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UNIVERSITÀ DEGLI STUDI
DI PALERMO
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Dottorato di Ricerca in Ingegneria delle
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SSD ICAR 04 – XXII ciclo

Rheology and Curing of Tyre Rubber Modified Bitumens

Ph.D thesis of:

Davide Lo Presti

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Rheology and Curing of Tyre Rubber Modified Bitumens

by
Davide Lo Presti

Tutors:
Prof. Eng. Bernardo Celauro

Coordinator:
Prof. Eng. Orazio Giuffrè

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Aknowledgements

Il 17 Marzo 2008 fù il mio primo giorno presso il Nottingham Transportation Engineering Centre. Il 18 Marzo 2011 difenderò la tesi esposta in questo lavoro, nella mia universitá, a Palermo. Tre anni esatti, ma quanto è cambiata la mia vita e quanto son cambiato io.

Tre anni fa invidiavo chi aveva un obiettivo ben preciso nella vita, studi tanti anni e poi non sai davvero che strada prendere. L'esperienza della tesi di laurea specialistica mi era piaciuta, ma e' stata l'opportunita' di poter approfondire gli studi all'estero che mi ha convinto a provare a vivere un dottorato di ricerca. Il risultato ultimo di tutto ciò è questa tesi, ma la conclusione più significativa di questa storia è la scoperta di una passione che ha segnato la mia vita e continua a riempirla : la ricerca.

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to my Family.

my strength. my pride

Table of Contents

Aknowledgements 5

Table of Contents 9

Introduction 14

1.1 End of Life Tyres (ELTs): from waste to resource 14
    1.1.1 ELTs in pavement applications 15
    1.1.2 ELTs management in Europe 16
    1.1.3 Future developments of the European ELTs market 20
1.2 Aim of this Research 22

2. Bituminous binder: an engineering material 24

2.1 Origin and manufacture 24
2.2 Composition and structure 29
    2.2.1 Chemical composition 29
    2.2.2 Fractionation of bitumen 30
    2.2.3 Bitumen as colloidal model 40
    2.2.4 SHRP findings on bitumen chemistry 48

  - 2.2.5 Relation between chemistry and performance of bitumen 53
- 2.3 Grading and Specifications 56
  - 2.3.1 Traditional grading systems 59
  - 2.3.2 Performance-related grading system 59

3. Rheology of bituminous binders 71

- 3.1 Base theory.. 71
  - 3.1.1 Principles of viscoelasticity.. 71
  - 3.1.2 Linear ViscoElasticity (LVE)... 72
  - 3.1.3 Viscoelastic behaviour of bitumen 73
- 3.2 Performance-related properties 75
  - 3.2.1 Traditional engineering properties of bitumen 76
  - 3.2.2 SHRP concepts and innovations.. 79
- 3.3 Rheometry... 85
  - 3.3.1 Dynamic Shear Rheometer (DSR) 86
  - 3.3.2 Dynamic Mechanical Analysis (DMA).. 95
  - 3.3.3 Rotational static tests.. 104
  - 3.3.4 Binder parameters related to asphalt rutting.............................. 105

4. Modification of bitumen 120

- 4.1 Principle of bitumen modification.. 122
  - 4.1.1 Bitumen modifiers.. 122
- 4.2 Polymer Modified Bitumen (PMB).. 127
  - 4.2.1 Polymers for bitumen modification.. 128
  - 4.2.2 Base bitumen for polymer modification..................................... 131
  - 4.2.3 Manufacturing of PMBs... 134
  - 4.2.4 Compatibility (Stability) of polymer - bitumen blends 135
  - 4.2.5 Rheological characteristics of PMBs.. 142
- 4.3 Tyre Rubber Modified Bitumen (TR-MB)... 146
  - 4.3.1 The material “Tyre Rubber” 148
  - 4.3.2 Tyre Rubber technologies in asphalt pavements 153
  - 4.3.3 Wet Process: Overview of processing conditions 161

4.3.4 Wet Process-High Viscosity: Technologies and Specifications 172
4.3.5 Wet Process-High Viscosity: Benefits, Issues and Limitations 186
4.3.6 Wet process-NO agitation: The new option 194

5. Effects of tyre rubber bitumen modification 202
5.1 Introduction 202
5.2 Experimental programme 203
5.2.1 Materials 203
5.2.2 TR-MB blending protocol 205
5.2.3 Physical and chemical characterization 205
5.2.4 Performance grading procedure 206
5.2.5 Rheological analysis 207
5.3 Results and discussions 208
5.3.1 Base binder 208
5.3.2 Modified bitumens 212
5.4 Summary of results 223

6. Desirable base binder properties for modification with tyre rubber 224
6.1 Introduction 224
6.2 Experimental programme 225
6.2.1 Materials 225
6.2.2 Blending protocol 226
6.2.3 Physical, chemical and mechanical characterization 227
6.3 Results and discussion 227
6.3.1 Base bitumens 227
6.3.2 Base binders 229
6.3.3 Modified bitumens 232
6.3.4 Rheological analysis 233
6.3.5 Storage stability analysis 238
6.4 Summary of results and critics 244
6.4.1 Base bitumen chemistry 244
6.4.2 Oil extender effect 244

6.4.3 Possible improvements of the processing conditions 245
6.4.4 Conclusions 246

7. New protocols to optimise laboratory curing of Tyre Rubber Modified Bitumen247
7.1 Introduction 247
7.2 Processing devices and procedures 248
7.2.1 Low shear protocol 248
7.2.2 High shear protocol 249
7.3 Materials and methods 252
7.3.1 Base bitumen selection 252
7.3.2 Tyre rubber properties 257
7.3.3 Bituminous binders 258
7.4 Rheological analysis 258
7.5 Results and discussions 259
7.5.1 Optimum rubber content estimation by using the low shear protocol 259
7.5.2 Optimum time estimation by using the high shear protocol 266
7.5.3 Performance comparison with PMBs 273
7.6 Summary of results 280

8. Curing variability effect on performance and stability of tyre rubber modified bitumens 282
8.1 Introduction 282
8.2 Experimental programme 283
8.2.1 Materials 283
8.3 Effect of temperature on Low Shear blends 284
8.3.1 Optimum blending time 284
8.3.2 Optimum rubber content 286
8.4 Effect of temperature on High Shear blends 292
8.4.1 Optimum blending time 293
8.5 Effect of Shear rate at fixed blending time 299
8.5.1 Mechanical strength (shear susceptibility) 302
8.6 Performance comparison with PMBs 303

8.6.1 Conventional properties 303
8.6.2 Rheological properties 305
8.6.3 Best performing blends 310
8.7 Processing conditions effects on blend stability 316
8.7.1 Storage stability analysis (SSA) 316
8.8 Summary of results 324

9. Conclusions and Recommendations for future researches 327
9.1.1 Rheological characteristics of TR-MBs 328
9.1.2 Curing of TR-MBs 329
9.1.3 Reccomendations for future research 333

References 335
List of Figures 355
List of Tables 366

APPENDIX A - SARA Analysis 369
APPENDIX B - SHRP Grading Procedure 377
APPENDIX C - DSR testing protocol 384
APPENDIX D - DSR data analysis 389
APPENDIX E - Results 402

Introduction

1.1 End of Life Tyres (ELTs): from waste to resource

The increasing number of vehicles on the roads of industrialised and developing nations generates millions of used tyres every year. About 1.4 billion tyres are sold worldwide each year and subsequently as many eventually fall into the category of end of life tyres (ELTs) (Tab. 1.1). Moreover, the amount of ELTs in Europe, US and Japan are about to increase because of the projected growing number of vehicles and increasing traffic worldwide. These tyres are among the largest and most problematic sources of waste, due to the large volume produced and their durability. Those same characteristics which make waste tyres such a problem also make them one of the most re-used waste materials, as the rubber is very resilient and can be reused in other products.

Table 1.1. End of Life Tyres recovery rate for 2009 (metric tonnes) (ETRMA, 2010)

	ELT recovery	ELT arisings	
EU27+CH+NO	2,494,000	2,621,000	95%
US (2007)	4,105,800	4,595,700	89%
Japan	737,000	814,000	91%

The U.S. Environmental Protection Agency reports that 290 million scrap tyres were generated in 2003 (EPA, 2007). Of the 290 million, 45 million of these scrap tyres were used to make automotive and truck tyre re-treads. With landfills minimising their acceptance of whole tyres and the health and environmental risks of stockpiling tyres, many new markets have been created for scrap tyres. One of the most successful applications is the use of ELTs in road pavements.

1.1.1 ELTs in pavement applications

The accumulation of end of life tyres and premature pavement failures are both interconnected and dependant of each other due to enormous increase in traffic density and axle loading respectively. To overcome these problems different techniques have been introduced, one of the most promising was introduced in 1960s when scrap tyres were processed and used as a secondary material in the pavement industry.

One application was introduced by two Swedish companies which produced a surface asphalt mixture with the addition of a small quantity of ground rubber from discarded tyres as a substitute for a part of the mineral aggregate in the mixture, in order to obtain asphalt mixture with improved resistance to studded tyres as well as to snow chains, via a process known as Dry Process (Epps, 1994).

In the same period Charles McDonalds, a materials engineer of the city of Phoenix in Arizona (USA), was the first to find that after thoroughly mixing crumbs of tyre rubber with bitumen and allowing it to react for a period of forty-five minutes to an hour, new material properties were obtained. This application, known as the “Wet process”, produced a new binder which captured beneficial engineering characteristics of both base ingredients. It became known as Asphalt Rubber.

Several experiences have shown that dry process results in applications which exhibit unstable performance (Papagiannakis & Lougheed, 1995; Van Kirk, 1991). In the USA experimental pavement sections have been placed in California, Florida, New York, Oregon, and Ontario and common negative results can be summarised in the following quote: “Performance of rubber-modified asphalt using the dry process has been mixed, with some early failures. Installations in service for several years generally show little

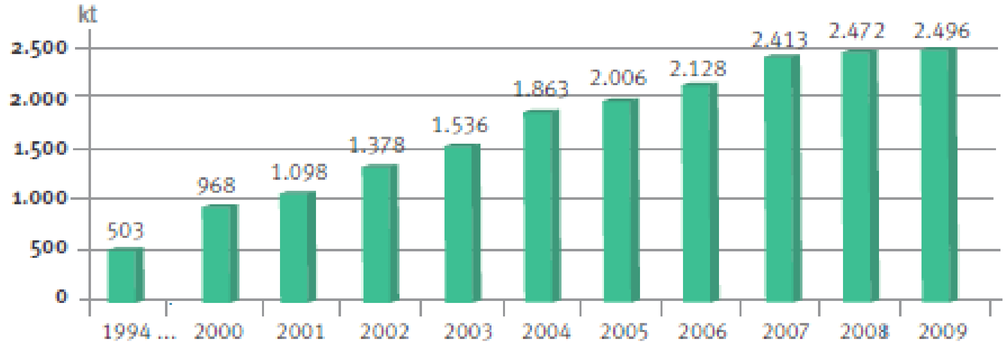
improvement over conventional overlays. Little to no evidence of ice debonding has been observed, except in laboratory tests". (Epps, 1994).
Whilst, extensive literature (§ 4.3.5) clearly shows the numerous successes obtained using Tyre Rubber bituminous mixtures produced with the Wet Process. However, Asphalt rubber is not a panacea. There are drawbacks to it, chiefly in terms of its workability, its recyclability, binder storage stability and the fumes it emits during the paving process. Asphalt rubber pavements are also more expensive than conventional asphalt pavements, and can be difficult for paving contractors not accustomed to working with the sticky product, which must be placed and compacted within a relatively narrow temperature window (Kuennen, 2004). For these reasons, in the early 90s, this technology was left as dead. In fact, asphalt rubber pavement was a promising concept that a few agencies were working with, but many others were not ready to implement it on a grand scale.

When in 1991, the United States federal law named "Intermodal Surface Transportation Efficiency Act" (ISTEA), mandated its widespread use, the Asphalt Rubber technology concept started to make a "quiet come back". In 1992 the patent of the McDonald's process expired and the material is now considered a part of the public domain. Since then, considerable research has been done worldwide to validate and find better use of this Tyre Rubber. Nowadays, these rubber bitumen type materials have spread worldwide as solutions for different quality problems (asphalt binders, pavements, stress absorbing lays and inlayers, roofing materials, etc.) with much different evidence of success demonstrated by roads built in the last 30 years.

1.1.2 ELTs management in Europe

In Europe there are 12 major tyre manufacturers: Bridgestone Europe, Continental, Cooper Tyres, Goodyear Dunlop Tyres Europe, Hancock, Marangoni, Michelin, Mitas, Nokian Tyres, Pirelli Tyres, Trelleborg Wheel Systems and Vredestein. Every year, 355 million tyres are produced in 90 plants, representing the 24% of world production (ETRMA Stat, 2010). In addition the EU has millions of used tyres that have been illegally dumped or stockpiled. The inadequate disposal of tyres may, in some cases, pose

Table 1.2. Evolution of the ELT recovery in Europe since 1996 (ETRMA stat, 2010)



	1994	*1996*	*1998*	*2000*	*2002*	*2004*	*2006*	*2008*
Re-use/export	11%	81%	11%	10%	11%	9%	9%	8%
Reconstruction	10%	12%	11%	11%	11%	12%	11%	10%
Material recovery	6%	11%	18%	19%	25%	28%	34%	38%
Energy recovery	11%	20%	20%	21%	27%	31%	31%	37%
Landfill	62%	49%	40%	39%	26%	20%	13%	6%
ELT manag. companies	1	3	4	4	7	11	13	15

a potential threat to human health (fire risk, haven for rodents or other pests such as mosquitoes) and potentially increase environmental risks.

Most countries, in Europe and worldwide, have relied on land filling to dispose of used tyres but the limited space and their potential for reuse has led to many countries imposing a ban on this practice. The current estimate for these historic stockpiles throughout the EU stands at 5.5 million tonnes (1.73 times the 2009 annual used tyres arising) and the estimated annual cost for the management of ELTs is estimated at € 600 million (ETRMA, 2010).

In order to face this problem, in 1989, a Used Tyres Group composed of experts from the main tyre manufacturers producing in Europe, was set up under the strategic guidance of the European Tyre and Rubber Manufacturers Association (ETRMA). This Group was dedicated to the management of end of life tyres (ELTs). Thanks to this group, since 1996, the collection rate has increased steadily while there has been a continuous decline in the landfilling of used tyres (Tab. 1.2). In 2009 the European Union was faced with the challenge of managing, in an environmentally sound manner, more than 3.2 million tonnes of used tyres of which 95% were recovered. This confirms Europe as one of the most active areas in the world in the recovery of ELTs. In the same year, 18 of the EU27 countries (plus Norway & Switzerland) recovered 90% and more of their annual used tyre arising. 15 of those 18 countries recovered 100% while a further attained between 80%

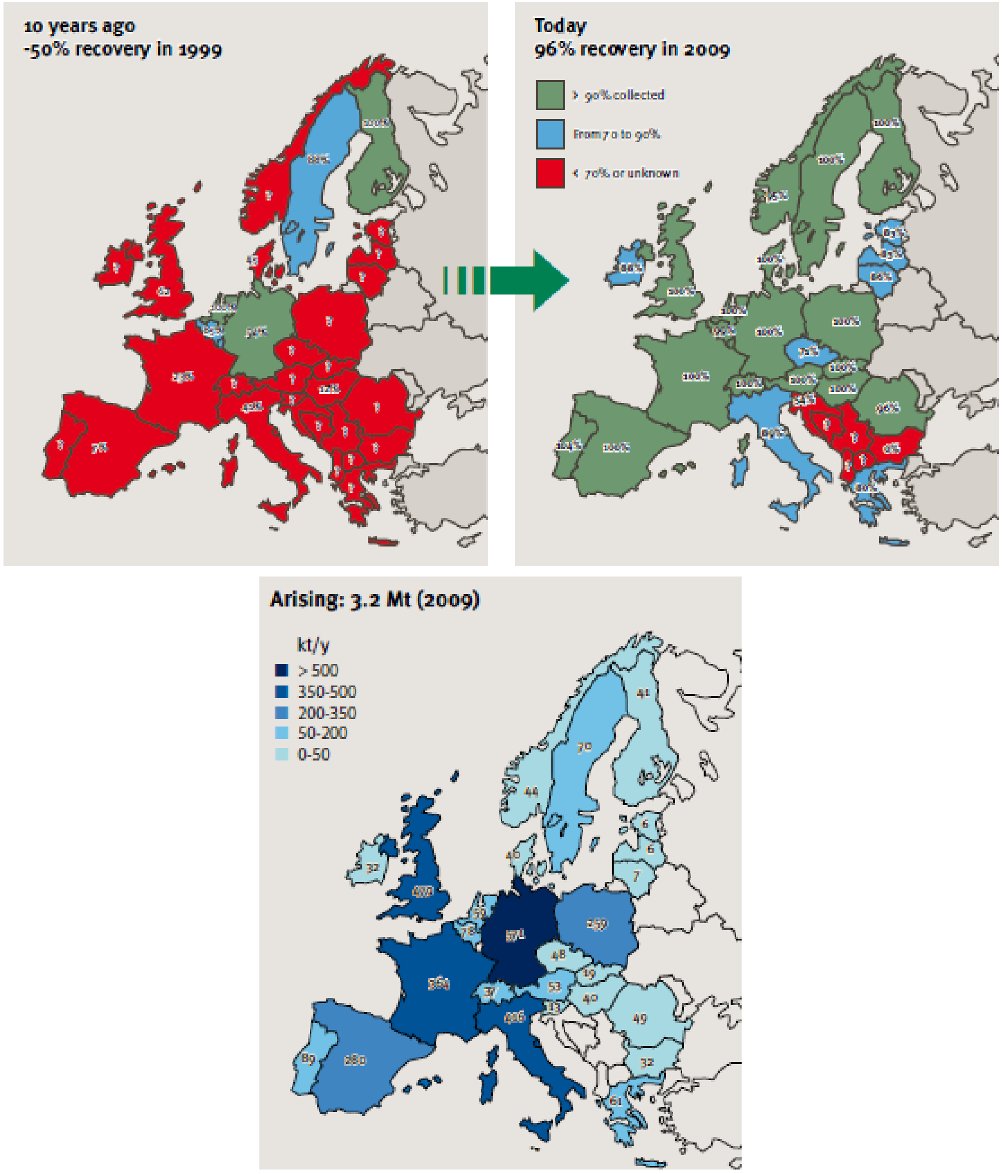


Figure 1.1. Histroy and Geography of the ELT management in Europe (ETRMA stat, 2010)

and 90%. The Czech Republic is above 70% whilst two countries are still depending on landfilling (ETRMA, 2010), (Fig. 1.1). European countries with recovery rates of 100% are those where stockpiles have been eliminated and a Producer Responsibility system has been operating for over 10 years (e.g. Nordic countries). In fact, today within the EU there are three different systems for managing end of life tyres (ETRMA, 2010):

Tax system. Under the tax system each country is responsible for the recovery and recycling of the end of life tyres. It is financed by a tax levied on (tyre) production and subsequently passed on to the customer. This is an intermediate system whereby the producers pay a tax to the State, which overall is responsible for the organisation and remunerates the operators in the recovery chain.

Countries: Denmark, Slovakia

Free market system. Under this system the legislation sets the objectives to be met, but does not designate those responsible. In this way all the operators in the recovery chain are under free market conditions and act in compliance with legislation. This may be backed up by voluntary cooperation between companies to promote best practices.

Countries: Austria, Bulgaria, Croatia, Germany, Ireland, Switzerland. Although operating under a freemarket system, United Kingdom features an hybrid system as collectors and treatment operators have to report to national authorities.

Producers Responsibility. The law defines the legal framework and assigns the responsibility to the producers (tyre manufacturers and importers) to organise the management chain of end of life tyres. This system appears to be the most suitable and robust for addressing and resolving end of life tyre arisings, in a sustainable manner for the long term, and to achieve a 100% recovery rate, in the most economical way. On the whole the European tyre manufacturers have demonstrated a clear preference for this system and have deployed determination and commitment to take this route. Currently, this system is adopted in 13 EU countries. Italy is expected to be operational in 2011 and other EU Member States are set to follow in the near future.

Countries: Norway, the Netherlands, Sweden, Belgium, Finland, Estonia, France, Poland, Portugal, Hungary, Romania, Spain, Greece, Italy (in 2011).

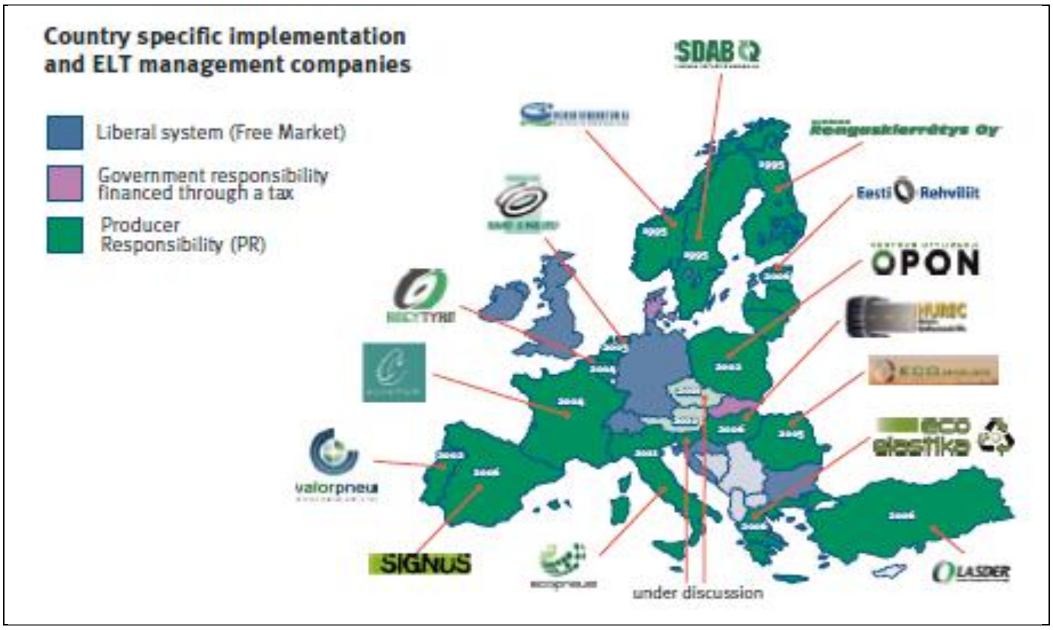


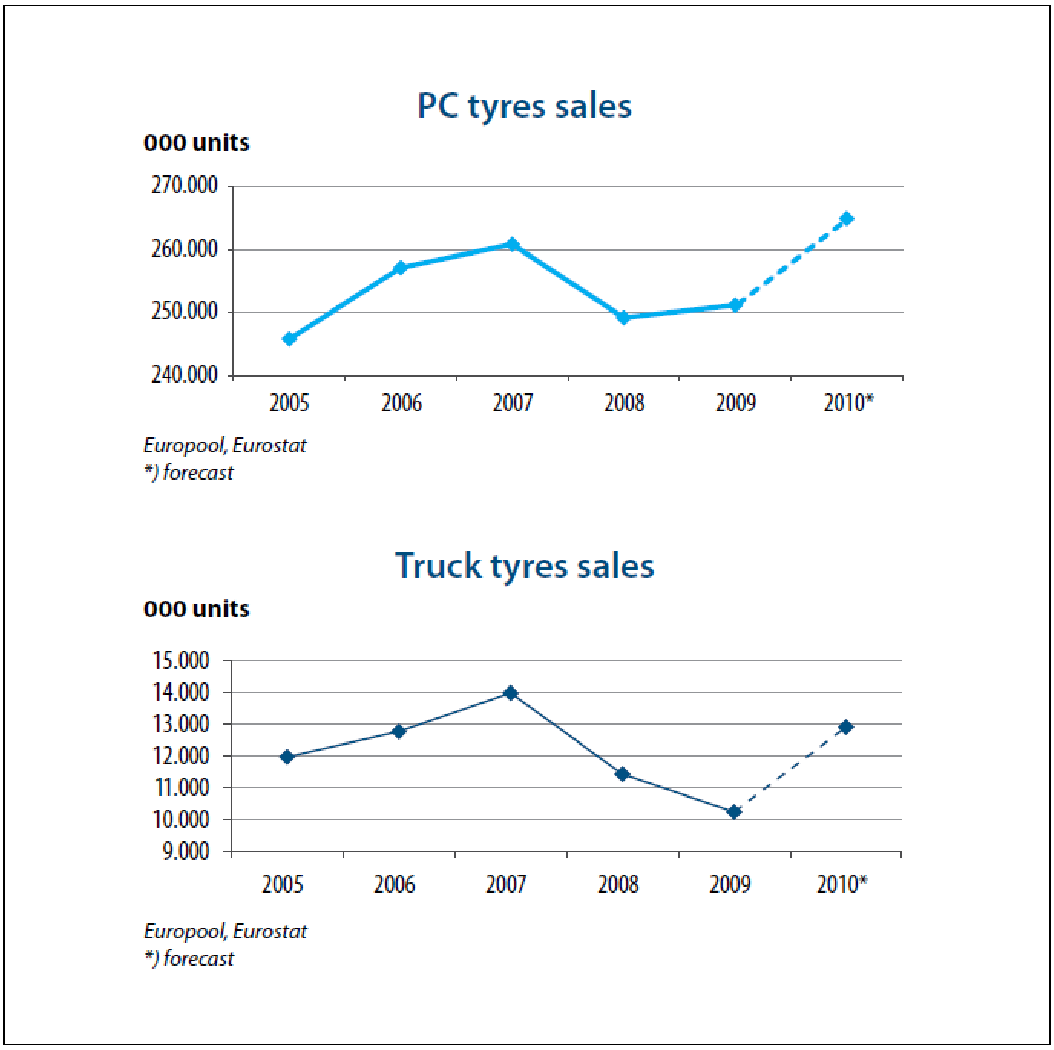
Figure 1.2. Country specific implementation & ELT managment companies (ETRMA stat, 2010)

1.1.3 Future developments of the European ELTs market

Country arisings and recovery rates demonstrate that ELTs management through the Producer Responsibility system achieves more robust results than the purely market driven approach, also because it allows the progressive elimination of landfilling (ETRMA, 2010). Despite an increase in the service life of tyres and the economic slowdown in Europe, the amounts of ELTs are about to increase because of the projected growing number of vehicles and increasing traffic (Fig. 1.3).

Therefore, the next goal of the European ELTs market is to continue promoting the adoption of the Producer Responsability System, in order to keep in improving the recycling of the ELT. This will be done by developing the organisation and professionalization of the different players (collectors, sorters and reprocessors) in the recovery chain with the creation of ELT management companies/associations at national level. The other main aim is, of course, supporting the creation of innovative engineering applications and products for industry, to create a sustainable market for derivatives of ELT. Within this framework, it is possible to place the use of end of life tyres in pavement engineering applications and also to understand why this “not new” technology is being relaunched worldwide.

It is also worth highlighting that, at the time of writing, the revised EU Waste Framework Directive (2008/98/EC) is providing potential for obtaining end of waste status for ELT derived materials.



Europool, Eurostat
**) forecast*

Europool, Eurostat
**) forecast*

Figure 1.3 Annual trends of sales on the European tyre replacement market (ETRMA stat, 2010)

There is an on-going development of quality standards for ELT derived materials at CEN level (TC366) which will surely contribute to a significant increase in the level of quality of tyre derived products while opening the market to new applications, promoting technology exchange and access to know-how and innovation, whilst protecting the environment. These efforts should for example help to further develop the use of ELTs in rubberised asphalt in road construction, which has high growth potential in Europe and it is still relatively underutilised: only few hundred kilometres of roads in total (ETRMA, 2010).

1.2 Aim of this Research

Although a considerable amount of research has been done and implemented in some parts of United States, Europe, Australia and South Africa, there are variations in outcomes of published work related to tyre rubber modified bitumens (TR-MBs). It may also be observed that the research done in one part of the country is not accepted by the other. Many publications and specifications based on research done in those areas reveal the variation in outcomes. Moreover, from the literature, it was observed that most of the research and practical applications control the modification process of tyre rubber modified bitumen only by empirical properties such as rotational viscosity. Based on the varied observation from country to country, and considering the development of new technologies related to tyre rubber modified bitumen, mainly the Wet process-No Agitation, still limited work has been done in the local environment and more research is needed to think about having this widespread within Europe.

Therefore, in the light of the available literature in this field, and current practical applications, it has been thought necessary to carry out a study in terms of detailed rheological properties of TR-MBs, in order to better characterise this material, and to understand how best to control the bitumen-rubber modification process also by varying the processing conditions.

The research programme was conducted in two phases, the first was at the Nottingham Transportation Engineering Centre, where the candidate developed skills on laboratory production methods, rheological measurements and data analysis of modified bitumen. The second phase, was done at the Road Infrastructure Department of the University of Palermo, where the influence of raw materials and processing conditions, on the production and final performance of TR-MBs, was studied.

The whole research was developed by using laboratory equipment which simulate as much as possible, the conditions present in the mixing plants. No special equipment, like those used for the wet process, have been used but only those apparatus that should be good for any other kind of polymer-bitumen modification in industrial dimensions.

New laboratory procedures have been defined. They are easily adoptable from other laboratories and permit the estimatation of the optimum tyre rubber content for a selected bitumen, and optimum processing time based on performance of the final blend. Moreover, these procedures allowed optimium testing time and material consumption, which are often precious resources.

The influence on the final product of the raw materials, such as bitumen, tyre rubber and oil extenders, were investigated by the production of several tyre rubber-bitumen blends at different processing temperatures and applied mixing shear stress.

Accurate selection of raw materials, storage stability, studied by means of rheological tests and image analysis, and comparisons with rheology and the anti-rutting behaviour of elastomer modified bitumens (SBS-MB) have led to produce high quality tyre rubber modified bitumens. The basis of deductions were results got by using traditional measurements but mostly performing performance-related characterisation and dynamic mechanical analyses. The results of the investigation indicate that the blended TR-MBs show large improvements with respect to the base bitumen, comparable with the SBS-MB under almost all the conditions. However, in order to use this binder for practical purposes, major work regarding the improvement of the storage stability of the TR-MBs still needs to be done.

2. Bituminous binder: an engineering material

2.1 Origin and manufacture

Bitumen is a product used for millennia as a building material in a wide variety of applications. Although it exists also in natural state, nowadays it is mainly obtained as a residue of petroleum processing. As defined in European Standard EN 12597:2002, bitumen is intended as "those organic compounds consisting essentially of mixtures of organic hydrocarbons completely soluble in carbon disulfide and with binding capacity”.

Bitumen is a heterogeneous organic compound usually derived from the distillation process of crude oil. Natural bitumen, instead, is in a more or less pure state and with various consistencies, in clusters underground, on the surface or also as primers of rocky and sandy formations. In this regards, the following can be cited: the formation of gilsonite, bitumen in an almost pure glassy state extracted in the U.S. state of Utah, bitumens of natural lake of Trinidad and Selenizza (Albania) and so-called Canadian tar sands. In Italy: asphaltic rocks of Sicily and Abruzzo.

The use of natural bitumen dates back to the ancient Sumerian civilization (6000 BC), Hindu (3000 BC) and Egyptian (2600 BC), who used them to waterproof marine and hydraulic works or as mastics for buildings. Natural bitumen has also been used in the very early: the first bituminous pavement built in the United States in 1876 on Pennsylvania Avenue in Washington, DC, consisted of a mixture, called sheet asphalt mixture of sand and natural asphalt of the lake Trinidad . Over time, the distribution of natural bitumens has been diminishing, however, with the development and refinement of processing techniques, able to provide bitumen in large quantities at a price more and more competitive, they are still used, but contribute with a negligible percentage of the annual world production of bitumen. Native bitumen deposits are found all over the world, in areas with suitable geological conditions in which the high permeability of the rock formations has enabled a process of natural fractionation of crude oil.

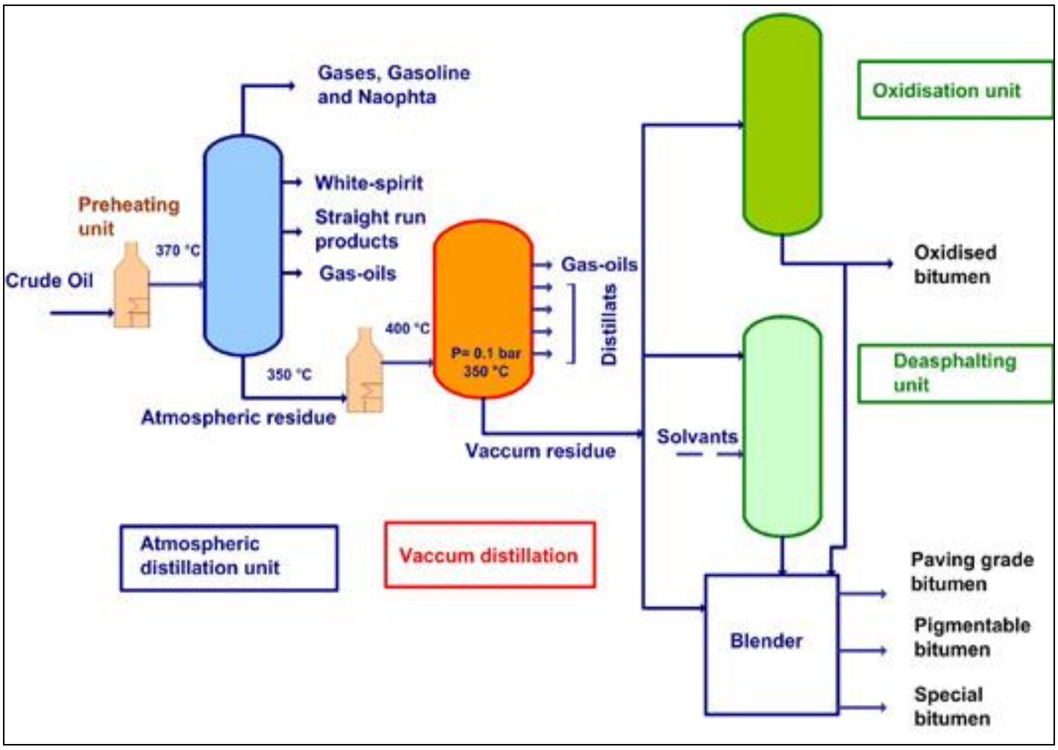


Figure 2.1. Distillation of bitumen (Total.com, 2010)

Being composed of the fractions with higher boiling point of the crude oil, the bitumen is traditionally obtained at the bottom of the vacuum distillation tower, which is designed to process the residue of a first distillation at atmospheric pressure (Fig. 2.1).

Some oils are not suitable for the production of bitumen due to the basic nature of the crude. Figure 2.2 shows the relative distribution of various fractions from different crudes. Among the extremely light oils there is the Gippsland (Australia) that contains a bitumen fraction less than one percent. On the other hand, the Sicilian oil, which is extremely heavy and contains more than 90% bitumen.

When it is also wanted to get other fractions, it is not possible or convenient to use oils with those extreme conditions. Therefore, the most common refined oils are usually chosen with a bitumen content of between 15 and 60% by weight. On this basis, the most qualified for the crude bitumen production are classified as medium and heavy. Examples of inappropriate crudes for bitumen production are "far east" oils (Indonesia and Australia), which contain a lot of wax. The wax cannot be totally eliminated from the bitumen by vacuum distillation and they can remain with a concentration up to 50% by the final weight of bitumen. The resulting product is of poor quality and with little adhesion to the aggregate (Siracusa et al, 2010).

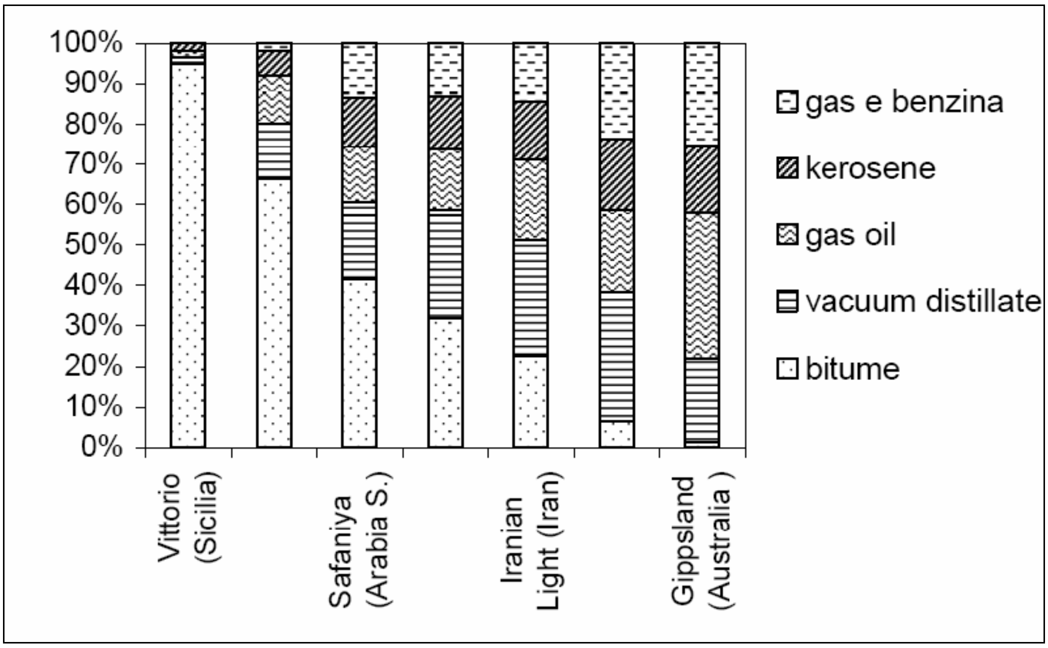


Figure 2.2. Composition of varium petroleum crude oils (concentrations in vol %) (Siracusa et al. 2010)

The material, obtained as previously described and then classified, can be directly used for different applications of civil engineering and the construction industry ranging from the manufacturing of sealing to the production of various mixtures for road pavements. When necessary, the distillation residue is also subject to oxidation, solvent extraction and/or mixing with other bitumen, which vary considerably depending on the production pattern of each refinery. These operations have the common purpose, to modify its chemical and rheological properties as detailed in other sections (§ 4.1.1).

According to the post processing used, the bitumen to be used for pavement applications can be classified as follows:

- **neat bitumen**. obtained through a fractional distillation of petroleum with processing temperatures reaching 350°C;

- **cutback bitumens.** Bitumen is ‘cutback’ by adding controlled amounts of petroleum distillates such as kerosene. This is done to reduce the viscosity of the bitumen temporarily so it can penetrate pavements more effectively or to allow spraying at temperatures that are too cold for successful sprayed sealing with neat bitumen. The materials used to cutback bitumen will evaporate after application to leave the remaining material similar in hardness to the original bitumen

- **fluxed bitumens.** mixtures of bitumen with flux. Flux is a petroleum product with high boiling point, such as oils for industrial processes or heavy distillates with initial boiling point greater than 350°C (Siracusa et al., 2010). After the application, original bitumen viscosity is still reduced because only limited evaporation of the solvent is present.

- **visbreaked bitumens**, resulting from the visbraking process in which heavy hydrocarbons are processed by a refinery, in light hydrocarbons, thus obtaining a product with less viscosity than that in input

- **hard grade bitumens:** These are manufactured in a similar way to paving grade bitumens. They have lower penetration values and higher softening points than paving grade bitumens. Hard paving grade bitumens are used in the manufacture of high modulus asphalts (Bitumenuk.com, 2010).

- **blown bitumen (oxydised).** Bitumens used in a wide variety of 'industrial' applications including roofing, flooring, pipe-coating etc. They are produced by passing air through soft bitumen/flux mixtures under controlled temperature conditions. (Bitumenuk.com, 2010). The process is based primarily on an oxidative condensation that causes the increase in molecular weight.

- **bitumen emulsions.** A dispersion of bitumen in water achieved by the use of suitable chemical emulsifying agents. They are normally produced using a penetration grade bitumen and suitable colloid mill. The contents of bitumen in emulsion is in a range from 40 to 80% by weight, and the application temperature from ambient to 90°C. The emulsified bitumen droplets may be anionic (negative charge), cationic (positive charge) or non-ionic (neutral)

- **polymer modified bitumen** Bituminous binders containing selected polymers to produce enhanced performance characteristics.They can be used in the same variety of applications as unmodified bitumens (Bitumenuk.com, 2010).

Storage and pumping temperatures

Bitumen should be stored in tanks specifically designed to minimize hardening (§ 3.3.2) and in particular: risk of overheating, oxidation and loss of volatiles. The latter are both related to the exposed surface to volume ratio of the storage tank which, for a cylindrical vessel, equals the reciprocal height of the filled part. Thus, vertical storage tanks with high height to radius ratio are preferable to horizontal tanks. Fortunately the residence time of bitumen in the tank is usually sufficiently low for any hardening to be insignificant. (Read & Whiteoak, 2003)

Bitumen should always be stored and handled at the lowest temperature possible, consistent with efficient use. Working temperatures are calculated on the basis of viscosity measurement and are supported by operational experiences. For normal operations, i.e. the blending and transferring of liquid hot bitumen, temperatures of 10 to 50°C above the minimum pumping temperature (145-185°C) are recommended, but the maximum safe handling temperature of 230°C must never be exceeded. The period during which bitumen resides in a storage tank at elevetad temperatures should be minimized to prevent hardening of bitumen. If bitumen must be stored for an extended period, say a period exceeding one week without the addition of fresh material, the temperature should be reduced to approximately 20 to 25°C above the softening point (70 – 90°C) of the bitumen. Moreover, in case of prolonged storage the bitumen should be tested before use to ensure its continued suitability for the proposed application.

When a polymer modified bitumen has to be stored in standard plant, it is important to ensure that the modified binders are storage stable. Different polymers and different polymer/bitumen combinations require different storage regimes and pumping temperatures. Essential information on storage should always be ascertained from the relevant product information sheet and such advices must be applied rigidly. Not all polymer modified bitumens are stable in storage and the management of these binders can be radically different to the one above exposed (Read & Whiteoak, 2003).

2.2 Composition and structure

The characteristics of the bitumen from the oil refining is dependent on both the type of the starting crude and from the production process. Though the types of production process are similar (with the differences inherent in different production plant), the composition of crude is variable, not only between areas of production, but even within the same area.

2.2.1 Chemical composition

Bitumen is a complex mixture of organic compounds with high molecular weight, with a prevalence of hydrocarbons with a number of carbon atoms greater than C25 and high value of C / H, as well as small amounts of sulphur, nitrogen and oxygen, it also contains traces of metals such as nickel, iron and vanadium. (Lobbi F. et al, 2002).
The crude oil, does not generally contains unsaturated compounds, but it consists mainly of:

- aliphatic hydrocarbons;
- cycloalkanes (C5-C7);
- naphthenes;
- aromatic and polyaromatic compounds (asphaltenes).

The last three compounds are heavier and more stable products that can be found in the bottom of the topping column (atmospheric distillation), then sent to vacuum distillation. Consequently oils with higher percentages of these compounds are best suited to the production of bitumen.

Its elemental composition, even if highly variable, can be identified by the following scheme (Read & Whiteoak, 2003):

- Carbon: 82-88% by weight;
- Hydrogen: 8-11% by weight;
- Sulfur: 0-6% by weight;
- Oxygen: 0-1.5% by weight;
- Nitrogen: 0-1% by weight.

As can be seen, the chemical composition of bitumen is extremely complex. Thus, a complete analysis of bitumen would produce such a large quantity of data that correlation with rheological properties would be impractical, if not impossible. Thus, as explained in the next paragraph, the bitumen can be fractioned into a few different chemical families, depending on the molecule’s size and solubility in polar, aromatic or non-polar solvents.

2.2.2 Fractionation of bitumen

The need to separate the individual components of mixtures, sometimes very complex as is the case of bitumen, has led to the development of numerous techniques of investigation. They can be classified into three main categories. Depending on the separation scheme used, it is possible to use:

Selective solvents. They provide the sequential processing of bitumen with solvents of increasing polarity that precipitate fractions of decreasing polarity. Although these methods avoid contact between bitumen and reactive adsorbent or components that could alter irreversibly its properties, they are able to isolate fractions that typically are not sufficiently different.

Chemical precipitation procedures. After separation of asphaltenes through precipitation in n-pentane, the remaining solution of maltenes is treated with solutions increasingly concentrated of sulfuric acid (H2SO4), and then with fumes of sulfuric acid containing 30% of $S0_3$ (sulfur dioxide). This allows the precipitation and therefore the quantitative evaluation of three other molecular classes with progressively less reactivity: nitrogen bases and then first and second acidaffines. Finally, the constituents of maltenes not reacting with the sulfuric acid fumes are called paraffins.

Chromatographic techniques. In contrast to the previous techniques, such methods have been widely circulated mainly in the field of research. The term chromatography is now generally used to indicate the various separation techniques applicable to mixtures of substances based on the distribution between two phases that uses the same principle: the differences in the speed with which the different components of a mixture migrate to a stationary phase under the influence of mobile phase, which is responsible of dragging along the system, the solutes that make up the mixture in question. (McCabe et al, 2005). Modern chromatographic techniques, in their many variants, differ among themselves, as well as the solvents used, for the type of porous support and the technical assessment of the relative amount of each fraction. Below are reported: the operating principles of this technique and the main methods used for the chromatographic fractionation of the bitumen.

Principles of chromatography

Chromatographic techniques applied to the fractionation of bitumen, can be traced to one fundamental experiment:

The preliminary operation, common to all these methods, is the separation of the components more polar and less soluble, asphaltenes, by precipitation in a non-polar solvent paraffinic. The resulting solution is then placed in a chromatography column. The stationary phase consists of a liquid or granular (pratically a powder) of a size such to allow the sliding of the mobile phase without offering excessive resistance. The mixture to be separated is deposited on top of the column (without dilution) on a very thin initial layer. After loading the column, the mobile phase is added continuously (also known as eluent), which, flowing through the stationary phase, drags in a selective way the different components of the mixture, according to the affinity of each of the two phases (mobile and stationary). Thus, different bands are formed along the column. The substances most similar to the stationary phase are retained longer and therefore their pathway is slower. When leaving the column, the eluent is collected in fractions of known volume. If the chromatographic system is able to carry out its function, the various components of the mixture, as a result of the continuous addition of eluent, separate more and more and this allows to collect fractions completely separated from each other. At the end of the chromatographic separation, containers hold different amounts of each eluted substance. These can be determined by gravimetric methods, after evaporation of the solvent, or by measuring a physical property, such as absorption of the color.

Iterations that occur between the substance to be separated and the two phases, mobile and stationary, are not always properly describable and they are still not totally, because the acting mechanisms are several and different nature, and polarity, of the two phases usually plays a decisive role. The various chromatographic techniques are classified according to the main separation mechanism involved in each of them:

Adsorption. The stationary phase is a solid powder, typically an inorganic compound or an organic polymer. On the surface of the granules some active sites are present and they can interact with certain functional groups of molecules to be separated. This phenomenon is called adsorption, and therefore the method is called adsorption chromatography. If the mobile phase is a liquid, the method is called liquid-solid chromatography (LSC). When eluting, the molecules of each substance are distributed dynamically between the two phases, mobile and stationary, depending on the extent of adsorption.

Allocation. The stationary phase is a liquid that covers a solid support. Each component of the mixture is soluble in both phases, mobile and stationary, and it is distributed according to solubility of each of them. This allocation mechanism is used in liquid chromatography - liquid (CLL).

Ion exchange. The stationary phase is an ion exchange resin, comprising a polymer matrix with inert ionized surface groups, balanced by its counter-ion. The ion exchange is achieved when the anions, present in the mobile phase, replace counter -ions and stick on the resin. By using a resin with high concentration of the counter-ions, foreign ions of the mixture are removed and eluted. Ion-exchange chromatography (IEC) is based on this mechanism.

Exclusion. The larger molecules can slide only in the spaces between the particles of gel (stationary phase) and then leaving quickly the column. The smallest molecules, instead penetrate into the gel granules, which have a porous structure, and thus are slowed down. The result is a separation of molecules based on their size. Exclusion chromatography (SEC) is based on this mechanism.

Affinity. By using a reversible reaction, the molecules to be separated bind to specific functional groups of the stationary phase. Eluting with an appropriate stage, break the bonds with the stationary phase and these molecules are recovered. Affinity chromatography (AFC) is based on this mechanism.

Low Pressure Chromatography, (LPC)

In principle, the traditional column chromatography does not require special equipment and can be conducted in accordance with the details of the fundamental experiment described above. It is possible to use automated equipment to improve reproducibility separations and drastically decreasing downtimes, which are considerable when operating manually. Typically, the chromatographic analysis is characterized by the use of a column that is filled with a stationary phase (solid, liquid or gel) through which the mobile phase (a liquid organic or a low viscosity aqueous solution) is pulled through by gravity or gentle pressure. The eluted bands are then collected in fractions at the column exit (Fig.2.3).

The core of a LPC system is the column itself. It is made of glass or plastic, mostly transparent, generally the length varies from 10 to 100 cm and internal diameter from 0.5 to 5 cm (on these two quantities depends the effectiveness of trade between the two phases, solid and steady, indeed their relationship must be chosen very carefully). However, if the separation is performed to obtain large quantities of a substance, for of research purpose or purification, the size of the column can also grow a lot.

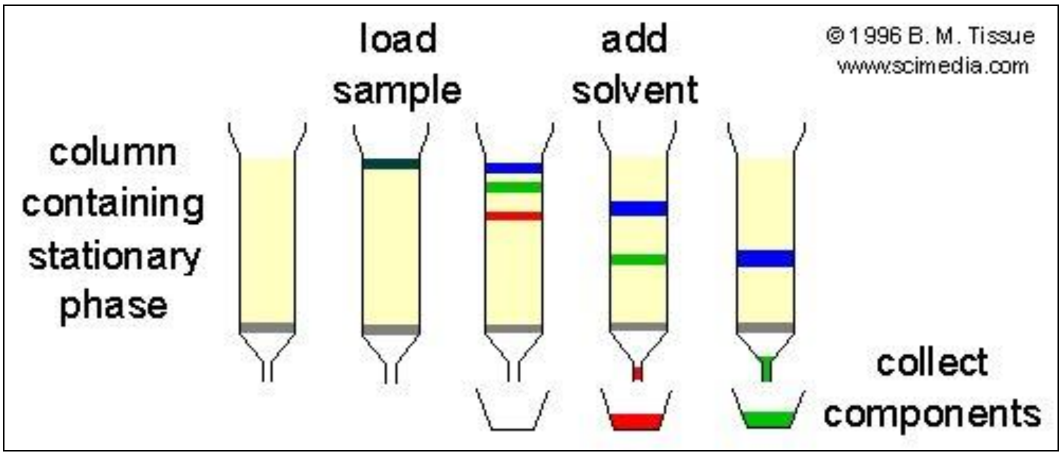


Figure 2.3. LPC process

Nowadays the reference method for the separation of maltenes into saturates, aromatics and resins, which together with the preliminary asphaltenes estimation forms the so-called SARA analysis, is the standard ASTM D4124. It is basically a LSC which is based on Corbett procedure but using other solvents for safety reasons and convenience (Corbett, 1969). The ASTM method prescribes also how to preliminary find the asphaltenes content and so assess the so-called SARA fractions (§ 2.2.3). The four groups are not well defined and there is some overlap between the groups; however, this does enable bitumen rheology to be set against broad chemical composition. (Read & Whiteoak, 2003).

The classification of different techniques in LPC is based on a criterion which takes into account both the physical state of the two phases and the mechanism of separation; the main techniques can be divided into:

Adsorption-allocation chromatography. This technique has two variations, which are very similar to each other from the operational point of view:

- *Liquid-Solid Chromatography*, LSC;
- *Liquid-Liquid Chromatography*, LLC;

The separation mechanism may involve adsorption phenomena, characteristic of the LSC, and allocation phenomena characteristic of LLC. Very often, these phenomena occur simultaneously, albeit with the prevalence of each other. As for adsorption, the molecules are distributed between two phases, solid (stationary phase), on which are adsorbed, and liquid (mobile phase) which is solubilised. With regards to the distribution, the stationary phase is a liquid, immiscible with the mobile phase, and the molecules are distributed between the two phases according to the solubility of each of them. The solubility, of course, depends on the physical-chemical affinity of the solute with each phase; so the molecules of the mixture to be separated establish more or less strong links with the stationary phase and are carried by the mobile phase in a different way: easily the least similar (and thus less soluble) to the stationary phase, with more difficulties the most similar (and therefore more soluble) to the stationary phase. If the separation mechanism is effective and sufficiently selective, the various components of the mixture give rise, to the bottom of the column, to bands well separated from each other.

Size Exclusion Chromatography, SEC. Also known as molecular sieve chromatography and steric exclusion chromatography, it separates the components of a mixture according to molecular size which, in the case of homologous series of compounds, are related to the molar masses. Typically the stationary phase is a polymer in gel form; the mobile phase can be an organic solvent, in the case of Gel Permeation Chromatography (GPC), or water or a buffer solution, this is Gel Filtration Chromatography (GFC). The gel, once packed with eluent and included in the column, is basically a set of particles, more or less rigid with high porosity, consisting of micro channels and pores of different sizes. When eluting, the molecules of the mixture can penetrate the gel particles, but only if they are smaller than the size of the pores, and then are held for different times depending on their size. The larger molecules are even excluded from the gel and therefore they pass through the column together with the eluent at the same speed. Unlike what happens in an ordinary sieve, larger particles move more quickly, while others are increasingly delayed with decreasing their size. Compared to a fix type of gel, the molecules of a mixture can have three different behaviors (Fig. 2.4):

1. molecules with dimensions such that can not penetrate into the pores are excluded from the gel;
2. Some molecules can penetrate only partially into the pores of the gel, occupying only a fraction of the internal volume, and therefore they are divided;
3. molecules smaller than the smallest pores of the gel can penetrate all the internal volume and they are therefore completely permeated by the gel.

Together with IEC, the SEC, has been used intensively to characterize the chemical properties of bitumen within the SHRP project (2.2.4)

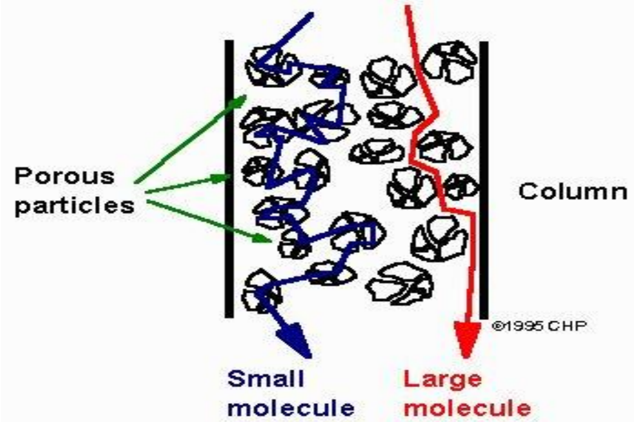


Figure. 2.4. SEC process.

Ion Exchange Chromatography, IEC. Separation of the components in a mixture of ionic character through the use of special equipment (Fig. 2.5). In order to perform such operation are used the so-called ion exchangers are used. These are polymeric resins on which molecular skeleton functional groups, with electric charge, are stacked and reversibly exchange ions with the solution of the mixture. On a cationic resin, active groups are negatively charged and exchange their counter-ion (positive) with ions of the same sign in the mixture. An anionic resin works in the opposite way.

In a column for IEC, migration and separation of different ionic components are due to the distribution of each of the two phases, mobile (usually a buffer) and stationary (the ion exchange resin).

Figure. 2.5. Example of IEC equipment

The behaviour of an ion during the separation thus depends on the balance that it has with the active groups (loads) of the resin which, before introducing the sample, are associated with a particular type of counter ion. Sometimes, the mechanism of ion exchange is overlapped by others (e.g. adsorption), which can also improve the chromatographic separation (Cozzi et al, 1997).

High Performance Liquid Chromatography, HPLC

HPLC is the natural evolution of the instrumental Low Pressure column chromatography and its variants. It is a chromatographic technique which separates two or more compounds present in a solvent, by using the affinity between the conventional stationary phase, placed inside the chromatographic column, and a mobile phase flowing through it. A substance similar to the stationary phase, more than the mobile phase, takes a longer time to pass through the chromatography column (retention time). Whilst, a substance with low affinity with the stationary phase, and high affinity with the mobile phase, goes through faster.

The test sample is injected at the beginning of the chromatographic column where it is "pushed" through the stationary phase, by the mobile phase, by applying pressure till the order of hundreds of atmospheres. To achieve high efficiency in separation, it is necessary that the particle size of the filling is very small (usually having diameters ranging from 3 to 10 μm). For this reason it is mandatory to apply high pressure in order

Figure. 2.6. Example of HPLC equipment

maintain a reasonable speed eluent flow and also an appropriate analysis time. A detector (mass spectrometer) is applied at the end of the column and a computer, that allows a continuous analysis of the output column, is able to quantify and /or identify the substances injected.

The main advantages of this technique are: the small size of the column that avoid the longitudinal deviations (longitudinal movements of the mobile phase) and alternative routes, constant and adjustable elution rate (mobile phase passing through the column), reduced speed of the whole process, small amounts of compound needed (in the order of 5-10 micrograms of sample dissolved in an appropriate solvent), improved accuracy and precision. The main disadvantage of the HPLC apparatus is that it is much more expensive than a traditional column chromatography (about 20-30 thousand euros for a complete set-up). Due to the high pressures, instrumentation for HPLC (Fig. 2.6) is usually more complex than the equipment used for other chromatographic techniques (Skoog & Leary, 1995).

Thin Layer Chromatography - Flame Ionisation Detector, TLC-FID

The TLC-FID is one of the most widely used techniques for the fractionation of bitumen. Through this investigation it is possible to trace the three functional groups that characterize the maltenes, namely, saturates, aromatics and resins. The technique is fast and cheap, but with the defect of lack of reproducibility. This type of thin-layer chromatography uses, as the fixed phase of the process, a porous surface represented by a stick coated with silica (Chromatod). Impurities on the stick are removed by the preliminary operation of burning with a hydrogen flame. Applied to one end of these sticks is 1μg of a 0.5% solution of test sample in dichloromethane, which is the mobile phase of the process. The chromatogram, which represents the amount of substance detected as a function of time, is being developed for ascension of the mobile phase in a closed room, pre-saturated with the eluent phase. In and orderly time frame, the stick is suspended in a tank with solvent of increasing polarity (hexane, toluene and dichloromethane / methanol in the ratio 95 / 5). The fractions of bitumen are individually dragged up from the solvent for the capillary that is held back by gravity. The separation into four fractions in the case of bitumen is clearly visible due to its natural color.

The quantitative detection of individual fractions separated on the chromarod is made via a flame ionization detector (FID Flame Ionisation Detector). A flame with hydrogen moves along the rod and when it encounters the acidic fraction of bitumen separated using column chromatography, it causes the combustion and pyrolysis cleavage, producing, positively charged ions and electrons. Due to this process, a stream of charges and then an electrical signal is generated within the measuring circuit. The response of the FID detector is proportional to the number of carbon atoms in the molecule. The sensitivity is then related to the molecular weight of the organic substance eluted. The FID detector most adopted in the field of research is the Iatroscan (Montepara & Giuliani, 1998). This technique is particularly suited to the study of asphalt because the asphalt is substantially free of chemical species that do not produce a signal with FID detector, but as mentioned earlier, it has a low reproducibility.

The chromatogram

Most of the chromatographic separations described earlier, ends in the recording of the chromatogram. The chromatogram is the path that describes the evolution of the detector signal versus time or volume of eluent, starting from the moment the mixture is introduced into the column (t = 0).

The detector is a tool placed at the bottom of each device that records the passage of a substance eluted. The eluent is selected so that it does not provide any response or otherwise to provide a constant response over time. Therefore, when the detector register only the passage of the eluent, only a baseline that can be considered as "zero" (response of the solvent) is obtained. When the eluted substances begin to pass through the detector, the path bends and reaches a maximum, they then quickly reform the original level. The complete path obtained for each flowed substance is called chromatographic peak.

Under ideal conditions the chromatographic peak has the shape of a perfectly symmetrical bell curve, because it is due to the inevitable dispersion process that undergoes any substance (theoretically in a symmetrical manner) while flowing through the column. (Cozzi et al, 1997). Whenever a substance is detected, the chromatogram shows a peak, which is higher or lower depending on its concentration (Fig. 2.7).

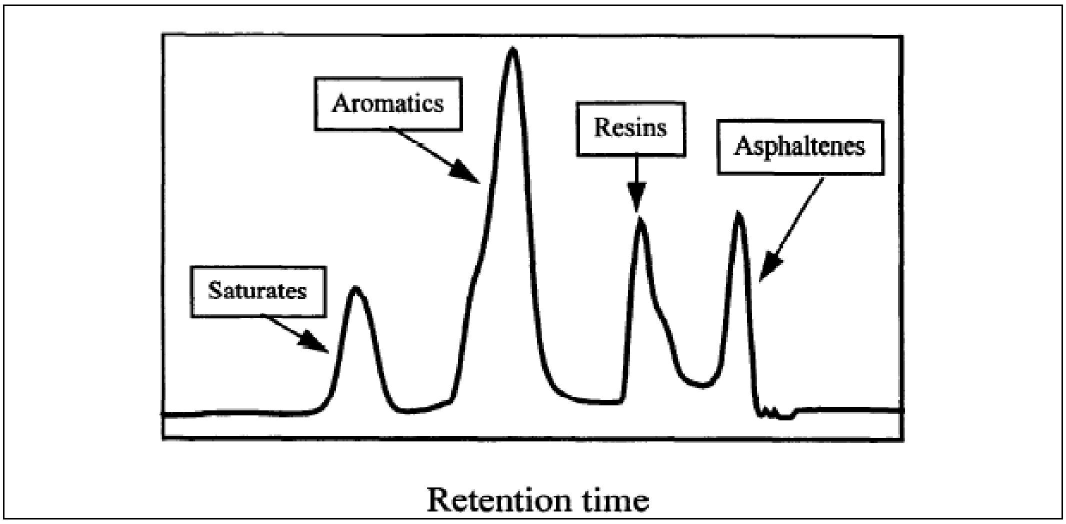


Figure 2.7. – Example of a bitumen Chromatogram (Isacsson & Lu, 1997).

2.2.3 Bitumen as colloidal model

Traditionally, bitumen is regarded as a colloidal system consisting of a suspension of high molecular weight asphaltene micelles dispersed in a lower molecular weight oily medium identified as maltenes (Fig. 2.8) (Lu et al, 1999).

Indeed, very early in the study of crude oils, it was observed that mixing oils with several volumes of normal alkane solvents (propane, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane) resulted in the precipitation of black, friable solids called *asphaltenes*. These solids are relatively enriched in heteroatoms (nitrogen, oxygen, sulfur, metals) and are more aromatic than their parent oils. Asphaltenes are involatile, so they become concentrated in residual fractions. Deasphaltened oils (otherwise known as *petrolenes* or *maltenes*) differ

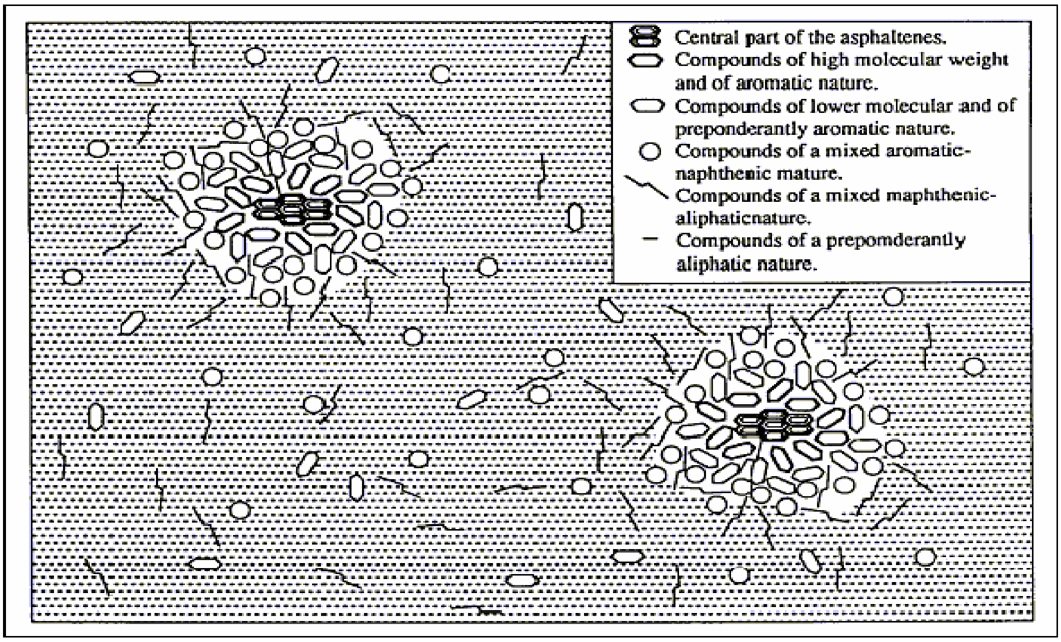


Figure 2.8. – Colloidal nature of bitumen (Read & Whiteoak, 2003)

in properties from whole crude oils; for example, maltenes are much less viscous than whole crudes. Therefore asphaltenes, which normally make up a few mass percentage of crudes, are the principal viscosity-enhancing components, as they are with bitumens.

From these observations, Nellensteyn (Nellensteyn , 1924) introduced the concept that petroleum residua are colloidal dispersions of asphaltenes in maltenes (which serve as a solvent phase) peptized by polar materials called *resins*, which may be isolated from maltenes. Mack (Mack, 1932) studied rheological properties of asphalts and also concluded that asphalts are colloidal. He proposed that asphaltenes are dispersed throughout the maltene phase as large agglomerations, which are stabilized by association with aromatic components of the maltenes. Labout (Labout, 1950) proposed that in asphalts having highly aromatic maltene fractions, asphaltenes are well dispersed (peptized) and do not form extensive associations. Such asphalts were designated *sol-type* asphalts. In asphalts with less aromatic maltene fractions, asphaltenes are not well dispersed and form large agglomeration, which in extreme cases can form a continuous network throughout an asphalt. These bitumens were designated *gel-type* asphalts (Fig. 2.9). Pfeiffer and Saal (Pfeiffer & Saal, 1940) suggested that asphalt dispersed phases are composed of an aromatic core surrounded by layers of less aromatic molecules and dispersed in a relatively aliphatic solvent phase.

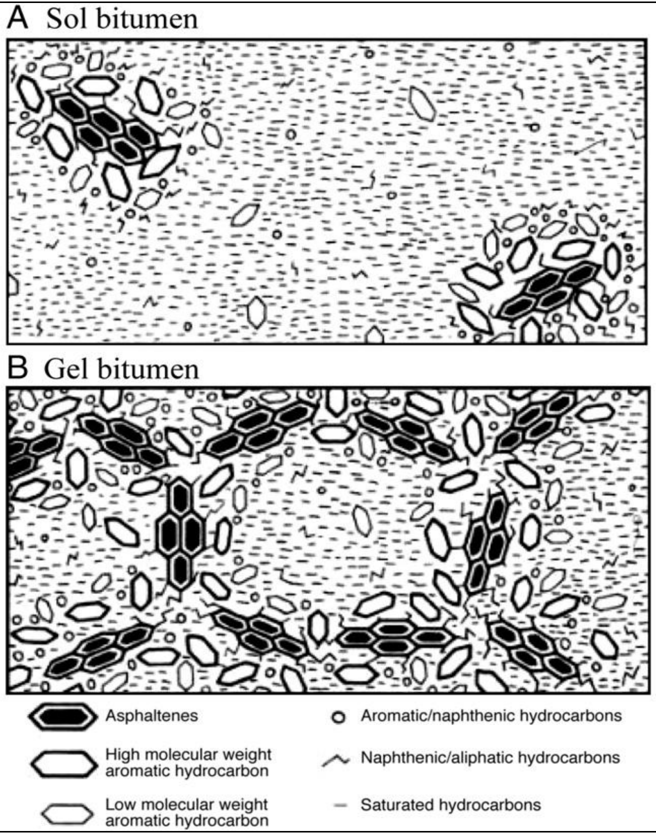


Figure 2.9. - Modello colloidale dei bitumi SOL e GEL. (Lesueur D.,2009).

They did not claim that there are distinct boundaries between asphalt dispersed and solvent phases, as in soap micelles, but that there is a continuum from low to high aromaticity from the solvent phase to the centers of the entities making up the dispersed phase. Pfeiffer and Saal observed that asphaltenes, which they considered to be the core constituents of dispersed phases, have a marked tendency to absorb aromatic hydrocarbon solvents, and they assumed that the same tendency would prevail in asphalt systems; that is, the asphaltenes would attract smaller aromatic components of maltenes, which would surround and peptize the asphaltenes. The smaller aromatic molecules would be compatible with naphthenic and aliphatic components of the remainder of the maltene phase. Therefore, there is no contact between materials having greatly different surface tensions anywhere in the system, although differences in surface tension between the aromatic asphaltene cores and the more naphthenic and aliphatic solvent may be fairly large. Pfeiffer and Saal considered aromaticity gradients in their model and did not address distributions of heteroatom-containing molecules with polar functional groups.

They claimed that asphalt properties are a function of the strength of associations between fundamental components of dispersed phases and the extent to which dispersed phases are peptized by solvent phases.

Effect of temperature. Peptization is provided by a shell of resins that surrounds the asphaltene core with the thickness of this resin layer being temperature dependent (Figure 2.10a). At low temperature and in the case of high asphaltene content the bitumen can show a compact structure as shown in Figures 2.10b and 2.10c.

On the other hand, insufficient quantities of resins and aromatics (insufficient solvating power) may lead to an association of several micelles - from the latin “mica” meaning “crumb” - which may be simply expressed using the following thermal dependent equilibrium:

molecules <=> micelles <=> clusters

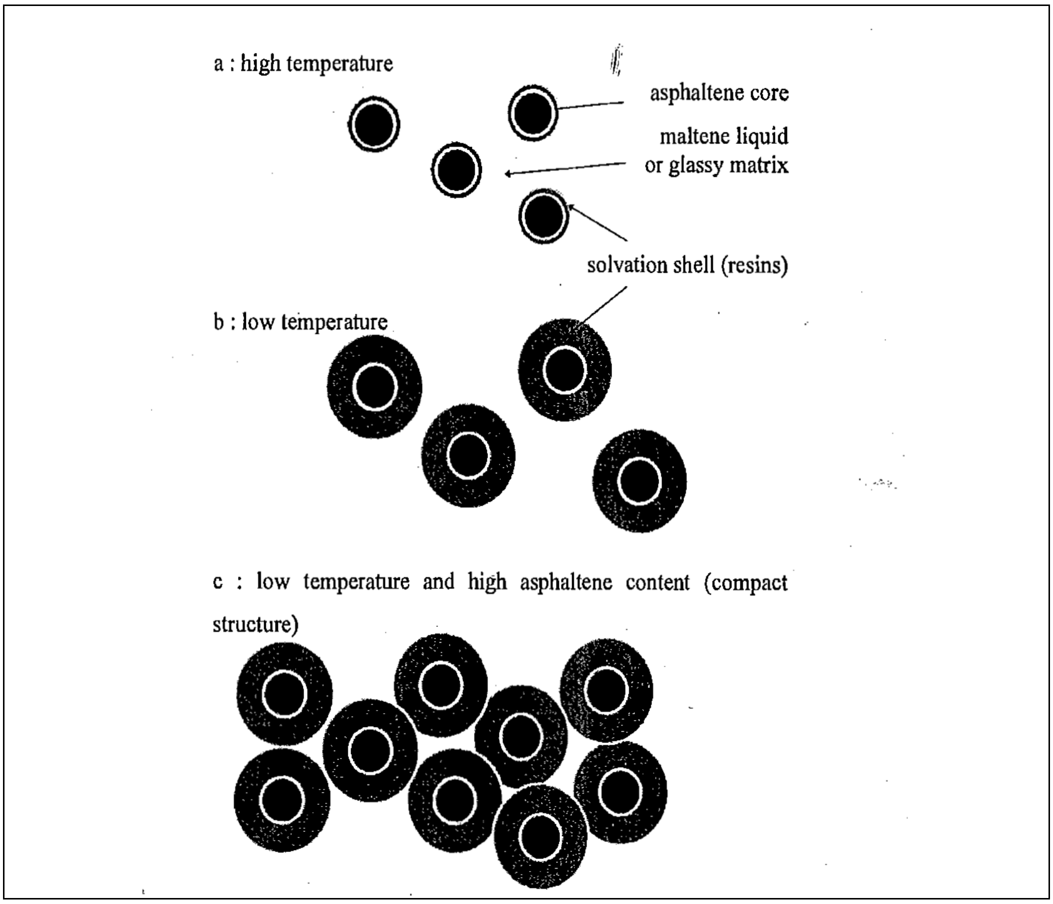


Figure 2.10. Colloidal structures against temperature (Lu et al, 1999).

The system is therefore formed by a liquid part (resins dissolved in a maltene matrix), in equilibrium with a solid part (resins peptizing the asphaltenes) and it is, of course, temperature dependent (Yen, 1990).

SARA fractions

The colloidal model proposed by Nellensteyn and modified by Mack, Pfeiffer and Saal, and later investigators enjoys widespread support among petroleum scientists. There is a great deal of evidence in favor of its validity.

Unfortunately, the simple optical methods that would easily verify or refute the model cannot be used because of the opacity of petroleum and all but its most dilute solutions.

Chromatographic techniques (§ 2.2.2), instead, have shown to be suitable. Indeed, by means of absorption chromatography (LSC), bitumen can be separated into four functional groups with related properties with regard to chemical reactivity and rheological properties despite its complexity. As seen above, these generic components are generally referred to as: Asphaltenes, Resinous components (polar aromatics), Aromatics (non-polar naphtene aromatics), and Saturates (Read & Whiteoak, 2003).

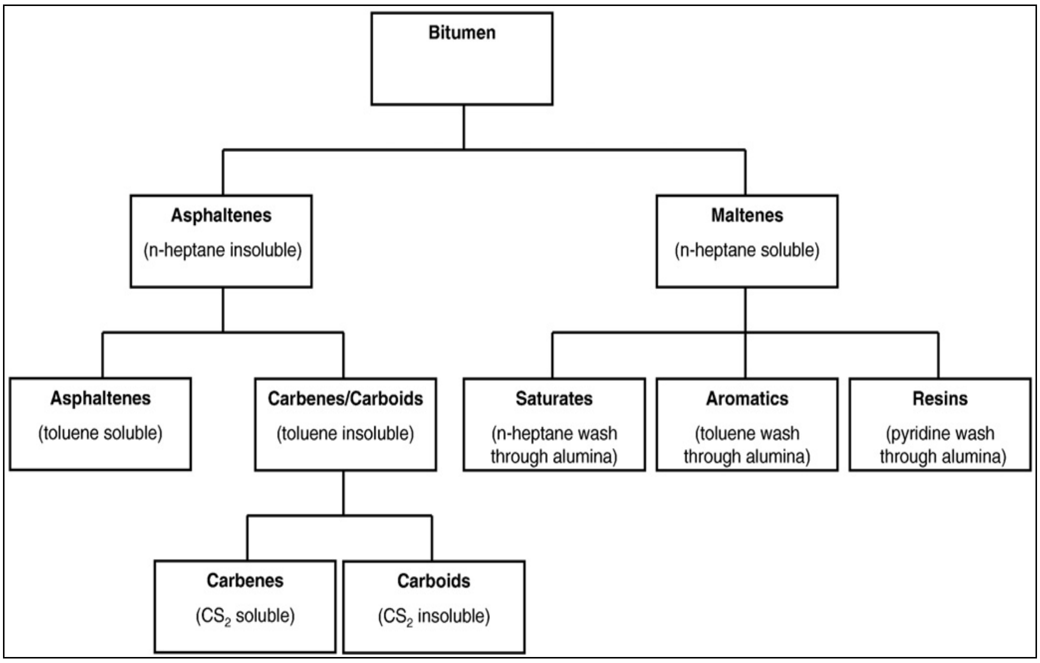


Figure 2.11. - Separazione del bitume in diverse frazioni in relazione delle classi di solubilità. (Lesueur, 2009)

The major obstacle to the characterisation of bitumen is the high molecular weight of the compounds, but the currently available methods do not allow to identify the single species present. To verify compliance of the bitumen to industry specifications, it has been used a qualitative analysis of organic the compounds, based on the principle of solubility classes (Fig. 2.11), which is able to separate the bitumen as follow:

- Carboids, unsolved to carbon disulphide (CS2);
- Carbenes, unsolved in carbon tetrachloride (CCl4);
- Asphaltenes, unsolved in the n-heptane, but completely soluble in carbon tetrachloride (CCl4);
- Maltenes, soluble in all solvents listed above, but identifiable by chromatography and infrared spectroscopy.

Carbenes and **Carboids**, are compounds that are not usually present after the oil distillation and they are formed in any heat treatment of the bitumen. Their absence is still a prerogative of pure bitumen. In fact, bitumen, it is defined as completely soluble in carbon disulfide, and a possible presence of carboids, higher than the prescribed limit set by the standard of 1% by weight of bitumen, is considered intolerable, causing removal of that bitumen for road paving use.

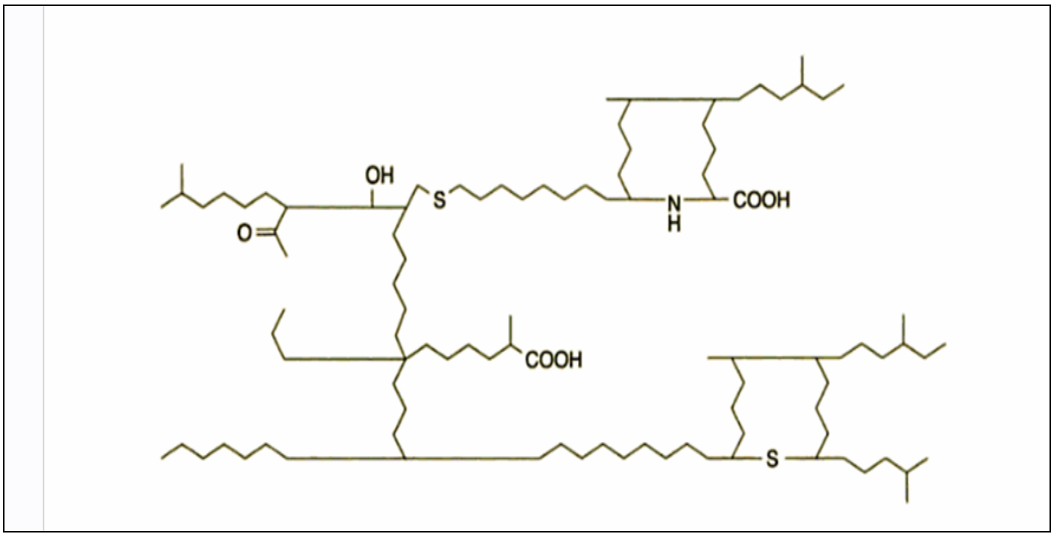


Figure 2.12. - Possible structure of the Asphaltenes (Read & Whiteoak, 2003).

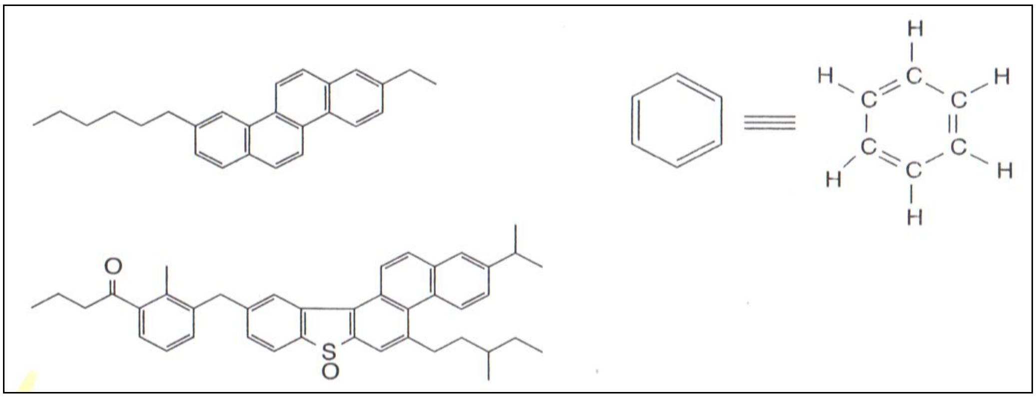


Figure 2.13. – Possible structure of Aromatics (Read & Whiteoak, 2003)

Asphaltenes (Fig. 2.12) present in the bitumen from a 5% to 25% by weight, are complex mixtures of hydrocarbons, consisting mainly of:

- condensed aromatic compounds, in which it is also found the presence of oxygen, nitrogen, sulfur and metals (V, Ni etc.), together with condensed rings and alkyl chains with up to thirty carbon atoms;
- heteroaromatic compounds containing sulfur and nitrogen in pyrrole or pyridine rings.

They are the specific components of the bitumen and represent, thanks to their properties and structure, the viscous part of the binder. Their high molecular weight (generally much higher than 2000 a.m.u. (atomic mass units), up to values of hundreds of thousands) makes them the fraction richest in macromolecules within the bitumen. They have structural configurations of the aromatic type (where the aromaticity means the lowering of ground state energy of the molecule), they are solid at room temperature with grainy, black-brown aspect. The effectiveness of their identification depends on the type of solvent used (Siracusa et al., 2010). Usually, also present within the asphaltenes are: amines and amides, oxygenated compounds (ketones, phenols or carboxylic acids), nickel and vanadium complexed with the porphyrin nitrogen systems.

Maltenes, are dividable into two subgroups:

- Resins
- Oil fraction, consisting of Aromatic and Saturates

Resins are the most polar compounds. Structurally very similar to asphaltenes, they are very viscous at room temperature, dark brown in color and with remarkable adhesive properties. Within the bitumen, resins work as dispersing agents of the macromolecular structures of asphaltenes. Compared to these, resins have a smaller molecular weight, estimated between 500 and 1000 a.m.u., but a much higher ratio of carbon aliphatic/aromatic carbon (C_{alif} / C_{arom}) due to the increased number of paraffinic chains. Some scientists assume that asphaltenes originated in nature by the oxidation of the resins.

*Oil fraction***,** is defined as such because of their high boiling points. It consists mainly of naphthenic and aromatic rings connected by long aliphatic chains. In fact, it is possible to distinguish two subgroups:

Aromatics, or aromatic oils (Fig.2.13), are a viscous brown liquid fraction, which contains several compounds with naphthenic and aromatic rings. Their molecular weight is between 500 and 1000 uma;

Saturates, or saturated oils (Fig.2.14) is viscous liquid fraction of yellowish-white color. They consist mainly of long-chain saturated hydrocarbons (some with branches), and cycloparaffins (naphthenes), with molecular weights ranging from 500 to 1000 a.m.u.
At room temperature, they are in the liquid state and are chemically low reactive. Their C_{alif} / C_{arom} ratio is definitely in favor of paraffins.

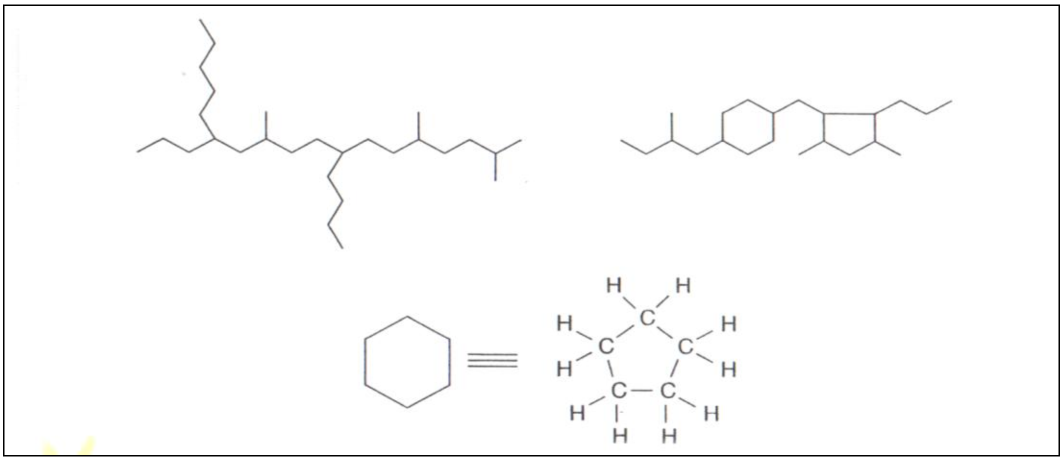


Figure 2.14. - Possible structure of Saturates (Read & Whiteoak, 2003)

The above mentioned fractions are contained in the bitumen approximately in the following percentages which can vary depending on the origin of crude oil and the distillation process (Siracusa et al., 2010):

Asphaltenes	%p	5 - 25;
Resins	%p	10 - 25;
Aromatics	%p	40 - 70;
Saturates	%p	5 - 20.

2.2.4 SHRP findings on bitumen chemistry

The colloidal model (§2.2.3) proposed by Nellensteyn and modified by Mack, Pfeiffer and Saal, and later investigators enjoys widespread support among petroleum scientists. There is a great deal of evidence in favor of its validity, for this reason it is used, throughout this research, to explain the peculiar features of bitumen properties.

It is important to recognise also the work conducted within the “Binder Characterization and Evaluation” section of the SHRP Project (SHRP reports 367 & 368, 1994), in which some problems of the colloidal model are highlighted and a new model and analysis techiniques are evaluated to better correlate the bitumen chemistry with its field-performances.

Microstructural model

In the colloidal model , the asphaltene content of a bitumen was an important indicator. Bitumen with large asphaltene concentrations, designated "gel" types, tended to behave differently from bitumens with few asphaltenes, designated as "sol" types. However, it was also observed that many bitumens are of an intermediate nature. Although it was established that asphaltenes are the principal viscosity-enhancing components of bitumen (and disproportionately influence other properties as well), it was observed that equiviscous bitumen, at a given temperature, could have varying asphaltene concentrations. Similarly, bitumens with identical asphaltene concentrations could have different rheological properties. Failure modes of bitumens (when mixed with aggregates) such as low-temperature cracking propensities, stripping behaviors, tendencies to rut, and susceptibilities toward oxidative aging could not be predicted except in general ways.

Therefore, within the “Binder Characterization and Evaluation” section of the SHRP Project (SHRP reports 367 & 368, 1994), scientists considered necessary to validate a better model of bitumen structure, which better relates bitumen chemical properties to performance-related physical properties, was required than was offered by the colloidal model.

A model based on that suggested by Pfeiffer and Saal (1940), but with modifications, was described to account for bitumen behavior. The authors designate this model the *microstructural model.* It was suggested that bitumens consist of a solvent phase composed of relatively aliphatic, non-polar molecules that are low in heteroatoms (save perhaps sulfide and thiophenic sulfur and ether and ester oxygen) and that this phase disperses *microstructures* (structural units formed from molecular associations) consisting of more polar, aromatic, asphaltene-like molecules. Many of the molecules composing the dispersed phase were assumed to be polyfunctional and capable of associating through hydrogen bonds, dipole interactions, and π-π interactions. It is these interactions that allow formation of primary microstructures. It was speculated that the primary microstructures could associate into three dimensional networks under the proper conditions. These networks, and the primary microstructures themselves, may be broken up by heat and shear stress. It was suggested that three-dimensional structuring is suppressed by an effective solvent phase but promoted by an ineffective solvent phase. Oxidative aging increases the number of polar molecules that become part of the dispersed phase, leading to more structuring, but also increases the solvent power of the dispersing phase (Anderson et al., 1994 - SHRP 367).

The above model rationalises important physical properties of bitumens, such as non-Newtonian rheological behavior, temperature dependence of viscosity, molecular structuring that causes isothermal reversible age hardening (steric hardening), and many others. According to the model, oxidative aging is rationalised by the buildup of polar molecules as a result of the reaction of oxygen with reactive molecules, many of which are nonpolar, and by the loss of low molecular weight, nonpolar molecules by volatilization. The result of this process is a decrease in bitumen solvent moieties and an increase in molecular associations to the point that remaining reactive molecules are less accessible to oxygen at any given temperature. Details of the model had not been quantified to the extent that a given value of some structural property may be correlated with a certain range of physical properties. The model proposed is descriptive, not quantitative (Anderson et al., 1994 - SHRP 367).

Two of the most fundamental chemical properties of any organic substance are molecular weight and chemical functionality. Many physical properties, particularly rheological properties, are in theory functions of molecular weight and (for complex mixtures) molecular weight distribution. Chemical functionality determines the extent of intermolecular associations; it therefore influences effective molecular weights, as distinct from true molecular weights, of organic materials. Hence, chemical functionality governs those physical properties that depend on effective molecular weight. Chemical functionality also influences aging and stripping behaviors. Therefore, within the SHRP project not only the model was considered improvable. Indeed, to better evaluate the implications of the microstructural model, other techniques (in addition to asphaltene precipitation) that should be able to separate the components of bitumens into distinct chemical fractions and into fractions of differing molecular sizes, need to be investigated.
The microstructural model of bitumen structure postulates that the more polar, aromatic components of bitumens engage in extensive associations at bitumen service temperatures. Therefore, in the native state, the dispersed associated structural units will be of larger molecular size than the solvent components. It should be possible to separate the two moieties by techniques that separate mixtures according to molecular size. During such a separation, the fundamental bitumen structural units must be bonded strongly enough that they will not be broken up. A candidate technique for this objective is SEC. Because the dispersed associated materials are believed to be significantly more polar than materials that compose the solvent, it must also be possible to separate the two components by techniques that effect chemical separations. Two such candidate techniques are ion exchange chromatography (IEC) and conventional absorption liquid chromatography (LC). If the model is correct, materials isolated by all techniques that correspond to either dispersed or solvent moieties should be similar in properties. If the separations cannot be made, the model is incorrect or needs revision. Inability to perform an effective SEC separation would indicate that association forces are much weaker than predicted. Inability to make meaningful IEC or LC separations would indicate that the residua are more homogeneous than the model will allow.

The technique of ion exchange chromatography (IEC) had been shown to provide good separations of petroleum fractions into neutral, acidic, and basic components, but had only been used in one bitumen study. The advantages of the technique were that neutral materials free of polar heteroatoms could be obtained, and that acidic and basic species could be separated. These results cannot be achieved by asphaltene precipitation.

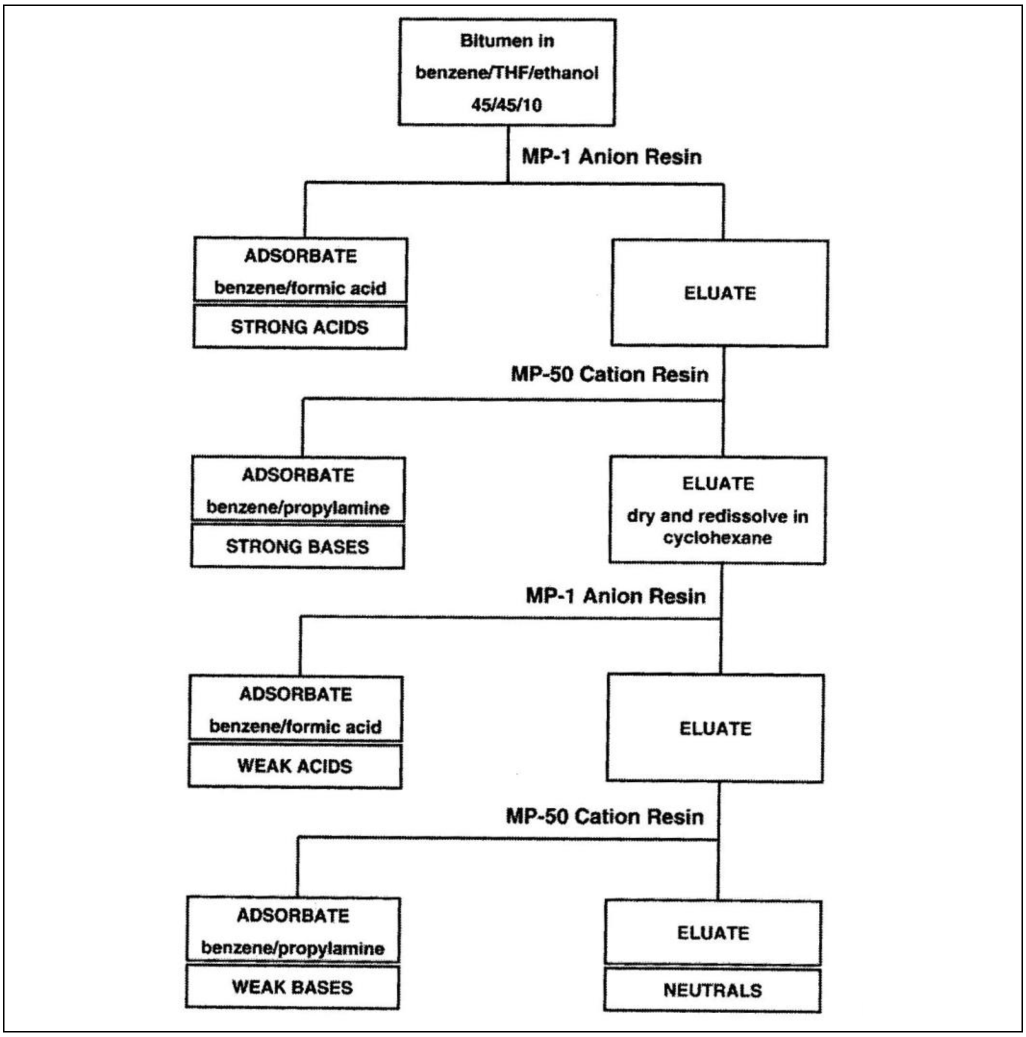


Figure 2.15. Separation of bitumen in strong and weak acids, strong and weak bases and neutrals trough IEC (Anderson et al., 1994-SHRP 367)

IEC fractions

Ion Exchange Chromatography (IEC) gives a complementary picture of bitumen chemistry and has found increasing interest in the past 20 years. It separates bitumen into five fractions corresponding to strong and weak acids and bases, and neutral components, but the recovered fractions do not exhibit the progressive range of properties found in the SARA fractions. It therefore proves more complicated to understand bitumen structure

based on these IEC fractions. They are however of great interest when the chemical and interfacial properties of bitumen are studied. Bitumen components were separated into IEC fractions starting from the pioneering work of Boduszynski and co-workers in 1977. (Boduszynski et al., 1997) The most used set-up however is the one developed by SHRP researchers (Lesuer, 2009). It allows to separate bitumen components into strong and weak acids, strong and weak bases and neutral fractions (Fig. 2.15). In order to separate amphoteric species, a second set-up was proposed by SHRP researchers, as pictured in Figure 2.16. It uses only cyclohexane as the solvent for bitumen. With cyclohexane, both amphoterics and bases adsorb into the cation resin. Amphoterics and resins are the separated though the anion resin. (Fig.2.16).

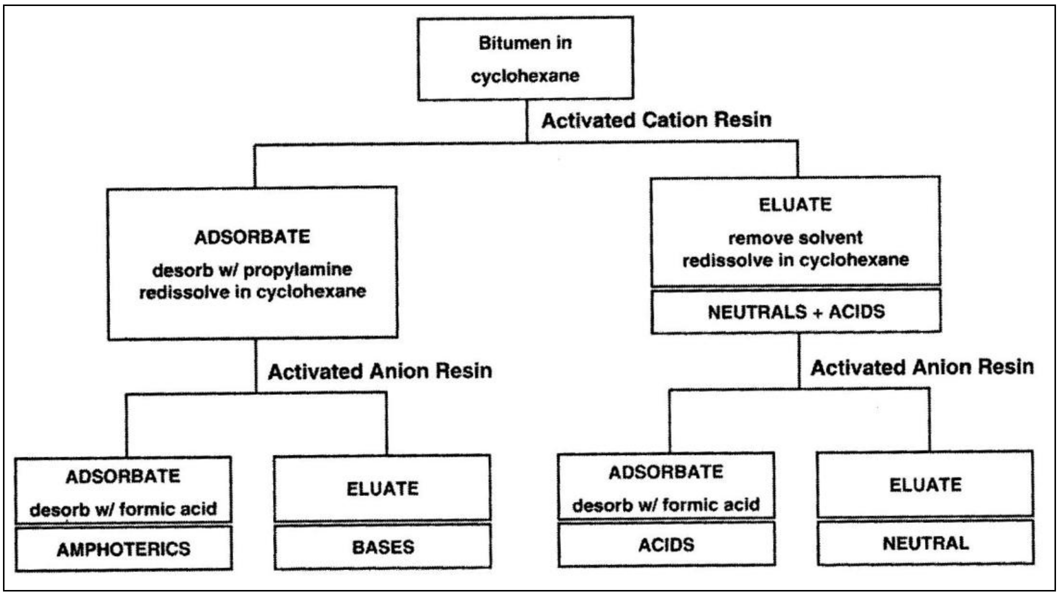


Figure 2.16. Separation of bitumen in acids, bases, amphoterics and neutrals trough IEC (Anderson et al., 1994-SHRP 367).

Combining the two above set-ups, it is possible to entirely characterise the bitumens and comparisons with the standard SARA analysis can be made (Fig.2.17).

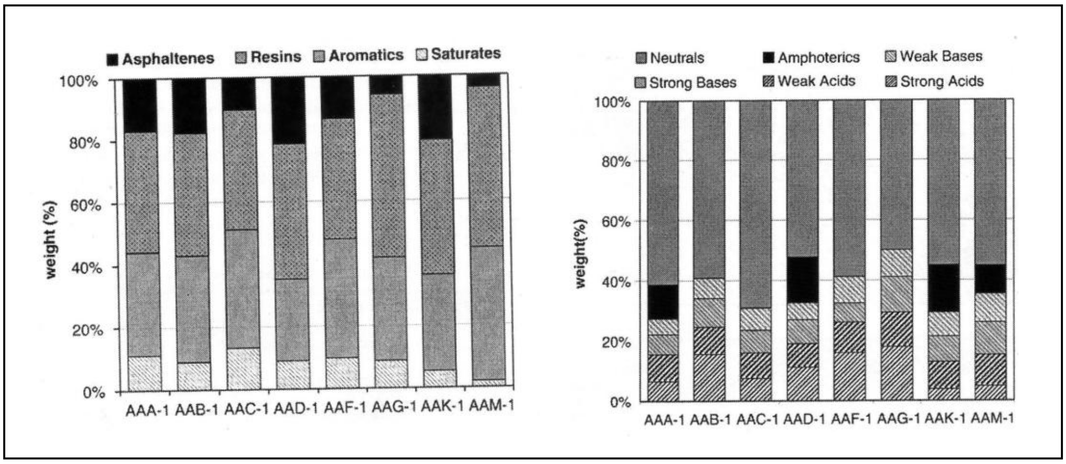


Figure 2.17 Separation into SARA and IEC fractions of some SHRP bitumens. Amphoteric were quantified for only 4 of them (after 24 Lesuer)

Given that the quantity of neutral compounds amounts to tipically 60 wt% of the total bitumen, this strongly suggests that the acidic, basic or amphoteric species are distributed mostly between the resins and the asphaltenes. The strong acids contain most of the polar groups, the weak acids and bases are enriched in sulfoxides and ketones. The neutral fraction is almost free of polar groups. Neutral fractions are liquid, The amphoteric fraction is a black friable solid and therefore resembles asphlatenes. Base fractions form a tacky solid resembling resins. (Lesuer, 2009)

2.2.5 Relation between chemistry and performance of bitumen

The behavior of bitumen, depending on its composition is a very complex problem and the main difficulty is that it is difficult to correlate their physical and mechanical properties to the nature and proportions of the constituents. Asphaltenes, resins and oils can be combined into structures that are stable, depending on the relationships that lie between them. Oils, since they are the dispersing agent, must have good solvent power with respect to asphaltenes. The resins are the determining factor for the stability of the system, having characteristics similar to both oils and asphaltenes (Siracusa et al., 2010). The macroscopic behavior of each component due to tis chemical properties have different effects:

- Asphaltenes, are responsible for the properties of consistency, resistance to mechanical stress and adhesion of bitumen;
- Resins give elasticity and ductility (being the "bridges " of the structure);
- Oils provide fluidity and are responsible of the flow properties of the bitumen, which is essential to effectively and quickly cover the stone that forms, together with the binder, the asphalt for paving.

Other researchers (Read & Whiteoak, 2003) have verified the following results: by holding the asphaltene content constant and varying the concentration of the other three fractions, it has been demonstrated that:

- increasing the aromatics content at a constant saturates to resins ratio has little effect on rheology other than a marginal reduction in shear susceptibility;
- maintaining a constant ratio of resins to aromatics and increasing the saturates content softens the bitumen; and
- the addition of resins hardens the bitumen, reduces the penetration index and shear susceptibility but increases viscosity
- rheological properties of bitumen depends strongly on the asphaltenes content. High asphaltenes content means high viscosity and, usually, high softening point

In addition, it has to be underlined, that physical behavior of bitumen is closely related to its production process. Some post-distillation processes are designed precisely to alter the chemical fractions of the binder, according to the specific requirements.

Suffice it to say that to produce a “harder” bitumen (i.e. with the lowest penetration index) the most volatile fraction, composed of saturated and aromatic fraction, has to be removed. This is done by increasing the temperature and / or the degree of vacuum in the distillation column. A hard bitumen has a higher content of asphaltenes than a "softer" grade although originating from the same crude oil.

By considering the previously introduced oxidized bitumen (§2.1), the paraffin component is not changed significantly by the process of oxidation, since it is virtually inert; resinous and aromatic fractions instead, react with oxygen to form asphaltenes. The final product, if compared to the initial bitumen, has got a higher content of asphaltenes and about the same amount of saturated fraction of departure. An oxidized bitumen has a higher content of asphaltenes than a bitumen with the same penetration grade, obtained from the same crude through vacuum distillation.

SARA indices

In order to evaluate the relationship between the chemical composition and the physical properties of bitumens, and to assess the stability of this system, there are few key parameters to control: the ratio of aromatics to saturates, the ratio of resins to saturates and that of resins to asphaltenes. When these ratios decrease, asphaltene micelles will coalesce and form larger aggregates. These two ratios are expressed in terms of two indices: the *asphaltene index* and the *colloidal index.*

Asphaltene Index, I_A: This is the changing rate of asphaltene content and it is calculated using n-heptane asphaltene precipitation.

$$I_A = \frac{Asphaltenes + \mathrm{Resins}}{Aromatici + \mathrm{S}aturates}$$

A linear relationship between asphaltenes content and the index I_A is usually recorded, whilst the same index decreases with the increase of the resins content (Oyekunl, 2005).

Several studies (Yang et al.,2003; Baginska & Gawel, 2004, Oyekunl, 2005) have demonstrated that the most suitable parameter to describe the stability of the colloidal system bitumen is the following colloidal index:

Colloidal Index, I_C: introduced by Gaestel and co-workers (Gaestel et al., 1971) is the dispersing capability of maltenes to asphaltenes. It is also evaluated using n-heptane asphaltenes.

$$I_C = \frac{Asphaltenes + \mathrm{S}aturates}{Aromatici + \mathrm{Resins}}$$

The colloidal index typically ranges from 0.5 to 2.7 for current road bitumens. A higher colloidal index means that the asphahenes are more peptized by the resins in the oil based medium (Loeber et al., 1998). The index value grows proportionally with the aging of the bitumen. Indeed, a typical behavior of a dispersed system of type SOL shows a $I_c < 0.7$, with ageing this evolves to a marked character GEL having a $I_c > 1.2$ (Leseur, 2009).

An interesting interpretation of the colloidal index is given by its reciprocal which is called coefficient of dispersion "X" and is equal to:

$$X = \frac{Aromatics + \mathrm{Resins}}{Asphaltenes + Saturates} = \frac{1}{I_C}$$

This kind of representation gives the possibility to compare the resin/(asphaltene + saturate ratio) with the aromatic/(asphaltenes + saturates) ratio, and at the same time obtaining intermediate straight lines (isolines) characterised from having a constant slope equal to $1/I_c$.

2.3 Grading and Specifications

In the history of engineering use of bitumen, before introducing performance-related concepts, various systems were developed in order to describe the physical properties and rheology of bitumen at service temperatures. All of them were based on simple empirical tests:

- Fraass breaking point: brittleness range,
- Penetration: semi-solid range,
- Softening point: beginning of fluidity range,
- Viscosity: fluidity range

Frass breaking point test. It is the temperature at which bitumen first becomes brittle (as indicated by the appearance of cracks) when a thin film of bitumen on a metal plaque is cooled and flexed under specific conditions.

Penetration test. The Penetration is a measure of the consistency of the bitumen expressed as the distance in tenths of a millimetre (decimillimetre) that a standard needle is allowed to penetrate vertically into a sample of the bitumen, under a specified load and loading time, at a fixed temperature of 25°C. Therefore the greater the penetration of the needle the softer the bitumen and vice versa. The Penetration test can he considered as an indirect measurement of the viscosity of the bitumen at a temperatttre of 25°C.

Softening Point test. The Ring and Ball Softening Point test is an empirical test used to determine the consistency of a bitumen by measuring the equiviscous temperature at which the consistency of the bitumen is between solid and liquid behaviour. Therefore, regardless of the grade of the bitumen, the consistency will be the same for different grade bitumens at their respective Softening Point temperatures.

Viscosity. It is the fundamental characteristic that defines the flowing properties of a binder. Within traditional systems it has been defined and measured in two ways (Read & Whiteoak, 2003):

- absolute or dynamic viscosity, measured in Pascal seconds, is the shear stress applied to a sample of bitumen in pascal divided by the shear rate per second; 1 Pa s=10P(poise). The absolute viscosity of a bitumen can be measured using a sliding plate viscometer.
- kinematic viscosity, measured in units of m^2/s, or more commonly mm^2/s; 1 mm^2/s=1cSt (centistokes). It is measured using a capillary viscometer.

The two viscosities are related by the equation:

kinematic viscosity = dynamic viscosity/density

Temperature susceptibility. Temperature susceptibility is defined as the rate at which the consistency of bitumen changes with a change in temperature. Traditionally it is possible to predict this property by assessing the softening point at high temperatures and the fragility point at lower temperatures. The window between the two extremes is called the service temperature of the bitumen with the two extremes being dependent on the crude source and bitumen grade. Should the binder be exposed to temperatures above the softening point bleeding/rutting could occur and below the fragility point, cracking may be observed (Fig. 2.18).

The Penetration Index (P.I.) (Pfeiffer & van Dormal, 1936), is probably the most used method to predict temperature susceptibility of a selected binder. Considering that Penetration value (pen) of 800 corresponds to the Penetration at Softening Point temperature (SP) for low wax content bitumens (maximum wax content of 2 percent), and assuming that the Penetration test temperature will be 25 °C, the P.I. can be obtained from the following equation:

$$PI = \frac{1952 - 500 \log \mathrm{pen} - 20 \cdot \mathrm{SP}}{\mathrm{PI} - 50 \cdot \log \mathrm{pen} - \mathrm{SP} - 120} \tag{3.5}$$

According to Roberts (Roberts et al., 1991), PI values for most good paving binders are between +1 and –1. High temperature susceptibility occurs when the binder has PI below –2.

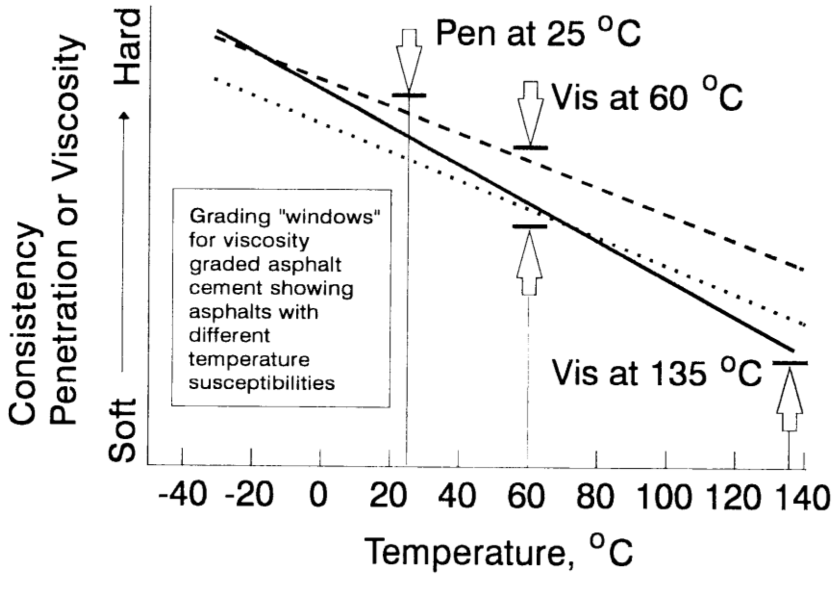


Figure 2.18 – Typical viscosity of a binder over its working temperature range.

2.3.1 Traditional grading systems

For many years, the physical properties and rheology of bitumen at service temperatures, has been adequately characterised and/or predicted by the values of simple traditional tests as penetration and softening point and also by measuring its viscosity (§3.2.1).

The two most common bitumen grading systems were the *penetration-graded* and *viscosity-graded* systems, both of them base on the empirical tests explained before.

The primary purpose of these specifications was to grade bitumen according to its consistency, so do not address specific distress modes or ensure long term field performance. Examples of bitumens as graded by the penetration and viscosity grading system are presented in Table 2.1

Table 2.1. Penetration and viscosity graded bitumens (Airey, 1997)

Penetration grade	Penetration @ 25°C (dmm)	Viscosity grade	Viscosity @ 60°C (dmm)
40/50	40-5-	B24	170-300
60/70	60-70	B12	105-165
80/100	80-100	B8	55-100
150/200	150-200	B4	25-50

These specifications have at times been modified to relate the specification criteria to field performance, but these modified specifications still tended to be largely based on empirical parameters, such as Penetration, ductility and Fraass breaking point. The result was that it was still difficult to reliably relate the specification criteria to pavement performance. The traditional grading systems cannot therefore completely describe the viscoelastic properties of bituminous binders, which are needed to relate fundamental physical binder properties to performance.

2.3.2 Performance-related grading system

Traditional grading systems cannot provide a proper rheological evaluation of bitumen. Moreover, the increasing use of polymer modified binders required the development of new technology as the conventional bitumen test procedures were proving to be inadequate.

Based on these considerations, research in pavement engineering has redefined the concepts underlying the mechanical characterization of binding to a performance-related type of classification. This is addressed through a system based on the determination of performance-related properties, which are characteristic parameters theoretically related with the performance exhibited by the pavements in service. This was made possible by the development and widespread use of equipment (§ 3.3.1), that overcome limitations in traditional tests (§ 3.2). which have been developed, and used for decades, in the study of un-modified bitumens and therefore unsuitable for a performance evaluation of modified bitumen.

Primary pavement distress mechanisms

In order to meet the requirements of performance-related specifications, it is fundamental to identify the distress mechanisms that are critical to field performance, select and develop material response parameters that relate to the critical distress mechanisms, and incorporate these response parameters into specification-type test methods and specification criteria. For a performance-related specification, indeed, it is essential that the specification properties be fundamental material properties so that the properties can be related in a mechanistic manner to the pavement response and, in turn, to pavement performance (SHRP report 367, 1994).

The three primary methods of pavement distress are:

High temperature permanent deformation. The majority of deformation defects result from the plastic deformation of the surface course or the surfacing. This can occur under the high shear stresses imposed by braking, accelerating or turning traffic. The primary factor influencing plastic deformation is the composition of the mixture. Plastic deformation is greatest at high service temperatures, for which 60°C may be taken as a maximum ins situ temperature (Read & Whiteoak, 2003).

Load-associated fatigue cracking. Fatigue is the phenomenon of cracking under the repeated application of a stress that is less than the tensile strength of the material. When a wheel load passes over a point in an asphalt pavement, the pavement flexes and a tensile strain is induced at the underside of the base layer. Continuos flexure and relaxation over many years produces the possibility of fatigue cracks initiating at the underside of the asphalt base and propagating upwards. The fatigue resistance of a bituminous mixture is especially sensitive to binder volume. The simplest means of increasing the predicted fatigue life of the bituminous pavement is to construct the pavement using binder-rich lower asphalt layer (Read & Whiteoak, 2003).

Thermal cracking. Cracking that results from extreme cold is generally referred to as low-temperature cracking whereas cracking that develops from thermal cycling is normally referred to as thermal fatigue cracking. Thermal cracking will occur when the bitumen becomes too stiff to withstand the thermally induced stress and it is related to the coefficient of thermal expansion and the relaxation characterisitics of the mixture.Both these properties are related to the nature of the bitumen. The general mechanism responsible for these two forms of cracking is considered to be similar. The main differences are (Read & Whiteoak, 2003):

- Low temperature cracking is a single event phenomenon that is the result of the full depth of asphalt being put into thermal tension under conditions where stress relaxation cannot occur;
- Thermal fatigue cracking is more dependent on the properties of the surface course material, and cracks first have to initiate at the surface and propagate though the surface course before the affect the lower asphalt layers.

Of the listed above, thermal cracking is predominantly found in countries with very cold winters (more than 15 degrees under zero), therefore, it is of marginal relevance in most of Europe. In addition, to improve the mechanical properties of permanent deformation and fatigue resistance, it is essential that bituminous materials are resistant to the effects of the environment. This phenomenon is termed “durability”, and it is concerned with the resistance of the bituminous material to two other fundamental mechanism (Airey, 2002):

Oxidative Ageing (bitumen hardening). When exposed to the atmosphere in the form of film, bitumen loses its initial softness becoming gradually a fragile substance. The mechanism is complex because of the complex nature of the bitumen. The process is difficult to study under real conditions because road traffic with the trickle of oil, gas oil and wax from the tire pollute the asphalt. However, the study in the laboratory, under controlled conditions, showed that the action of the atmospheric oxygen (oxidation), enhanced by solar radiation, is the main cause of degradation, followed by the evaporation of volatile components (loss of volatiles), from the re-orientation of the bitumen molecole and slow crystallization of the waxes at ambient temperature(Steric or physical hardening) and finally from the movement of the oily components that exude from the bitumen into the mineral aggregate (exudative hardening).

Moisture damage (water damage). Durability of a pavement is strictly related also to the possibility of being in contact with water which can be resposnisble of two different damage phenomenon:

- Failure due to hydraulic pressure: Once water has entered a road pavement, water damage is initially caused by hydraulic pressure, i.e. vehicles passing over the road pavement impart considerable sudden pressure on the water present in the road pavement, this pressure forces the water further into the road fabric and breaks it up, this process can be very rapid once it begins. Water that has entered the road pavement and is subject to the process of freezing (expansion) and thawing during the winter also brings about the swift failure of the road pavement. Eventually the water will descend to the subgrade layer below the road pavement and weaken this layer and deep seated failure of the road will begin (Highway Maintainance.com,2010).
- Failure due to binder stripping: Most aggregates have a greater affinity for water than they do bitumen, and with the presence of water and movement of the aggregate it is quite possible for the binder film on the aggregate particle to be broken and water to come in to contact with the aggregate surface. Once the integrity of the binder layer has been broken it will depend upon the chemical nature of the aggregate particle and the viscosity of the binder as to how long it will be before stripping of the aggregate particles becomes an engineering problem. Depending on the viscosity of the binder and the thickness of the binder film surrounding the aggregate the stripping of the bitumen will occur hardly at all, fairly slowly or quite quite quickly (HighwayMaintainance.com,2010).

American experiences: SHRP and NCHRP

Although the international literature is rich in contributions that testify the new trend in the experimental analysis of binders, two projects deserve a special mention: SHRP: Strategic Highway Research Program, initiated in the USA in 1987 and ended in 1993, and NCHRP (National Cooperative Highway Research Program). This two projects leaded to the establishment of new equipment, test protocols and criteria for selection of asphalt binders based on their expected performance in work. Researchers of SHRP and NCHRP were searching for more fundamentally sound measures of the rheological properties of bituminous binder and this efforts leaded to the definition of a technology called "Superpave" (Superior PERforming PAVEments.).

Superpave, is a system of standard specifications, test methods, and engineering practices that enable the appropriate materials selection and mixture design of Hot Mix Asphalt (HMA) to meet the climatic and traffic conditions of specific roadway paving projects. Through use of this system, highway engineers and constructors can build pavements that last longer, require less maintenance and have a lower life-cycle cost than pavements designed using previous engineering methods. The utility of this method has been demonstrated, and it now is accepted within the bitumen industry.

SHRP Project. The Strategic Highway Research Program (SHRP) was originally conceived in response to a perception within the highway industry that, after the Arab oil embargo of 1972, the quality of paving-grade bitumen had in many instances deteriorated to an unacceptable level. This perceived deterioration was, and still is, cited as the cause of an unacceptable rate of early pavement failures. Because of this perception, the primary objective of the bitumen-related portion of SHRP was to develop performance-related specifications for bitumen cement binders and bitumen concrete mixtures that protect against early pavement failure. The existing specification tests for bituminous binders, and their associated test methods, are not performance-related and therefore cannot be used either to relate the chemistry of bitumen to performance or to develop performance-related specifications that warrant pavement performance. Indeed, performance-related physical and chemical test methods are needed to characterize bituminous binders to properly develop performance-related specifications and to ascertain the quality of current paving-grade bitumens (SHRP report 367, 1994).

NCHRP Project. The SHRP carried out a major research program to develop the Superpave performance-based specifications and test methods for bituminous binders and similar tests and a mix design practice for HMA mixes. One goal of this program was to make the specifications and tests “transparent” to the use of modified binders—that is, to ensure that the specifications would accurately measure the enhanced performance characteristics of the modified binders. However, the SHRP bitumen research was carried out almost exclusively with unmodified bitumens, so the applicability of the Superpave specifications and test methods to modified binders was not validated.

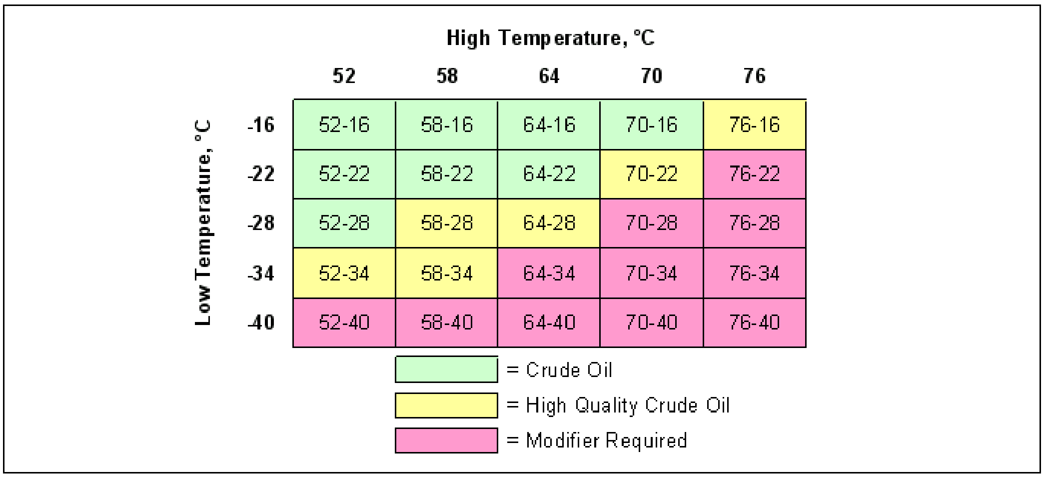
In practice, modified bituminous binders graded according to the requirements of AASHTO MP1 do show marked improvements in selected performance characteristics compared with neat bitumen. However, users and producers of modified bituminous binders remain concerned that the current specification and test methods do not fully measure the performance enhancement contributed by the modification.

A new project called NCHRP Project 9-10, “Superpave Protocols for Modified Asphalt Binders,” was undertaken from various American researchers in order to recommending changes to AASHTO MP1 (Fig.B.1), and its supporting test methods, to fully characterize modified bituminous binders and validating those recommendations through laboratory performance testing of modified HMA. The research team found that the current AASHTO MP1 specification does not adequately characterize the performance of modified bitumens; typically, the binders’potential performance is underestimated. Therefore, new suggested specification parameters and test protocols were developed for three concepts in particluar: permanent deformation, fatigue cracking and low-temperature cracking. In addition, the research developed a practice in the AASHTO format for characterization of modified bitumens and new test methods for storage stability, particulate additive content, and laboratory mixing and compaction temperatures (NCHRP report 459, 2001).

Superpave performance grading system. As mentioned before, one of the main motivation of the SHRP project was to produce pavements which performed well in service (SUPERPAVE). Thereby, one of the results of this project was the “Superpave asphalt binder specifications” which categorises grades of bitumen according to their performance characteristics in different environmental conditions. The specification was intended to control permanent deformation, low temperature cracking and fatigue failure of asphalt pavements. This is achieved by controlling various physical properties measured with the SHRP equipment mentioned above. In this specification, the physical properties remain constant for all grades but the temperature at which these properties must be achieved varies depending on the climate in which the binder is to be used (Shell handbook). Such a fundamental grading system should have the benefit of being applicable to both unmodified bitumens and speciality products such as Polymer Modified Bitumens (PMBs).

Superpave performance grading is reported using two numbers the first being the average seven-day maximum pavement temperature (°C) and the second being the minimum pavement design temperature likely to be experienced (°C). Thus, a PG 58-22 is intended for use where the average seven-day maximum pavement temperature is 58°C and the expected minimum pavement temperature is -22°C. Notice that these numbers are pavement temperatures and not air temperatures (these pavement temperatures are estimated from air temperatures using an algorithm contained in the LTPP Bind program (FHWA website, 2010).

As a general rule-of-thumb, PG binders that differ in the high and low temperature specification by 90°C or more generally require some sort of modification (Fig. 2.19) (PavementInteractive.org, 2010). A detailed description regarding a laboratory optimization of the procedure to grade an unknown binder with the Superpave performance grading system is provided in the Appendix B.



Low Temperature, °C	High Temperature, °C 52	58	64	70	76
-16	52-16	58-16	64-16	70-16	76-16
-22	52-22	58-22	64-22	70-22	76-22
-28	52-28	58-28	64-28	70-28	76-28
-34	52-34	58-34	64-34	70-34	76-34
-40	52-40	58-40	64-40	70-40	76-40

🟩 = Crude Oil
🟨 = High Quality Crude Oil
🟥 = Modifier Required

Figure 2.19. Prediction of PG for different crude oil blends (PavementInteractive.org, 2010)

European experiences: CEN

Current European specifications for bituminous materials are based upon empirical test methods, although the process towards developing performance-realted specifications has been underway for some time. (Southern, 2007). In order to take a systematic approach to this next generation binder specifications, the European bitumen/asphalt industry has made major efforts in recent years to define the requirements for paving binders.

The Comité Européen de Normalisation / European Committee for Standardisation (CEN), formed in the early sixties, was charged with preparing common rules and standards to be used in all member countries to ensure no barriers to trade. As part of that programme, new harmonised European specifications for paving grade bitumens are being developed in two stages:

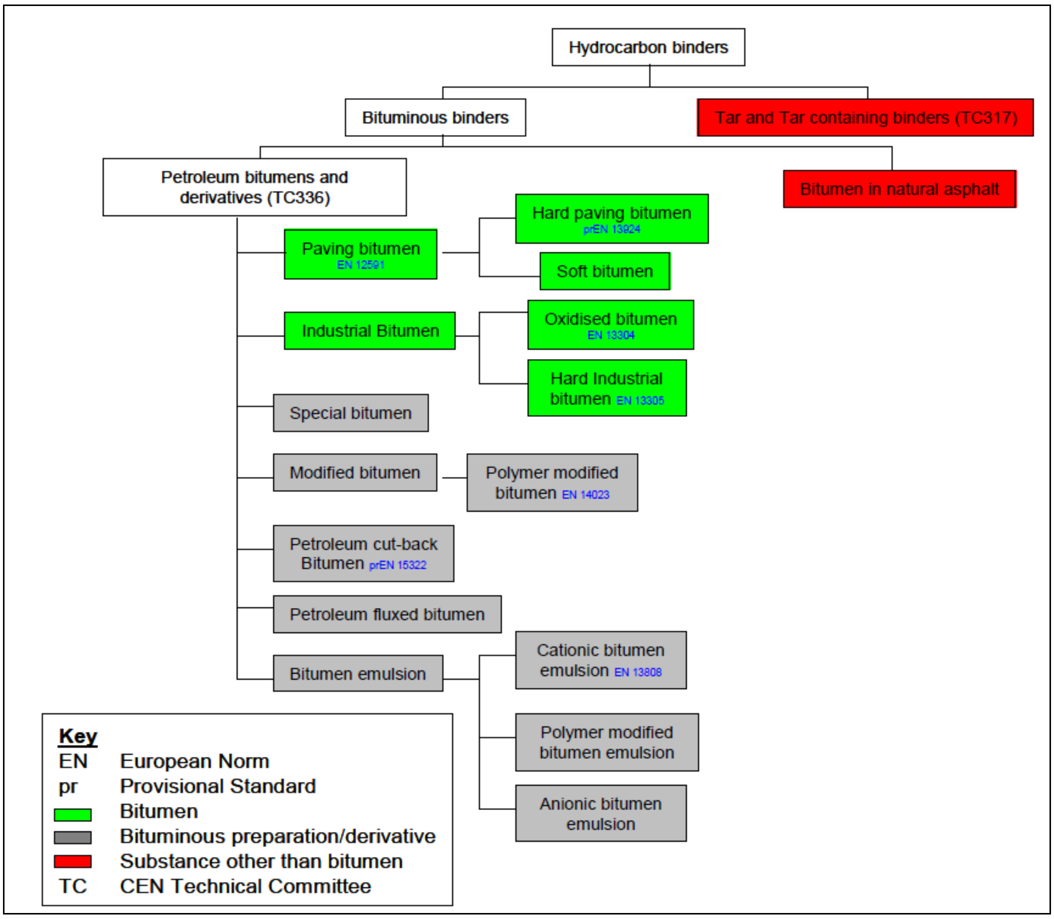


Figure 2.20. Structure of bituminous binders working groups (Southern, 2007)

First Generation (CEN TC19/SC1, since 1990): A first step in harmonising standards for bituminous materials in EU was to ensure that test methods and grades of bitumen & bituminous materials could be specified across all member states. The second step was to produce fully harmonised standards, albeit still based upon existing test methods. This is the stage at which European standards for bitumen and bituminous preparations are currently in the EU. At the time of writing the standards for Paving bitumen EN 12591, Hard paving grade bitumens EN 13924 and polymer modified binders EN 14023 are under revision prior to introduction as harmonised standards (Southern, 2007).
As is the case with many legislative issues the process for harmonisation of standards is highly bureaucratic. Standards are normally produced by technical committees, comprised of representatives nominated by their national standards body (or associate member body). Work items, proposed by working groups (WG's) are approved during plenary meetings and the work is carried out in either task groups (TG's, that report to working groups), or in the working group directly. Shortly after CEN was set up a technical committee responsible for standardising petroleum products was formed; TC19. Some years later a working group was formed to standardise bituminous binders, this was split into 5 groups to standardise different types of binder, ranging from penetration (paving) grade bitumens, through Industrial (oxidised) bitumens, cutback and fluxed binders, bitumen emulsions and polymer modified binders. Today only two working groups are still active; WG1 – Paving bitumens and WG2 – bitumen emulsions, cutback & fluxed bitumens. The structure of the working groups is shown in Figure 2.20.

Second Generation (CEN TC336, since 2000): The next task of the working groups, in order to meet the requirements of the so-called Construction Products Directive (CPD), is to produce "harmonised technical specifications that are performance based". The new standards should reflect the binder contribution to the performance of the asphalt pavement, with the inclusion of existing or new properties and test methods, as appropriate. The overall purpose of the specification system will be to ensure that binders can be evaluated on a fair and comparable basis, that the appropriate binder can easily be selected for a particular application and that the binder can be used with confidence in its quality. Ideally, the system should be suitable throughout Europe, for all types of climate and traffic conditions, for a large variety of pavement applications, and applicable to all categories of binders: conventional, multigrade and modified bitumens. (BiTVal, 2006)

BiTVal Project. The Bitumen Test Validation (BiTVal) project was set up by FEHRL (the Federation of European Highway Research Laboratories) in response to a request from TC 336, together with other stakeholders in the industry to assess the relevance of the results of bitumen tests on the required properties of bituminous mixtures.

It is, of course, recognised that the binder properties alone do not determine pavement performance. Other parameters, such as aggregate characteristics, mixture design, manufacture and laying are also considered as important. A process is being followed to ensure that, for the second generation standards, the performance relationships of a binder property are assessed before a specification is developed. The BiTVal project has been developed to assist that process (Southern, 2007).

The BiTVal project is expected to:

- Deliver the appropriate answers for assessing the suitability of test methods for characterising the relevant performance of related bitumen properties.
- Establish their relevance and correlation to the asphalt pavement performance.
- Give the required level of confidence in the future European specification system.

The first key outputs of the BiTVal project is a database, covering publications of the identified bitumen properties and their relationship to asphalt properties and/or road performance, and a FEHRL report to TC336 WG1, summarising the performance-related aspects for each test method, together with recommendations for their use in the next generation of standards. In the BiTVal project, all the binder tests that might be used by TC336 WG1 have been reviewed together with the conditioning/ageing procedures that might be used to assess binder durability. The BiTVal database has been searched for correlations between all these tests and the following critical performance characteristics, in asphalt mixture tests and/or pavement performance assessments . (BiTVal, 2006):

- Permanent Deformation.
- Stiffness.
- Low Temperature Cracking.
- Fatigue Cracking.
- Adhesion

The overall conclusions in terms of recommendations for a bitumen test to assess the potential asphalt properties are:

- The oscillation ZSV test, which is relatively simple and provides good correlations for permanent deformation.
- The DSR binder stiffness and/or penetration for stiffness, with the DSR test preferred because the penetration test is not suitable for PMBs.
- Either BBR limiting temperature or a DTT parameter for low temperature cracking, with the concept of critical cracking temperature, combining both the BBR and the DTT results, as an alternative for the future.
- The empirical characteristics (such as penetration, softening point and viscosity) and some rheological characteristics before and after ageing (such as RCAT or RTFOT and PAV) remain the best criteria to assess the fatigue of asphalt.
- The approach of using surface energies of materials enables some fundamental insights about adhesion to be gained, although equilibrium in an asphalt mixture is probably never realised.

However, the preferences are conditional and further research is required. These research needs are prioritised as:

- Essential – Oscillation ZSV test (for deformation resistance), critical cracking temperature (for low temperature cracking) and control aggregates (for adhesion).
- Important – Direct tensile test (for low temperature cracking), fracture toughness test (for low temperature cracking), bitumen fatigue test (for fatigue) and relationship with site data (for adhesion).
- Desirable – Creep ZSV/repeated creep tests (for deformation resistance), DSR relationship with site data (for stiffness) and relationship with site data (for low temperature cracking), (BiTVal, 2006).

CEN technical report. CEN/TC336 WG1 produced a CEN Technical Report (TR)11 summarising the status of work towards performance related specifications. The document contains a synthesis of TC 336 WG 1 (Paving bitumens) work on the development of second generation (performance-related) specifications for paving grade bitumens. It will be regularly updated by TC 336 when new information or test methods become available. The TR summarises and illustrates the ongoing work in the standardisation area with reference to the process of developing from traditional “empirical” based specifications to new “performance-related” specifications for paving bitumens, as required by the Mandate M/124.

It was decided that it would be better to maintain such a report as an ‘informative’ document, which can be regularly amended and updated by TC 336 WG 1 as appropriate. The technical report contains a list of candidate test methods for high, medium and low temperature properties as well as ageing regimes (Southern, 2007).

3. Rheology of bituminous binders

Rheology is literally “flow science”. Rheological experiments do not merely reveal information about the flow behaviour of liquids, but also the deformation behaviour of solids. The connection here is that large deformations produced by shear forces cause many materials to flow. All forms of shear behaviour, which can be described rheologically in a scientific way, can be viewed as lying in between two extremes: the flow of idealviscous liquids on one hand and the deformation of idealelastic solids on the other (Mezger, 2002). Bitumen is a thermoplastic material that, under most pavement operating conditions, shows a behaviour which is between these extremes and it is based on the combination of both the viscous and the elastic portion and therefore is called viscoelastic.

3.1 Base theory

3.1.1 Principles of viscoelasticity

In normal conditions, an elastic solid has a defined shape and the application of external forces moves him to a new form of equilibrium. The solid stores all the energy obtained from the work done by external forces and such energy allows the firm to return exactly to its original shape. An ideal solid subjected when stressed deforms elastically: the energy spent in deformation is preserved in the form of elastic potential energy and it is returned when the applied stress is removed. Hooke's law describes the behavior of elastic bodies, for which the stress is directly proportional to the deformation of the material and it is independent of strain rate. The elastic modulus defines the resistance to deformation of the solid and it is a property that depends on the specific material and its thermal history. Hooke's law is valid for both normal stresses and shear stresses (Belincioni et al, 2004):

$$\tau = \mathrm{G} \cdot \gamma \tag{3.1}$$

where:

- τ = stress [Pa]
- G = Shear modulus [Pa]
- γ = strain [m/m]

In contrast, the ideal fluids undergo completely irreversible deformations, in other words, all the energy used to impose the deformation is dissipated as heat and can not be restored by removing the stress (a purely viscous behavior).

Newton's law describes the behavior of purely viscous fluids, for which the stress is proportional to the strain rate and is independent of the strain level. The viscosity of a fluid “η” defines its resistance to the irreversible positioning change of its volume elements, (Belincioni et al, 2004). Hooke’s law is defined as follow:

$$\tau = \eta / \dot{\gamma} \tag{3.2}$$

where:

- τ = stress [Pa]
- η = viscosity [Pa s]
- $\dot{\gamma}$ = strain [m/m]

3.1.2 Linear ViscoElasticity (LVE)

Hooke's law and Newton's law govern the behavior of perfectly elastic and perfectly viscous materials. In nature, of course there are always intermediate behaviors which are between these extremes and they are based on the combination of both the viscous and the elastic portion and therefore are called viscoelastic. The extent of deviation from Newtonian or purely elastic behavior is not an intrinsic property of a material, but depends on the its physico-chemical state. There are two major types of deviations from the purely Newtonian or Hookean behavior:

Non-linear visco-elastic response: deformation in a solid, or deformation rate in a liquid, may not be directly proportional to the applied stress but they may have a more complex dependence.

Linear visco-elastic response: when deformation and deformation rate are directly proportional to the stress, the stress-strain relationship is linear:

$$\tau = \tau_E + \tau_V = G\gamma + \eta\dot{\gamma} \tag{3.3}$$

This simple equation is the constitutive behavior of linear viscoelastic and implies that stress related to strain and strain rate are additives. In most of the materials the linear behavior is obtained with infinitesimal deformation or strain gradients; in the case of “finite” strain or strain-rate, the stress-strain relations are much more complex, because the material exceeds the region of linear viscoelasticity (LVE).

Obviously there is not a value that places the well-defined border between "infinitesimal" and "finite" stress, but it depends on the type of material and its physical and chemical state (eg stress level, temperature, loading time).When infinitesimal strains are applied to solids the validity of Hooke's law extends to most real solids, instead fluids follow Newton's law for infinitesimal strain rate.

3.1.3 Viscoelastic behaviour of bitumen

Bitumen is a viscoelastic material that behaves as a glass-like elastic solid at low temperatures and/or during rapid loading (short loading times – high loading frequencies)

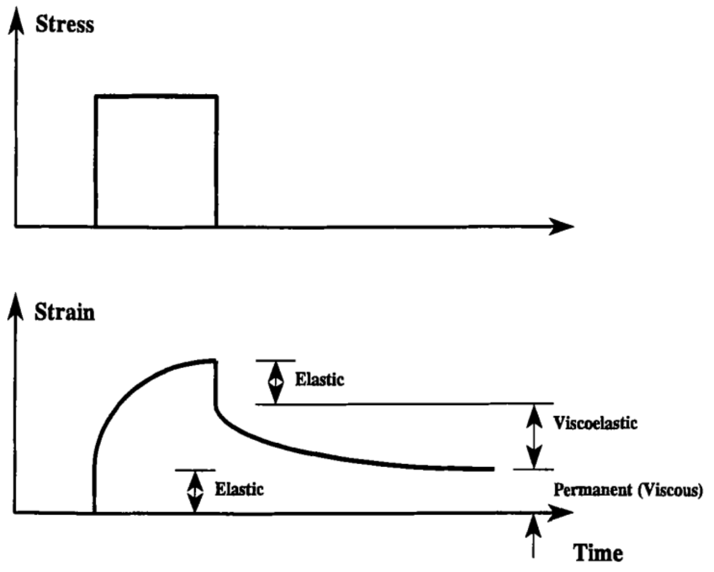


Figure 3.1. Mechanical response of a viscoelastic material (Airey, 1997)

and as viscous fluid at low temperatures and/or during slow loading (long loading times – low loading frequencies). At normal pavement temperatures, the bitumen has properties that are in the viscoelastic region and, as it is possible to see in Figure 3.1, it exhibits both elastic and viscous behavior and displays a time-dependent response.

As mentioned before, the non-linear response of viscoelastic materials, is extremely difficult to characterize in the laboratory and to model in practical enginering problems. Fortunately, under normal pavement operating conditions, in terms of loads and temperatures, bituminous binders can effectively be treated as LVE materials (SHRP report 368, 1994). Linear behavior is fulfilled at low temperatures and short loading times (high frequencies), where the material behaves as an elastic solid. The linearity is also

high temperatures and long loading times (low frequencies) where the material behaves entirely as a Newtonian fluid. It is in the range of moderate temperatures and loading time (field conditions) that non-linearity is prominent (Van der Poel, 1954). It is, therefore, in these conditions that is important, while testing, to ensure bituminous binders to remain within the LVE range by limiting the applied strain, or deformation, within certain boundaries.

According to Ferry (Ferry, 1971) the shape of the linear viscoelastic (LVE) response of a bitumen, including polymer modified bitumens, can be sub-divided into four zones:

- a terminal or flow zone,
- a plateau zone (only present in the case of a network),
- a transition zone, and
- a glassy zone.

The LVE response of bitumen and therefore the shape of the master curve can more generally be divided up or separated into three regions or zones of behaviour:

- At low temperatures or short loading times (high frequencies), bitumen behaves as glassy solid. The stiffhess therefore approaches a limiting value of approximately 1 GPa in shear and 3 GPa in tension-compression or bending. In this region the stiffhess is only slightly dependent on temperature and/or time of loading.

- At intermediate temperatures or loading times (frequencies), bitumen undergoes a gradual transition from glassy to fluid behaviour. This transition is characterised by large amounts of delayed elasticity. The stiffness modulus changes dramatically in this region as a function of temperature and/or loading time.

- At high temperatures or long loading times (low frequencies), bitumen behaves as a viscous fluid. The bitumen is considered to behave as a Newtonian fluid and for low to moderate stresses and strains the shear strain rate is proportional to the shear stress.

The general shape of the master curve of a bitumen is shown in Figure 3.2.

3.2 Performance-related properties

The increasing use of polymer modified binders required the development of new technology as the conventional bitumen test procedures were proving to be inadequate (Collins et al., 1991). One of the reasons for this is that many polymer modified bitumens tend to behave more as a polymer than as bitumen. The ductility, elastic recovery and toughness-tenacity tests are modifications that have been added to the penetration-grade or viscosity-grade specifications in an attempt to relate the specification criteria to field performance, particularly for modified bitumens (Collins et al., 1991). However, there are

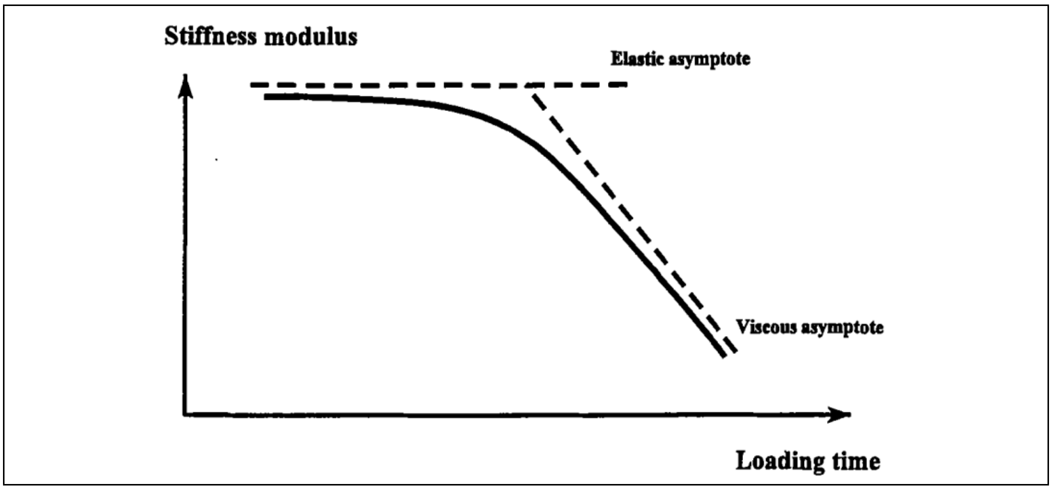


Figure 3.2. Linear viscoelastic response of bitumen

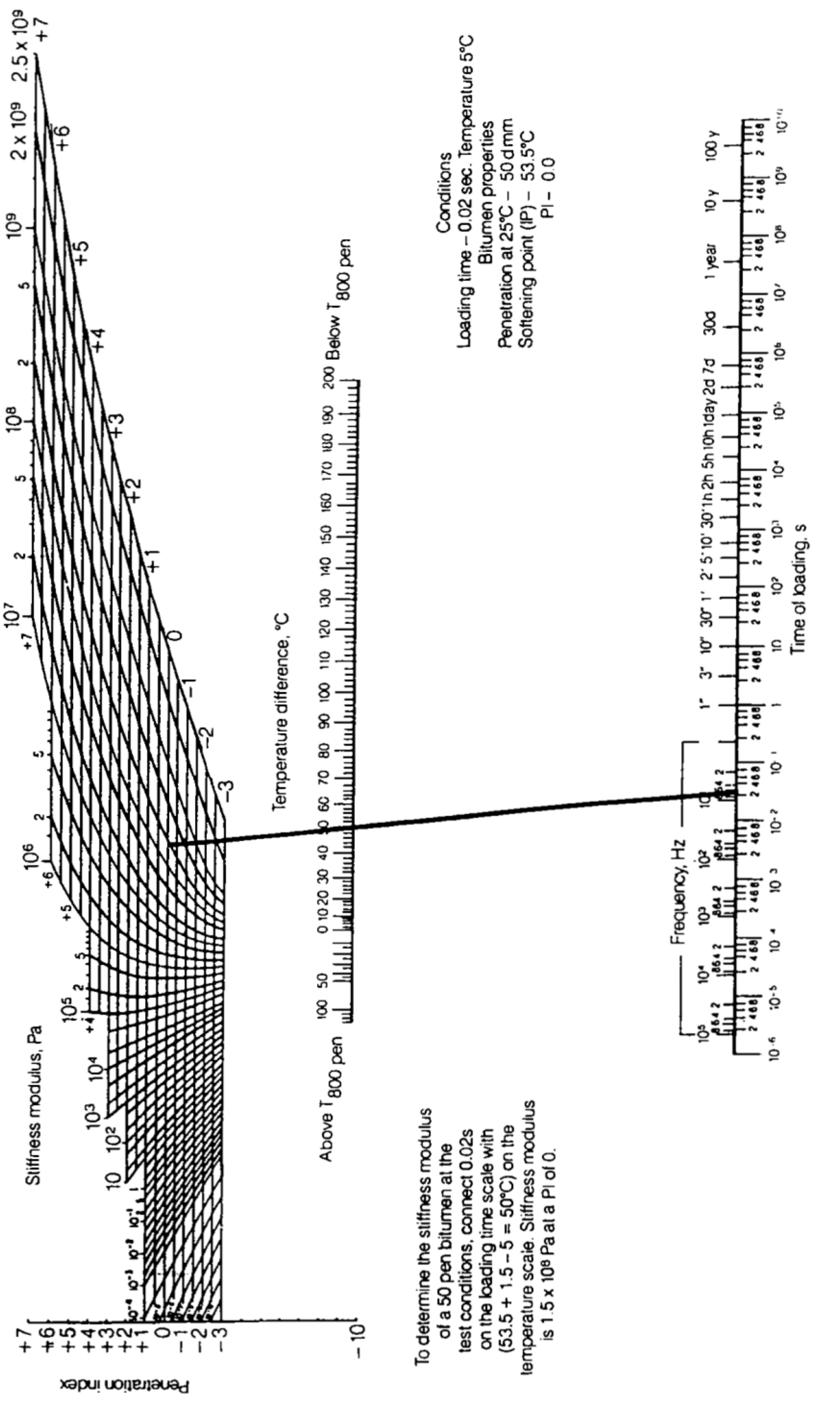
still problems with the use of a modified penetration-ductility specification, since both tests are inappropriate as fundamental measurements of low temperature rheology. This is because the stress fields within the test specimens cannot be defined, the strains developed during the test are very large and vary within the specimen and the stress-strain field cannot be easily modelled or calculated. For a complete description of the mechanical properties of bitumen it is, therefore, necessary to know engineering properties such tensile strength and the stiffness as a function of temperature and rate of loading.

3.2.1 Traditional engineering properties of bitumen

For most normal bitumens the tensile strength at low temperatures is approximately a constant, 4 MPa (Airey, 2002), therefore, to appreciate the mechanical properties of bitumen only the stiffness requires closer consideration.

In 1954 Van Der Poel introduced the concept of stiffness modulus as a fundamental parameter to describe the mechanical properties of bitumens by analogy with the elastic modulus of solids (Read & Whiteoak, 2003). Van der Poel found that due to the special nature of bitumen the value of stiffness is strictly dependent on temperature, T, and loading time, t. Consequently, the stiffness modulus has been defined as follows:

$$S_{t,T} = \frac{\sigma}{\varepsilon_{t,T}} \tag{3.4}$$



Conditions
Loading time – 0.02 sec. Temperature 5°C
Bitumen properties
Penetration at 25°C – 50 dmm
Softening point (IP) – 53.5°C
PI – 0.0

To determine the stiffness modulus of a 50 pen bitumen at the test conditions, connect 0.02s on the loading time scale with (53.5 + 1.5 – 5 = 50°C) on the temperature scale. Stiffness modulus is 1.5 x 10^8 Pa at a PI of 0.

Figure 3.3. Van der Poel's nomograph (Read & whiteoak, 2003)

In order to measure, or better, to predict the Stiffness, Van der Poel developed a simple system that could be used to predict or estimate the stiffness of bitumen using routine, empirical binder tests such as Penetration and the ASTM Softening Point. Van der Poel assumed a more or less hyperbolic shape for stiffness as a function of time. The shape of the master curve is estimated from the Penetration Index and the Ring-and-Ball temperature. Van der Poel concluded that the stiffness of a bitumen depended on:

- Time of loading or frequency,
- Temperature,
- Hardness of the bitumen, and
- Rheological type of bitumen.

The rheological stiffness property of bitumen could therefore be estimated by entering the following information into the nomograph:

- Temperature, ASTM Softening point,
- Loading time, and
- Penetration Index, PI.

Although the van der Poel nomograph has been succesfully used as means of predicting the stiffness of bitumens, it does have a number of shortcomings.

The stiffness obtained from the nomograph requires that the bitumen satisfies time-temperature equivalency and is therefore not valid for certain bitumens with a high wax content (Phillips, 1997).

Van der Poel's nomograph provides only an estimate of the stiffness of the bitumen within an accuracy factor of two and, since it is based on unmodified bitumens, is unable to give a realistic stiffness value for modified binders. The stiffhess estimates obtained from the nomograph may also be in considerable error at low temperatures and long loading time (Fig. 3.4). Given the poor reliability of these nomographs and their uncertain applicability to modified asphalts, a more direct measurement of low-temperature stiffness is necessary. (SHRP report 367, 1994).

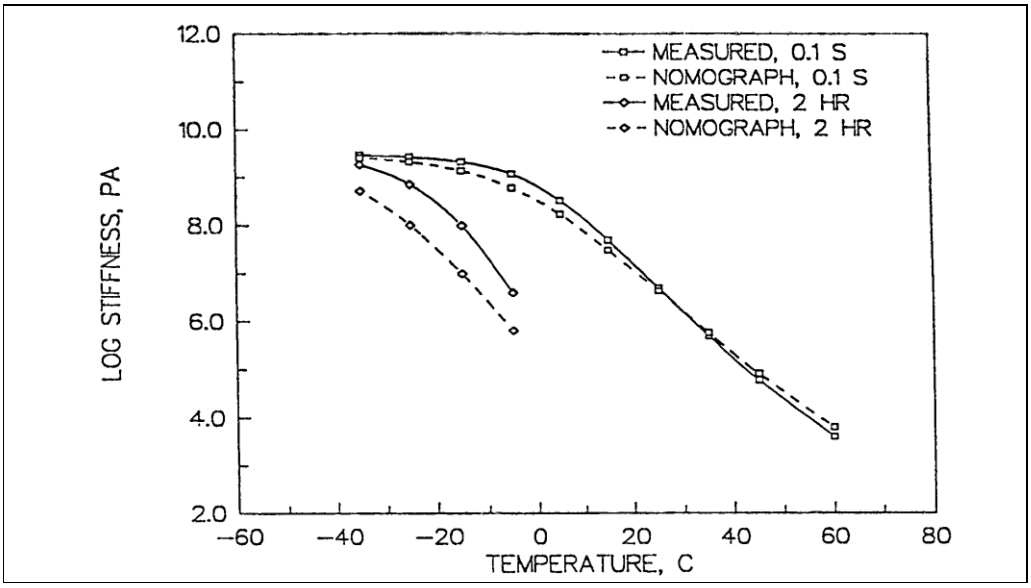


Figure 3.4. Measured stiffness versus Van der Poel's nomograph predicted Stiffness (SHRP 367, 1994)

3.2.2 SHRP concepts and innovations

Within the SHRP project (SHRP report 368, 1994), to fully control the potential performance of a bituminous binder, the mechanical properties over the entire range of temperatures to which pavements are subjected was accurately measured and specified. The continued use of penetration or ductility measurements in the SHRP project was considered undesirable, and the tests were replaced by more fundamental tests that can be used to define a rational rheological model for temperatures ranging from 200°C to as low as -40°C. Rational measurements and parameters that accurately describe the time and temperature dependence of the stress-strain response of plain and modified binder, were developed and the major tool used to study physical properties was rheometry (SHRP report 368, 1994).

SHRP equipments and methods

New procedures and equipments were developed in order to study the rheology of both neat and modified bitumens. The first issue addressed by the SHRP project was that asphalt, or rather the bitumen, is subject to a vast change in temperature from mixing,

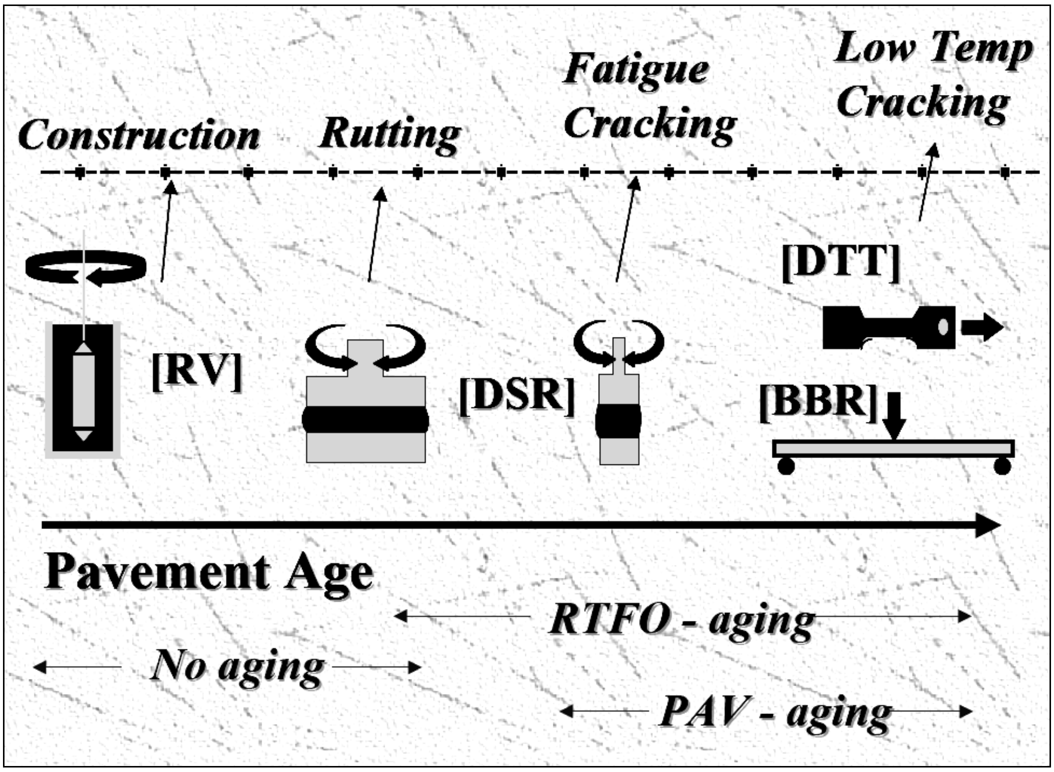


Figure 3.5. SHRP equipments and criteria

laying and compaction to end use. It also established that the pavement, depending on its location, may undergo relatively large changes in temperature.

Secondly, the SHRP project recognized that binder would change during its service life and determined ageing criteria. Thirdly, rheological characterization of the binder was considered of fundamental importance to the structural design of the road. The methods and equipments introduced by the SHRP project are outlined below.

High temperature properties: Rotational Viscometer (RV).

At elevated pavement service temperatures, greater than approximately 60°C and at mixing and compaction temperatures, unaged bituminous binders generally behaves as a Newtonian fluid (shear-rate independent) and ca be properly characterized by capillary viscometry. Aged binders, even at the upper range of pavement service temperatures, exhibit significant non-Newtonian behavior, so capillary viscometry is less applicable to them (Puzinauskas 1979). Furthermore, even unaged modified binders at mixing and

Figure 3.6. Brookfield rotational viscometer (PavementInteractive.org, 2010).

compaction temperatures exhibit significant shear-rate dependence when tested in capillary viscometers (SHRP report 369, 1994).

The Brookfield rotational viscometer was investigated as a replacement for the capillary tube viscometers at mixing and compaction temperatures. Techniques for obtaining a continuous viscosity-temperature curve were investigated; however, it was concluded that significant changes in equipment design would be necessary in order to make such measurements. Instead, the Brookfield viscometer was adopted as a specification test for evaluating the pumpability characteristics of both plain and modified binders (SHRP report 369, 1994).

Intermediate temperature properties: Dynamic Shear Rheometer (DSR).

The dynamic shear rheometer was selected as one of the primary test devices for characterising bituminous binders and was studied extensively in order to determine testing protocols and the equipment limitations. The equipment permit to measure the stiffness modulus by applying a shear stress and recording the deformation and other viscoelastic properties in creep or dymanic test (§ 2.4.4). The dynamic shear rheometer was found acceptable for measuring the stiffness of bituminous binders in the temperature range where the dynamic shear modulus varies from approximately 10 MPa to 1 kPa. A linear response region for bituminous binders in this stiffness range was determined and was subsequently incorporated into the SHRP binder specification (*AASHTO T315)*. Parameters specified are based on both the binder complex shear modulus ($|G^*|$) and the phase angle (δ) measured at intermediate to upper pavement service temperatures (SHRP report 369, 1994). A more detailed description of the DSR and viscoelastic properties is provided in the following section (§ 3.3.1)

Low temperature properties: Bending Beam Rheometer (BBR) and Direct Tension (DT). The bending beam rheometer (BBR) was developed in order to obtain reliable stiffness measurements at low temperatures where the stiffness of bituminous binders is greater than 10 MPa and where the compliance of the dynamic shear rheometer can otherwise lead to errors in the test measurements.

The developed technique was mainly based on the guidelines of the ASTM D790 Standard Method Test for measuring flexural properties of plastics and other elastomers (SHRP report 369, 1994). BBR is a simple device which measures how much a beam of bitumen will deflect under a constant load at temperatures corresponding to its lowest pavement service temperature when bitumen behaves like an elastic solid (Fig. 3.9). The creep load is intended to simulate the stresses that gradually increase in a pavement as the temperature falls. (Read & Whiteoak, 2003) It was shown that the stiffness values obtained with the dynamic shear rheometer and the bending beam rheometer can be related to each other using linear viscoelasticity. Together, the dynamic shear rheometer and the bending beam rheometer are sufficient to completely define the rheological properties of bituminous binders in the time and temperature region of interest for specification and research purposes (SHRP 369, 1994). By combining the bending beam and dynamic shear data, bituminous binders were shown to be thermorheologically simple and it was demonstrated that time-temperature superposition is valid. Time-temperature superposition was subsequently used to establish rheological master curves, allowing the bituminous binders to be described over a wide range of loading times and test temperatures (SHRP report 369, 1994).

The direct tension test procedure was further developed to study the fatigue and the fracture properties of the bituminous binders at low temperatures. The test procedures include a unique set of grips for aligning the specimen, a noncontact extensometer for measuring specimen deformation, and silicone rubber molds for preparing the test specimen.(Fig. 3.8). These test are necessary only when very stiff binders with also poor ductility are tested (SHRP report 369, 1994).

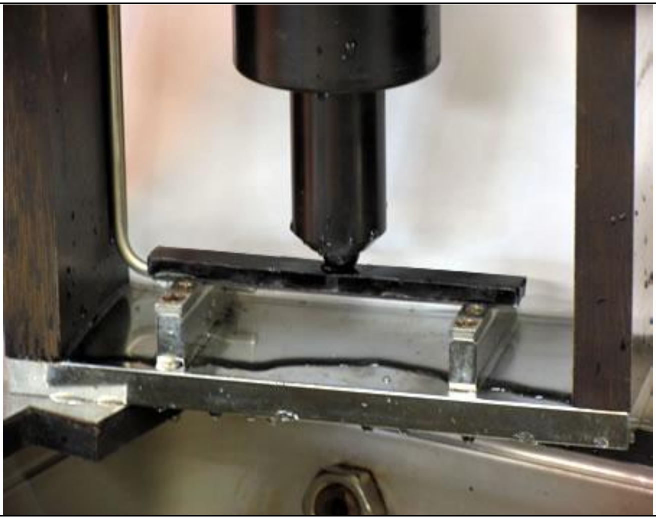


Figure 3.7. Close-up of the BBR beam on its supports (PavementInteractive.org, 2010).

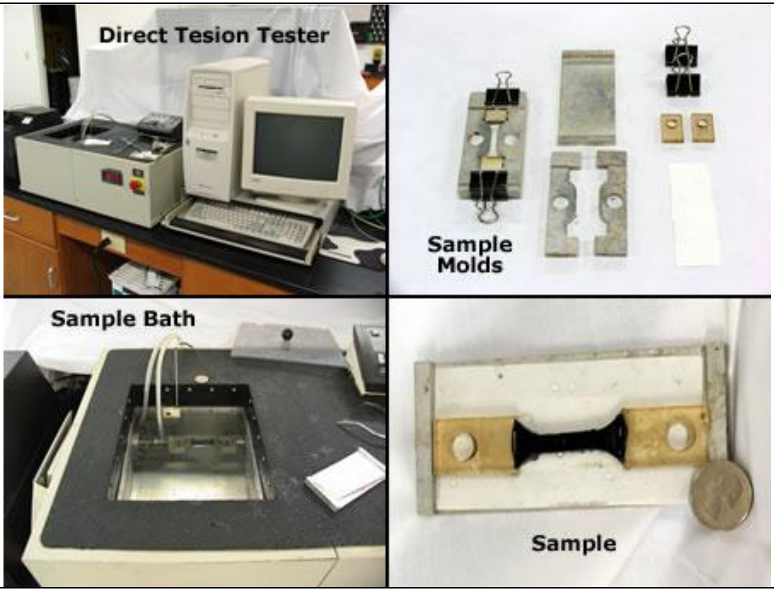


Figure 3.8. DTT equipment (PavementInteractive.org, 2010).

Short-term ageing: Rolling Thin Film Oven Test (RTFOT).

The aging studies completed during SHRP project were focused primarily on long-term, inservice oxidative aging, therefore the existing method of RTFOT was adopted as specification to simulate short term aging of bituminous binder (SHRP report 369, 1994).

The Rolling film oven test is an ageing test and measures hardening by both oxidation and evaporation. In this test, a thin film of bitumen is continuously rotated around the inner surface of a glass jar at 163°C for 75 minutes, with an injection of hot air into the jar every 3 to 4 seconds. The amount of bitumen hardening during the test, as drop on penetration and softening point increase, well relates with that observed during the manufacture of a bitumen. (Read & Whiteoak, 2003).

Figure 3.9. RTFO equipment (PavementInteractive.org, 2010).

One of the main problems with the rolling thin film oven (RTFO) procedure for modified binders is that these asphalts, because of their high viscosity, will not roll inside the glass bottles during the test. Also, asphalts are capable of creeping out of the bottles during the test. To solve this problem, within NCHRP project (NCHRP 457, 2001), two modifications were considered: (1) using a number of steel spheres to create shearing forces to force the spreading of thin films and (2) using a steel rod to induce the same action. Initial evaluations indicated that the steel rod is more practical, simpler to use, and easier to clean. The optimum conditions were achieved using steel rods that were 127 mm long by 6.35 mm in diameter and by tilting the oven slightly (2 degrees) to keep these asphalts from rolling out of the bottle. Several modified asphalts were tested in the modified RTFO. The results indicate that steel rods in the RTFO test can be used to alleviate the problem reported for aging modified binders in RTFO bottles. For all the tests conducted, it was observed that the rods inside of the bottles uniformly spread the asphalt binder (NCHRP 457, 2001).

Long-term ageing: Pressure Ageing Vassel (PAV).

An accelerated pressurised aging test was developed to simulate long-term, in-service oxidative aging. Initially, the test procedure was based on pressurising test samples with pure oxygen for 6 days at the maximum pavement temperature. This was found to be impractical because of safety problems associated with pure oxygen and the time required to conduct the test. As a consequence, air was subsequently used at temperatures ranging from 90 ° to 110°C for 20 hours. In the PAV test, bitumen in a thin film on a tray is placed in a rack into the PAV and the material is aged at a pressure of 2070 KPa. After validation of the test, by comparing samples of material aged in the laboratory and recovered from the field after 12 years, it was concluded that the specification for fatigue and thermal cracking should be based on PAV-aged material (SHRP report 369, 1994).

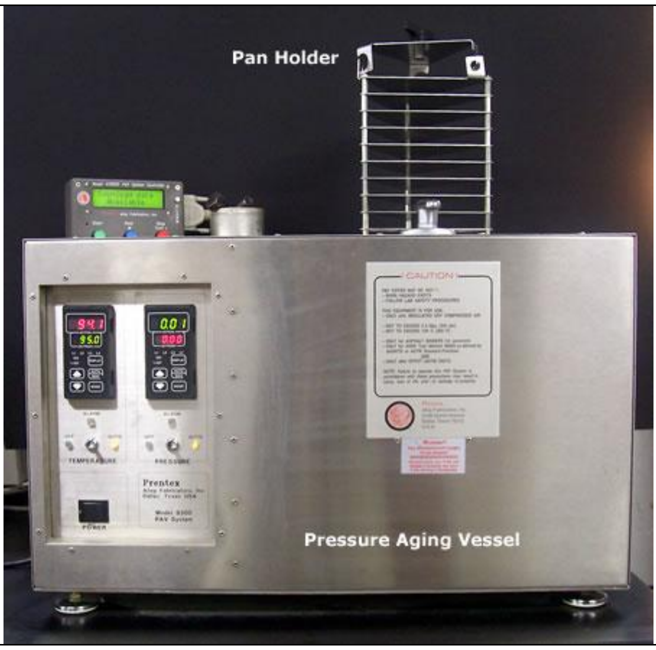


Figure 3.10. PAV equipment (PavementInteractive.org, 2010).

3.3 Rheometry

Rheometry is the measuring technology used to determine rheological properties of a material. It includes measuring systems, instruments, tests and analysis methods. As mentioned before, the intensive use of rheometry within pavement engineering studies was introduced during the SHRP Project (SHRP report 368, 1994) in which rheometry was used to study the viscoelastic properties of bitumen and to determine the effects of shear, shear rate, and temperature.

Rheometry was also later adopted by European TCs and it is currently used to study the rheology of bitumen, therefore to measure its viscoelastic properties and to determine the effects of shear, shear rate, and temperature.

3.3.1 Dynamic Shear Rheometer (DSR)

In the SHRP project, (§2.4.1) the dynamic shear rheometer was selected as one of the primary test devices for characterising bituminous binders because its technology, if well used, is able to provide a extremely accurate characterisation of bituminous binders and their visco-elastic properties within the whole range of service temperatures

In order to properly describe the rheology of bitumen in practical applications it is enough to test the bituminous binders within the linearity range (LVE). Indeed, non-linear response, especially for viscoelastic materials, is extremely difficult to characterise in the laboratory and to model, but fortunately, linear methods of characterisation and analysis are generally more than adequate for engineering design problems (SHRP report 368, 1994). This assumption greatly simplifies the characterisation and modeling of the physical behavior (rheology or stiffness) of bituminous binders (SHRP report 368, 1994).

The rheological tests are performed by subjecting a sample of bitumen, after thermal conditioning, to stress or strain regimes known by reading the corresponding deformation response and stress. The amplitude of the responding stress is measured by determining the torque transmitted through the sample in response to the applied strain. The stress and strain parameters are therefore calculated as:

$$\sigma = \frac{2T}{\pi r^3} \tag{3.5}$$

where:

σ = shear stress

T = torque

r = radius of parallel disks

$$\gamma = \frac{\vartheta r}{h} \tag{3.6}$$

where:

γ = shear stress

ϑ = deflection angle

h = gap between parallel disks

The shear stress and strain in equation 3.5 and 3.6 are dependent on the radius of the parallel disks and vary in magnitude from the centre to the perimeter of the disk. The shear stress, shear strain and complex modulus, which is a function of the radius to the fourth power, are calculated for the maximum value of the radius. The phase angle, δ, is measured by the instrument by accurately determining the sin wave forms of the strain and torque. The dynamic shear rheometer (DSR) is perhaps misnamed. Dynamic forces are not considered; the word "dynamic" refers to the manner in which the stresses or strains applied to the test specimen (SHRP report 369, 1994).

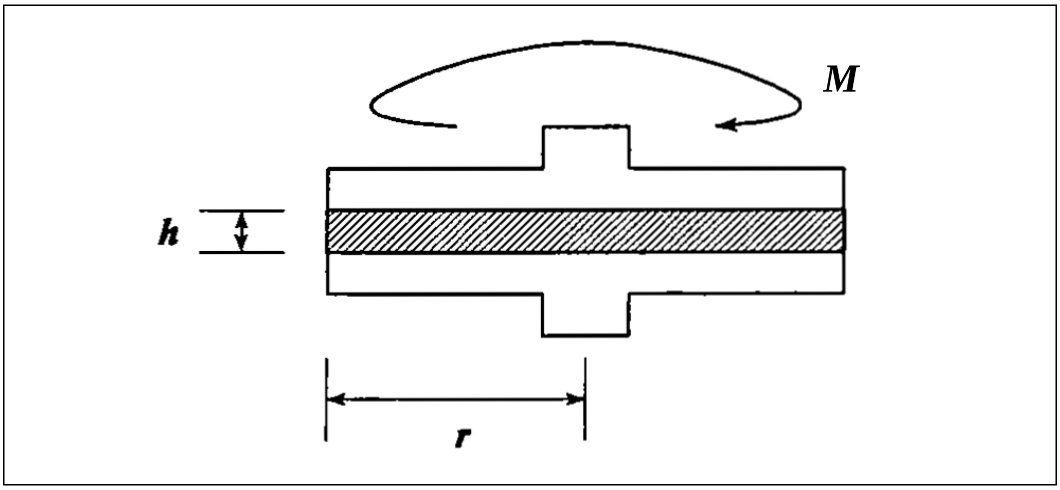


Figure 3.11. Dynamic Shear Rheometer testing geometry

In fact, DSR could be used for viscosity measurements, or tests in which stiffness and other viscoelastic characteristics of the sample are measured. Viscosity measurements are rotational tests or creep tests (§ 3.3.3), they are useful methods to measure long time load behavior of the binders. The latter are named dynamic tests because the stress/strain is applied in a oscillatory regime (§ 3.3.2); this allow significant extension to the range of material characterisation by also considerably reducing test time. In fact, the tests carried out at a certain frequency ω are qualitatively equivalent to results obtained at a testing time $t = 1/\omega$.

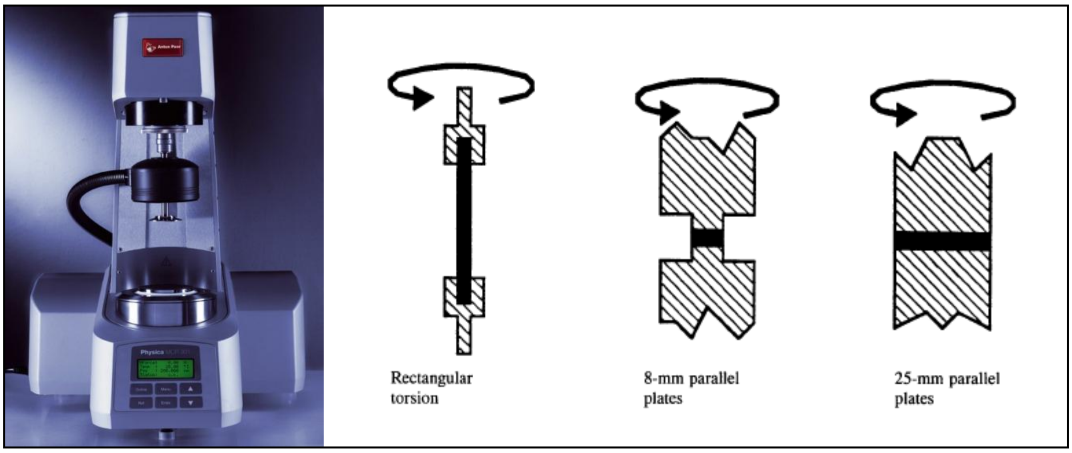


Figure 3.12. DSR and testing geometries used to characterise bituminous binders

Hardware

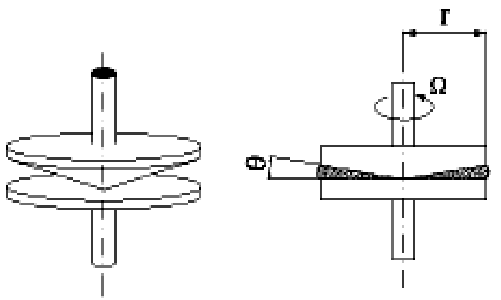
Dynamic shear rheometers consist of three major parts: (1) the rheometer, (2) the controller, and (3) the computer. The rheometer normally includes a housing or frame, a motor for applying the strain or stress to the specimen, a transducer for measuring the response of the specimen, and a temperature control and measurement system. The controller is simply an interface between the rheometer and the computer and contains the data acquisition and signal conditioning hardware for the motors and transducers used in the rheometer. The rheometer is usually operated and programmed by a personal computer. (SHRP report 370, 1994).

Measuring systems

Shear strains or stresses may be applied to test specimens in the DSR by mounting the test specimens between plates or twisting beams of material in torsion (Fig. 3.11)

The sample is placed between two surfaces, put in rotation to each other. Typically, the top plate is put in motion while the lower one is stationary.

DSR is usually equipped also with a cone and plate geometry that is required only when the test measurements are in the nonlinear region. Cone and plate configuration permits measurement with a constant shear rate, and therefore shear stress, fundamental in measuring viscosity of non-Newtonian fluids For each value of the radius "r", the flowing speed is the ratio between the speed of rotation of the cone and the distance between the two plates (Fig. 3.13).



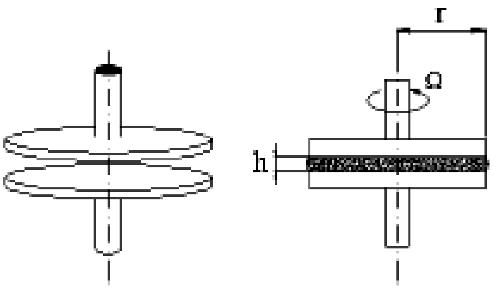
$$tg\vartheta \cong \sin\vartheta \cong \vartheta$$

$$\dot{\gamma} = \frac{v}{h} = \frac{\Omega r}{r \cdot tg\vartheta} = \frac{\Omega r}{r \cdot \vartheta} = \frac{\Omega}{\vartheta}$$

$$M = \frac{2\pi r^3}{3} \cdot \tau = \frac{2\pi r^4 \Omega}{3 \cdot h} \cdot \eta$$

Figure 3.13. DSR cone and plate geometry

The parallel plates configuration, instead, does not allow direct measurement of viscosity for non-Newtonian materials as the flow speed is not the same throughout all the flow areas; indeed, the distance “h” between the two plates is constant and the equation of the shear rate and torque becomes as indicated in Figure 3.14. Consequently, for a non-Newtonian fluid, the viscosity and the measurement of viscoelastic parameters, vary from center to the outer surface of the sample.



$$\dot{\gamma} = \frac{v}{h} = \frac{\Omega r}{h} \rightarrow \dot{\gamma} = \dot{\gamma}(r)$$

$$M = \frac{2\pi R^3}{3} \cdot \tau = \frac{2\pi r^3 \Omega}{3\theta} \cdot \eta$$

Figure 3.14. DSR parallel plates geometry

Results accuracy

Measuring systems geometry. In SHRP specifications, parallel plates geometries (8mm or 25mm) are normally used for the testing because the specification measurements are in the region of linear behavior. (SHRP report 370, 1994).

The specific plate diameter and sample thickness (plate gap) used in testing a given binder depends not so much on temperature as on the modulus of the binder.

When the complex shear modulus of the binder is greater than approximately 30 MPa, (it usually happens at temperature close to the glass transiction point) parallel plate geometry should not be used because the compliance of the rheometer can be sufficient to cause errors in the measurements. Although the range of moduli that can be successfully measured with different size plates will vary according to the design (resolution and compliance) of each rheometer, the following guidelines may be used (SHRP report 370, 1994):

- Use the BBR or torsion bar geometry when the complex modulus (G*) > 30 MPa.
- Use 8-mm parallel plates with a 2-mm gap when 0.1 MPa < G* < 30 MPa.
- Use 25-mm parallel plates with a 1-mm gap when 1.0 kPa < G* < 100 kPa.
- Use 50-mm parallel plates when G* < 1 kPa.

Results from the SHRP program, can be used to indicate that 8 mm diameter plates should be used at intermediate pavement design temperatures, 0 to 40°C, where the specification limit is 1.00 or 2.20 kPa (G*/sinδ) for tank and rolling thin film oven test (RTFOT) residue, respectively. At the maximum pavement design temperatures, 40 to 80°C, parallel plates 25 mm in diameter should be used where the specification limit is 5.00 MPa (G*sinδ). (SHRP report 370, 1994).

Although these recommended guidelines provide a useful indication of plate and gap geometry, care should be taken when using them over wide frequency sweep and for different bitumens. This is particularly relevant at the transition between the different sample geometries and, therefore, it is recommended that there should be an overlap of rheological testing with two disk and gap configurations being used at the transition points (Airey, 1997)

Gap setting. Gap setting can vary depending on the stiffness of the binder and the relative machine compliance, but also depending on the nature of the material. Modified binders have got polymer in the matrix that could falsify the measurement if the gap is too low. As a rule of thumb the gap setting has to be set at least 3 times higher than the maximum dimension of the modifier.

The zero gap setting should be established at a temperature as close as possible to the testing temperature. The fixtures and plates change their dimensions with temperature; therefore, different zero-gap settings will result at different temperatures. The gap dimension enters into the calculation of the shear modulus as a first-order term and the error resulting from an incorrect gap can be readily determined. For example, when the target gap is 2.00 mm, a 20 μm gap error will result in a 1 percent error in the measured shear modulus. (SHRP report 370, 1994).

Sample preparation. Mainly three methods exist to prepare sample for DSR testing:

1) *Hot-pour method*: binder is annealed until it is fluid enough to be poured directly on the lower plate of the DSR. After pouring and lowering the upper plate, trimming is necessary to obtain the desirable sample dimension.
2) *The silicone mould method:* hot binder is poured on 8mm or 25mm silicon mould of height approximately 1.5 times the testing gap. Once the binder is cooled, the disc is removed and centred on the lower plate of the DSR. After pouring and lowering the upper plate, trimming operations are usually necessary to obtain the desirable sample dimension.
3) *The weighing (mass) method*: binder is annealed until it is fluid enough to be poured directly on the upper plate of the DSR a place on supporting assembly and then on a balance with a resolution of 1 mg. The amount of bitumen is pre-calculated. The upper plate is then placed in the DSr and lowered to the desired gap. As the exact sample volume is placed between the plates, no trimming is necessary and no bulge is evident (Hunter & Airey, 2000).

Generally the repeatability of the three methods is more or less equal. Therefore, subject to good practice, any of the three methods would give good accuracy.

The specimen dimensions, regardless of the type of test used, must be carefully controlled to ensure maximum accuracy of test data. The sensitivity of test results to variations in specimen dimensions varies with test geometry. For parallel plate geometry, the dynamic modulus is proportional to the gap, and inversely proportional to the fourth power of the radius (§ 2.4.4). To limit errors caused by variation in the dimensions of the specimen to

3 percent or less, the radius of a 25-mm diameter specimen must be controlled to within about ± 0.8 percent, or 0.1 mm. (SHRP report 369, 1994).

*Trimming of the specimen***.** Excessive material or untrimmed material can cause the measurements to be considerably in error. Both under and over trimming are to be avoided. After the specimen has been trimmed and the gap has been closed to the target value, there should be a slight bulging at the periphery of the sample. A concave surface at the periphery of the sample is to be avoided, as it has a significant effect on the measured value of the shear modulus . To reiterate, if trimming is not done properly, the measurements may be considerably in error (SHRP report 370, 1994).

Temperature of the specimen. Asphalt properties are very sensitive to temperature. Therefore, the temperature of the asphalt binder between the plates should be kept uniform and within ± 0.1 °C throughout the conditioning period and throughout the test. Therefore, it is recommended that specimens as well as the upper and lower plates and spindles be submerged in a fluid bath or air oven that circulates fluid or air at a rate sufficient to keep the temperature of the specimen uniform and constant.

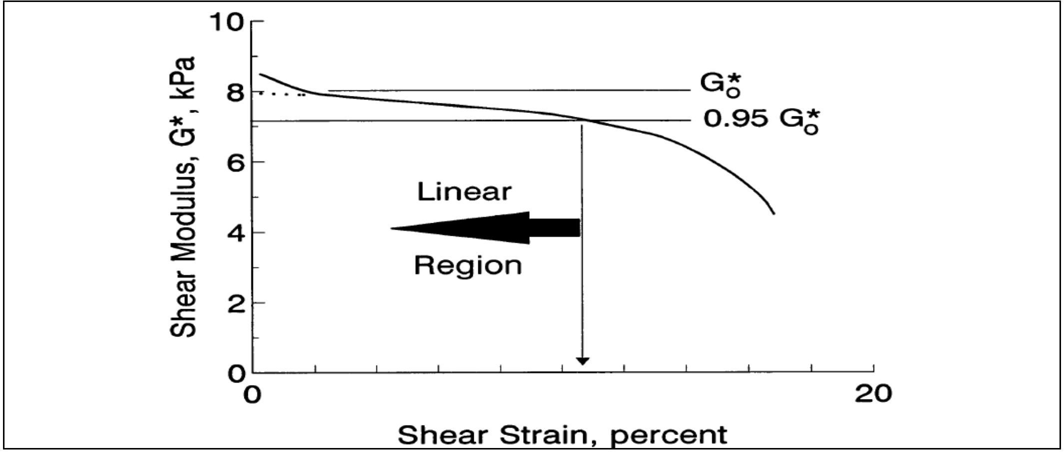


Figure 3.15. Strain sweep used to determine linear region (SHRP 370, 1994)

Conditioning temperature. Annealing times are fundamental factors in testing bitumen. In fact, annealing can reduce the measured modulus by as much as 40 percent (SHRP report 370, 1994).

Low temperature linearity. Characterisations based on linear viscoelastic behavior, must be limited to strains within the linear region (LVE), in order to ensure test repeatability and to better manage results. Linear viscoelastic behavior is encountered when a change in the strain level does not change the measured rheological properties. Therefore, the stress level (in case of a controlled-stress mode) or strain level (in case of a controlled-strain mode) at which testing is conducted must be selected so that the measured visco-elastic parameters are within the LVE limit.

In order to determine the region of linear behaviour of the material to be tested, strain sweeps, which are oscillatory test with variable amplitude and constant frequency values, are usually used. In this procedure, the strain level, to which a specimen is subjected, as gradually increased until significant nonlinearity appeared in the response.

In the SHRP program the limit of linear viscoelastic behaviour was defined as the point beyond which the measured value of G* decreased to 95 percent of its zero-strain value (SHRP report 370, 1994).

Conducting a strain sweep for each asphalt binder at each temperature is not practical and there would undoubtedly be considerable operator variability in judging the point at which G* decreases to 95 percent of the zero-strain value (Fig 3.15).

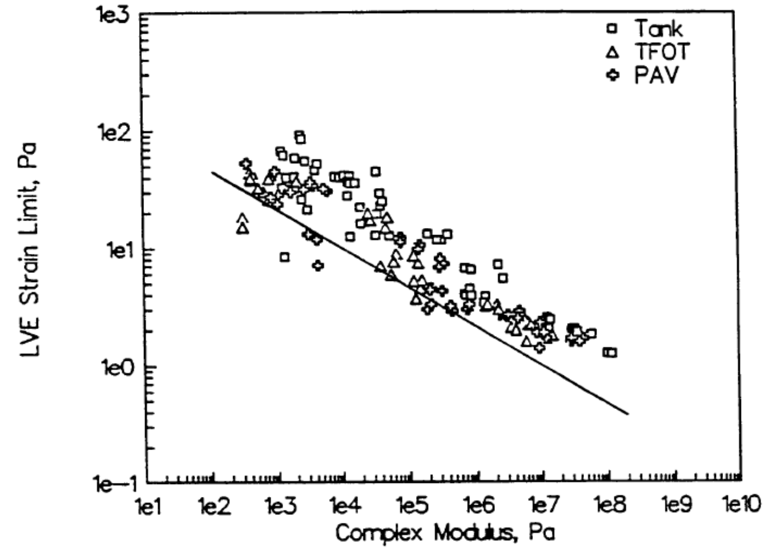


Figure 3.16. Linear viscoelastic strain limit as a function of complex modulus for unaged and aged asphalts (SHRP 370, 1994)

Therefore, SHRP specification suggest a "standard" set of strain values after testing more than 40 binders at different temperatures and aging conditions (Fig 3.16). The plotted points represent the strain level at which the modulus is reduced to 95 percent of its zero-strain value. Using the data in figure 3.16 as a guide, the specification

requires the strain to be controlled to ± 20 percent of the following (SHRP report 370, 1994):

$$\gamma = \frac{12.0}{(G^*)^{0.29}} \tag{3.7}$$

where:

γ = shear strain (%)

G* = complex modulus (KPa)

When testing in the controlled-stress rheometer, the stress should be controlled to ± 20 percent of:

$$\tau = 0.12 \cdot (G^*)^{0.71} \tag{3.8}$$

where

τ= shear stress (KPa).

High temperature Linearity. Another linearity check suggested by the researcher of the SHRP Project (SHRP report 369, 1994) regards a method to for declaring a binder a linear viscoelastic material or non-linear. It usually happens at highest service temperature. It is important to perform this check when an unknown bitumen has been graded with SHRP PG grading system, because test methods does not allow a nonlinear material to be tested. The determination is based on the change in complex shear modulus at 10rad/s (1,59Hz) when the strain is increased from to 2% to 12% at the critical upper temperature (high PG). The material is linear, if the ratio between G* at 2% and at 12% of strain is more or equal to 0,9 (AASHTO T315, 2005).

DSR specifications

EN 14770 and AASHTO T315 specifications describe static tests procedures, able to provide the viscoelastic parameters (eg, complex modulus and phase angle) under a continuous rotation, or in oscillatory regime (dynamic test). The tests are performed by applying a shear stress, continuous or oscillatory, in a controlled stress, or deformation, mode, by varying the temperature and / or frequency (for dynamic tests). In the most common configuration, the rheometer is equipped with two parallel plates with a fix gap setting . The plates have a diameter ranging between 8 and 25 mm; the recommended distance during the test can vary from 0.5 mm to 2.0 mm, according to the plates and testing conditions.

3.3.2 Dynamic Mechanical Analysis (DMA)

The rheology of bitumen can be accurately measured by dynamic mechanical analysis (DMA) using oscillatory-type testing, generally conducted within the region of linear viscoelastic response.

DMA allows the viscous and elastic (viscoelastic) nature of bitumen to be determined over a wide range of temperatures and loading times (Airey, 1997). The importance of carrying out test with variable frequency (frequency sweeps) is that here the time-dependent shear behaviour is examined. The tests carried out at a certain frequency ω are in fact qualitatively equivalent to results obtained at a testing time $t = 1/\omega$. Therefore, short-term behaviour is simulated by rapid movements (at high frequencies) and long term behaviour by slow movements (at low frequencies). There are two options for the specification of the number of oscillations per time unit: as frequency f with the unit [Hz] or as angular frequency with unit [1/s]. The following holds: $\omega = 2\pi f$

Definition of terms

The principal viscoelastic parameters that are obtained from rheological measurements, mainly with the DSR, are the complex shear modulus, G*, and the phase angle, δ.

The complex shear modulus, G* is defined as:

$$G^*(\varpi) = \frac{\tau(\varpi)}{\gamma(\varpi)} \tag{3.9}$$

where:

$\tau(\omega)$ = sinusoidal function of shear stress

$\gamma(\omega)$ = sinusoidal function of shear strain

It provides a measure of the total resistance to deformation when the bitumen is subjected to shear loading. It contains elastic and viscous components which are designated as the storage modulus, G'(ω), and loss modulus, G''(ω), respectively. These two components are related to the complex (shear) modulus and to each other through the phase (or loss) angle δ which is the phase, or time, lag between the applied shear stress and shear strain responses during a test (Figs. 3.17, 3.18).

The larger the phase angle (δ), and so the damping factor, the more viscous the material: For purely elastic materials, the phase angle will be zero, whereas for purely viscous materials, it will be 90º.

The complex modulus can be represented also by the vectorial sum of the storage portion, G'(ω), of the complex shear modulus and the loss modulus, G''(ω), or also as the difference between the real part, G'(ω), and the, imaginary part G''(ω):

$$G^*(i\varpi) = G'(\varpi) - iG''(\varpi) \tag{3.10}$$

The ratio of the loss to the storage is the tan δ, and is often called damping. It is a measure of the energy dissipation of a material under cyclic load. It is a measure of how well a material can get rid of energy and is reported as the tangent of the phase angle. It tells us how good a material will be at absorbing energy. It varies with the state of the material, its temperature, and with the frequency (PerkinElmer, 2008).

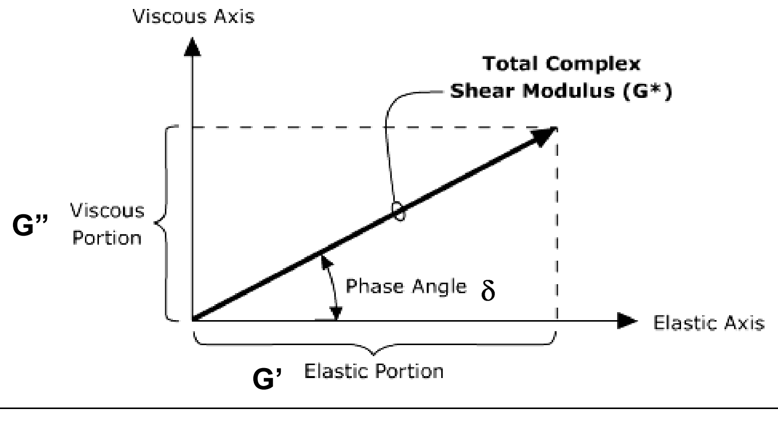


Figure 3.17. Vectorial representation of the relationship between the Complex Shear modulus and its components, (PavementInteractive, 2010)

Another function determined by performing a DMA is the complex viscosity, η*. Complex viscosity is frequency-dependent viscosity function an it represent the flow resistance of the sample subjected to oscillatory tests. It is defined, as a (normal) viscosity, as the ratio between the shear stress and the deformation rate measure in oscillatory tests:

$$\eta^*(\varpi)=\frac{\tau(\varpi)}{\dot{\gamma}(\varpi)} \tag{3.11}$$

Also, the complex viscosity function is equal to the difference between a real part, the so-called dynamic viscosity, η', and the out-of-phase viscosity, or imaginary part, η''.
The norm of the complex viscosity is related to the complex shear modulus as follows:

$$|G^*|=\varpi\cdot|\eta^*| \tag{3.12}$$

Oscillatory test

In order to perform a complete rheological characterisation it is fundamental to collect the rheological parameters, over a range of temperatures, by using oscillatory tests with variable frequency and constant small strain level within the Linear ViscoElastic response

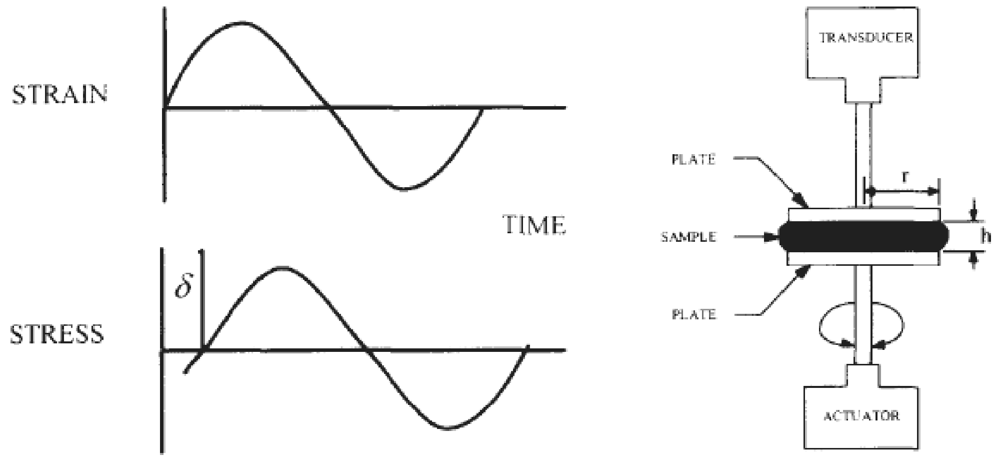


Figure 3.18. Dymanic oscillatory stress-strain functions and geometry (Lu & Isacsson, 1997)

(LVE). Indeed, as long as the γ amplitudes remain below the limiting value γ_l. the G' and G" curves show constantly high plateau, i.e. the structure of the sample is stable under this low-deformation condition. At amplitudes higher than γ_l, the limit of the LVE range is exceeded. In this case, the structure of the sample has already been irreversibly changed or even completely destroyed (Mezger, 2002).

If the material is neat bitumen, the SHRP formula (§ 3.4.1) works pretty well, if more accuracy is necessary an amplitude sweep, at the testing temperature, must always be carried out (Mezger, 2002). As a rule of thumb, in order to remain within the LVE range, the strain must generally be less than 0.5% but can be increased at higher temperatures.

(Airey, 1997). If it is necessary the LVE limits of a bituminous binder can be determined, by performing amplitude sweeps at the lowest testing temperature (§ 3.3.1).

Before performing a frequency sweep, the limit γ_l of the LVE range must be determined first for each new unknown sample (Mezger, 2002).

In order to characterise the in-service rheology of the bituminous binder, it is important to perform the tests over the whole range of service temperatures. Therefore, the binder is characterised within a range of 0°C – 80°C, usually with a step of 5°C and with thermal conditioning time of 15-20 minutes for any temperature.

Data analysis and representation

The following parameters have been covered in the previous paragraph: G^*, G', G'', η^*, η', η'', δ, $\tan\delta$. The great number of parameters provided by oscillatory tests can be confusing, however no rheometer provides more tha two sets of parameters as raw data. These parameters are listed in the Table 3.1. In order to study the rheological characteristics of bituminous binders the data obtained from DMA need to be represented in a useful form. The most common data representation diagram and curves are discussed below.

Table 3.1. Raw data and rheological parameters for oscillatory tests (Mezger, 2002)

Oscillation test	Test setting	Result
CSD - Controlled Shear Deformation	deflection angle, $\varphi(t)$	torque $M(t)$, phase angle, δ
CSS - Controlled Shear Strain	strain $\gamma(t)$	shear stress $\tau(t)$, phase angle,δ

Cole-Cole Diagram. A Cole-Cole diagram is a graph of the loss (viscous) modulus, G", as a function of the storage (elastic) modulus, G'. The plot provides a means of representing the viscoelastic balance ofthe bitumen without incorporating frequency and for temperature as one of the axes (Airey, 1997).

Black Diagram. Another fundamental curve obtainable from the frequency sweep data is the Black diagram. A Black diagram is a graph of the magnitude (norm) of the complex modulus, G*, versus the phase angle, δ, obtained from a dynamic/cyclic test. The frequency and the temperature are therefore eliminated from the plot, which allows all the dynamic data to be presented in one plot without the need to perform TTSP manipulations of the raw data. For this reason the Black diagram is well known even as the finger print of the binder (Airey, 2002).

Figure 3.19 shows the typical trend of the Black Diagram of a bitumen. In section 4.2.8 the rheological characterisation of PMBs is shown through Black Diagrams.

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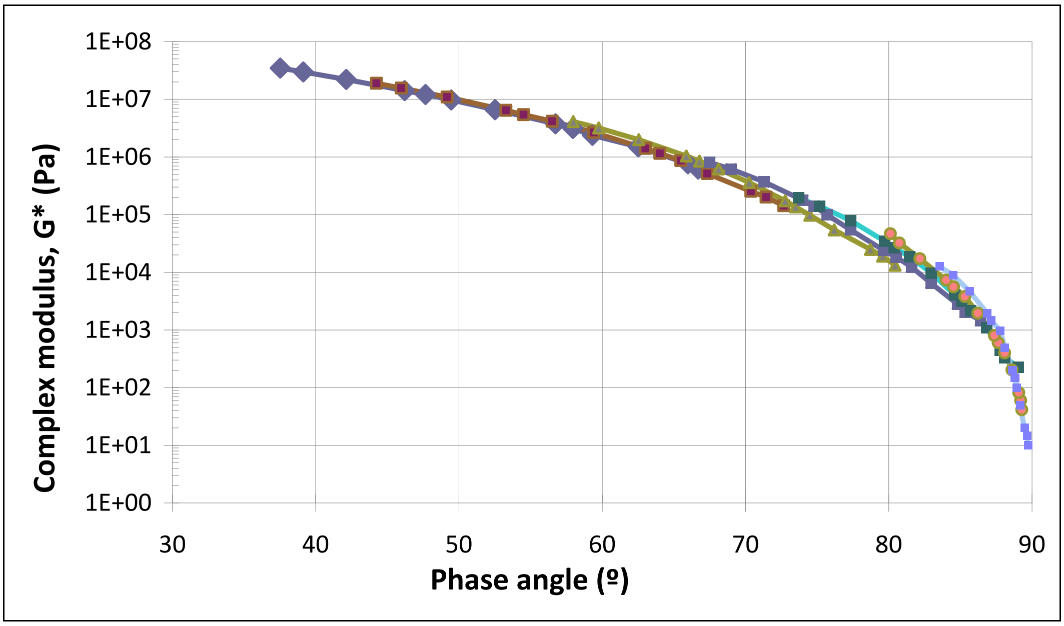


Figure 3.19. Typical trends of isochronal plots of bitumen for G* and δ

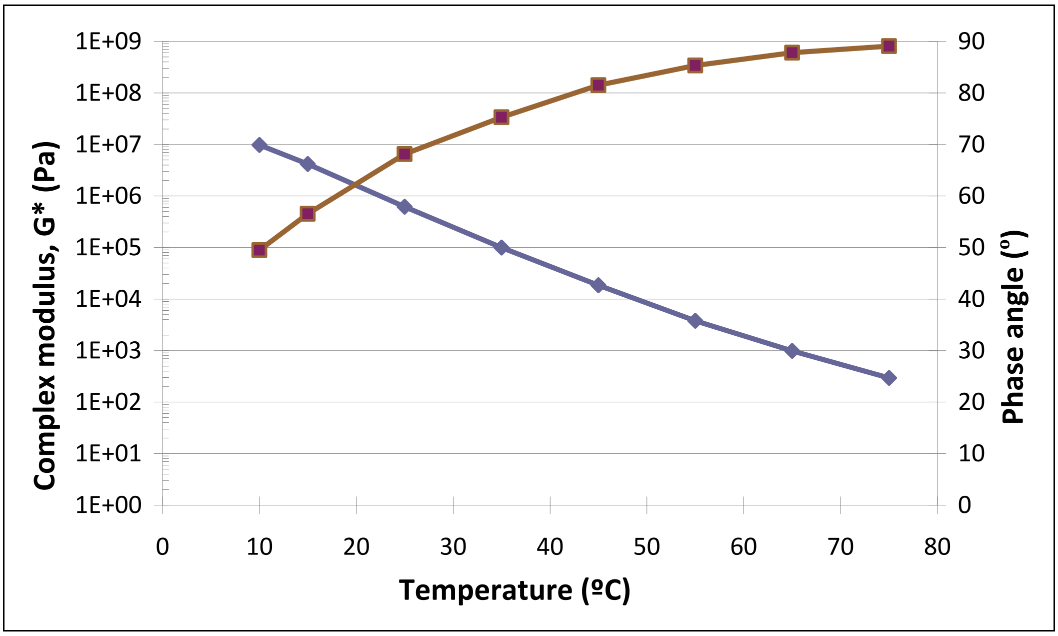


Figure 3.20. Typical trends of isochronal plots of bitumen for G* and δ

Isochronal Plots. An isochronal plot is an equation, or a curve on a graph, which represent the relation of the viscoelastic parameters with temperatures at constant frequency. Isochronal plots are really useful to state the temperature susceptibility of a bituminous binder (Fig. 3.20). Neat bitumen usually show isochronal plots for G* and δ like the one in Figure 3.20. Due to the effect of the polymer, especially at high temperature, Polymer Modified Bitumens have got significant variations on these trends. A description of the rhological characteristics of PMBs is reported in section 4.2.8.

Time-Temperature Superposition principle: Mastercurves. The results of the frequency sweeps, over the range of service temperatures, is represented by a series of isothermal curves which show the variability of the specific viscoelastic parameter with the frequency (Fig. 3.21). Although temperature and frequency sweeps give a good indication of the performance of binders, it is often useful to express both sets of data on a single axis.

One of the primary analytical techniques to analyse dynamic/cyclic mechanical data, born from this need and it involves the construction of the master curves, which represents the

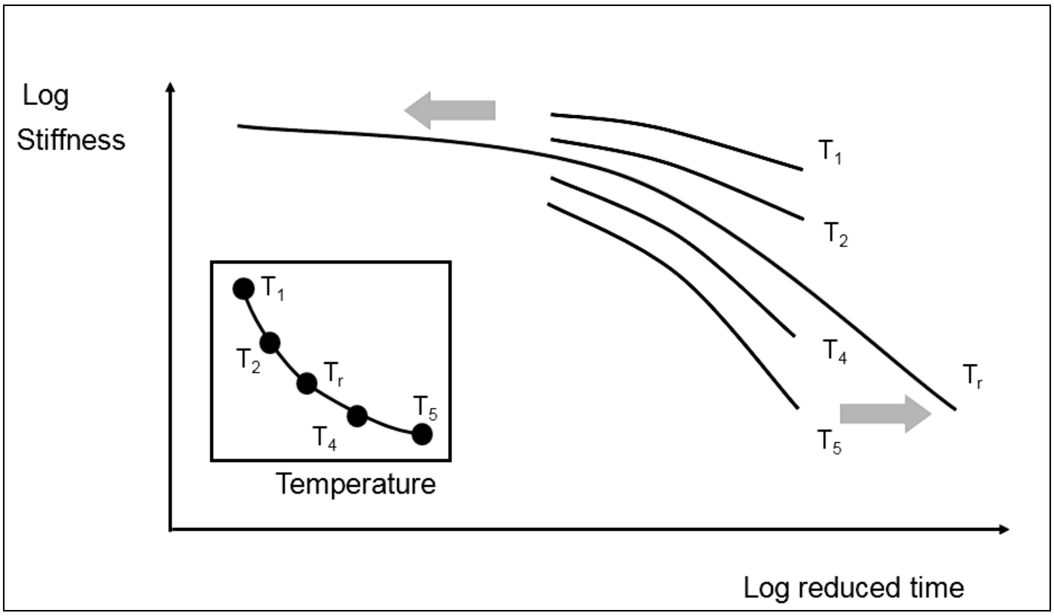


Figure 3.21. Time-Temperature Superposition Principle

viscoelastic behaviour of a bituminous binder at a given temperature for a large range of frequencies. The principle that is used to relate the equivalency between time and temperature and thereby produce the master curve is the Time Temperature Superposition Principle (TTSP), which mathematically is an application of Boltzmann's superposition principle. TTSP states that the effects of time and temperature are related, more specifically that response of the binders at high temperatures are related to their low frequency(time) behaviour and vice versa. For this reason it is possible to find the master curve by shifting each of the isotherms until they lie on the same plane as the curve at a reference temperature T_r (Fig. 3.21). Viscosity-temperature equations are used to characterise the temperature dependency of binder, therefore determine the shift factors needed for the TTSP. The shift factors a(T), can be defined in several ways depending on the adopted mathematical expression used to determine them (Airey, 1997).

When several frequency curves determined at different temperatures are shifted, each one according to its individual shift factor, and presented together in one diagram afterwards, the result is the so called “mastercurve”. Sometimes it is referred to as the “temperature-invariant mastercurve with reduced variable”. A positive value for lg a_T shows the shift of the frequency curve to the right in order to meet the mastercurve. A negative value shows the shift to the left (Fig. 3.23).

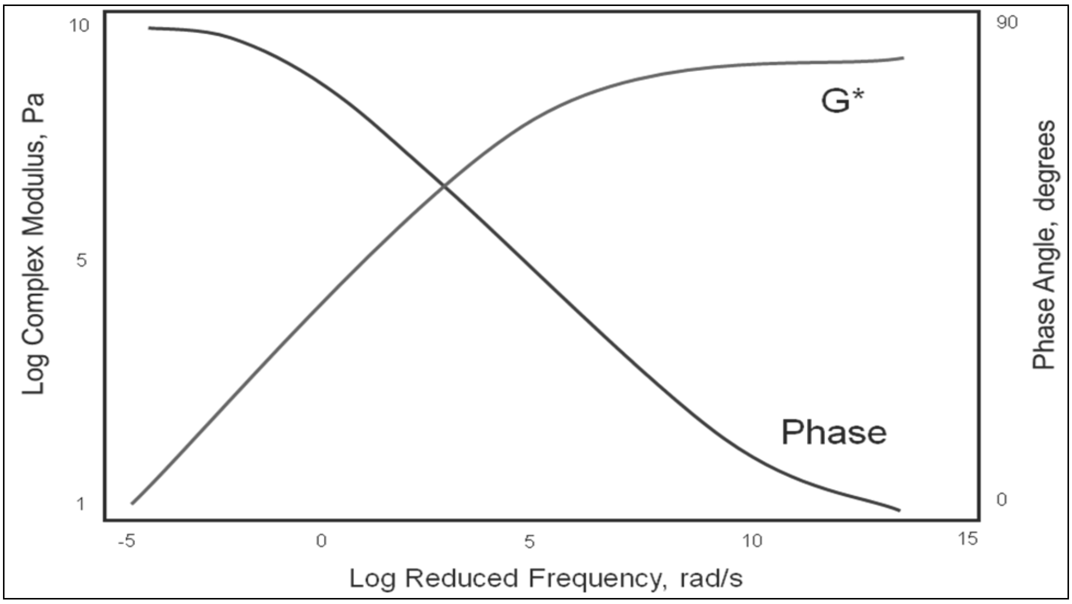


Figure 3.22. Typical trends of G* and δ mastercurves

The frequency mastercurve is plotted with lg (ωa_T) on the x-axis and, for example, with log G* or log δ on the y-axis (Mezger, 2002), (Fig. 3.22). In their simplest form, master curves are produced by manually shifting modulus versus frequency plots (isotherms) at different temperatures along the logarithmic frequency axis to produce a smooth master curve (Mezger, 2002). The shift factors may simply be reported in a graphical or tabular format, or they may be regressed or forced to fit some predetermined function such as described below WLF equation or the Arrhenius function (Airey, 997). (Fig. 3.23)

The Williams Landel and Ferry (WLF) equation (William et.al, 1955) has been widely used to describe the relationship between the shift factors and temperature and thereby determine the shift factors of bitumens. The equation is theoretical based on the free volume theory (Ferry, 1971) and makes use of temperature differences which makes it suitable for practical manipulations. The equation has also been found to be applicable to bitumen results. The WLF equation is:

$$\log a_T = \log \frac{\eta(T)}{\eta(T_R)} = \frac{-C_1 \cdot (T - T_R)}{C_2 + (T - T_R)} \qquad (3.17)$$

where:

a_T = shift factor at temperature T

$\eta(T)$ = Newtonian viscosity at temperature T

$\eta(T_R)$ = Newtonian viscosity at temperature T

C_l, C_2 = empirical determined coefficients

The WLF equation requires three constants to be detemined, namely C_l, C_2, and T_R. The constants C_1, and C_2 can be calculated with respect to the reference temperature, T_R, from the slope and intercept of the linear form of the WLF equation:

$$\frac{-(T-T_R)}{\log a_T} - \frac{C_2}{C_1} + \frac{1}{C_1} \cdot (T-T_R) \tag{3.18}$$

The temperature dependency of bitumens can be described by one parameter T_R, if universal constants are used for C_1, and C_2 in the WLF equation.

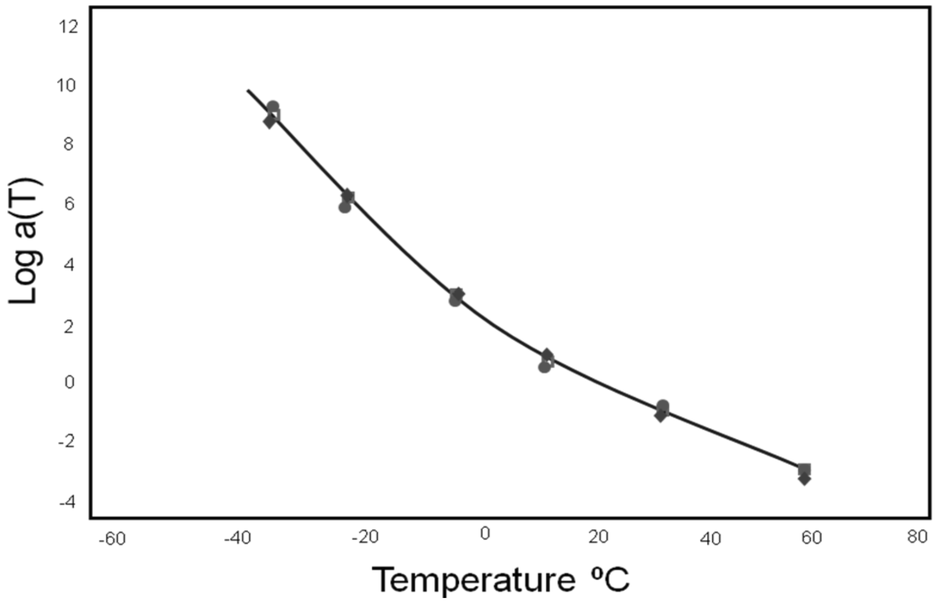


Figure 3.23. Example of WLF Shifting factor curve

Unfortunately, several studies (William et al., 1955; Brodnyan et al., 1960; Nielsen, 1995) have demonstrated that T_R, also known as standard reference temperature, Ts, or the defining temperature, Td, is difficult to determine, therefore setting the reference temperature and then calculating the other two constants is probably the best way to proceed.

Another equation that can be used to describe the relationship between the shift factors and temperature is the Arrhenius equation:

$$\log a_T = \frac{\Delta H}{2.303 \cdot R} \cdot \left(\frac{1}{T} - \frac{1}{T_R} \right) \tag{3.14}$$

where:

a(T) = horizontal shift factor

ΔH = activation energy, typically 250 kJ/mol

R = universal gas constant (8.314 J/°K-mol)

T = temperature, °C

T_R= the reference temperature, °C

The Arrhenius expression or function requires only one constant to be determined, namely the activation energy. The reference temperature, T_R, can be arbitrary chosen (Nielsen, 1995). The Arrhenius equation is useful for low viscosity liquids and polymer melts in the range $T>T_g + 100K$, where T_g is the glass-transition temperature. For melts of amorphous polymer at temperatures closer to T_g, it is better to use the WLF relation (Mezger, 2002). Considering that, T_g of bitumen is around -20ºC (Lesuer, 2009) and that the range of the isotherms to be shifted go from 0-80ºC, WLF equation is probably the most suitable method for bituminous binders.

3.3.3 Rotational static tests

The evaluation of the viscoelastic properties, through dynamic analysis, is one of the most investigated areas of rheology. The other topic of considerable interest is related to measurment of the viscosity of the sample, under sliding motion conditions. Rotational static methods are useful for measuring the viscosity of the bituminous binders, when they are subjected to long load times at intermediate pavement temperatures. DSR gives the possibility to conduct also such measurements.

Two are the main rotational tests: creep and relaxation tests. When a sample is subjected to a constant stress, an increase in the deformation takes place with time, this behaviour is called “creep”. Instead, when a constant strain is applied to a sample, the force necessary to maintain that strain is not constant but decreases with time, this behaviour is called “stress relaxation” (Azon.com, 2011).

To perform a creep test on a bituminous binder, it is necessary to apply a shear stress to the bitumen until the strain rate becomes constant. At low and intermediate service temperatures, longer times are required for delayed elasticity to be expended and steady state flow to occur. This results in the bitumen being subjected to very large strains causing geometric non-linearity. The delayed elasticity and geometric non-linearity can be overcome by assuming that the steady state strain rate has been attained at a series of shear stress levels and extrapolating the calculated apparent viscosities to a zero shear rate. This apparent viscosity at zero shear rate is known as the zero shear rate viscosity, η_0, and is equivalent to the maximum Newtonian viscosity of the bitumen at the test temperature (Airey, 1997). More details about the ZSV are reported in the next paragraph (§3.3.4).

A creep test can be performed stand alone or it can be combined with a “recovery” phase, where the costant stress of the creep phase is nulled and sample recovers the elastic deformations. In fact this type of test is usually performed to assess the accumulated permanent deforamtions due to the creep. Example of this tests for bituminous binders are the Repeated Creep Test and the Multiple Stress Creep Recovery where different cycle of creep-recovery are combined to find rutting parameters (§3.3.4).

3.3.4 Binder parameters related to asphalt rutting

As seen previously (§ 3.3) the road industry has redefined the concepts underlying the mechanical characterization of binders, toward a performance-related classification. On this basis, research have been focusing its attention on the determination of characteristic parameters of road materials that, on a theoretical basis, can be related to the performance of pavements in service. By focusing on the potential risk of rutting, which pavements can undergo at high temperatures, there are different opinions and methods proposed by various researcher and some of the most interesting are discussed below.

SHRP parameter: |G| /sinδ*

During the development of the SHRP (Strategic Highway Research Program), pavement rutting was interpreted in terms of accumulation of permanent deformation due to the repeated application of traffic loading. According to this definition, damage in binders was considered as a consequence of a cyclic stress-controlled phenomenon (Bahia and Anderson, 1995). According to this view, per each loading an amount of work is spent to deform the surface layer of pavement and a part of this work is recovered elastically, while the remainder is dissipated and appears in the form of permanent deformation and heat. By following this conception and by minimising that portion of work leads to the consequent minimisation of rutting. The contribution of resistance offered by the binder was then correlated to the portion of energy spent for permanent deformation and heat dissipation per each loading. This was considered to be directly proportional to the imaginary part, J", of the deformation complex compliance, J*. Consequently reversible cyclic shear analyses performed with Dynamic Shear Rheometer were proposed to characterise binder behavior. In such case a sinusoidal stress (or deformation) is applied on a viscoelastic material and the total dissipated work for damping effect per load cycle (W_c) can be calculated through equation 3.18 as the area of the hysteresis loop developed during each loading cyclic:

$$W_c = \pi \cdot \sigma_0^2 \cdot J''(\omega) = \pi \cdot \sigma_0^2 \cdot \left(\frac{1}{G^*(\omega) / \sin\delta} \right) \tag{3.15}$$

Therefore, in the SHRP philosophy, the performance indicator of the binder related to rutting of asphalt, is represented by the parameter: |G*|(ω)/sinδ, which must be maximised to increase the resistance to this phenomenon. In fact, intuitively, when a material tends to have a high complex modulus, |G*|(ω), and low phase angle, δ, turns out to be both more rigid and more elastic at the same time.

Although |G*|/sinδ is still used, as well as conventional parameters such as penetration, and penetration indecies (§2.3.1), it was found inadequate for describing the real anti-rutting performance of binders with high delayed elasticity (Shenoy 2002, Bahia et al.,2001 b) (Fig. 3.24). It is generally recognized that this occurs because the SHRP parameter is connected with the partially reversible energy of binders and consequently it is not fully associated with pavement damage (Bahia et al., 2001 b).

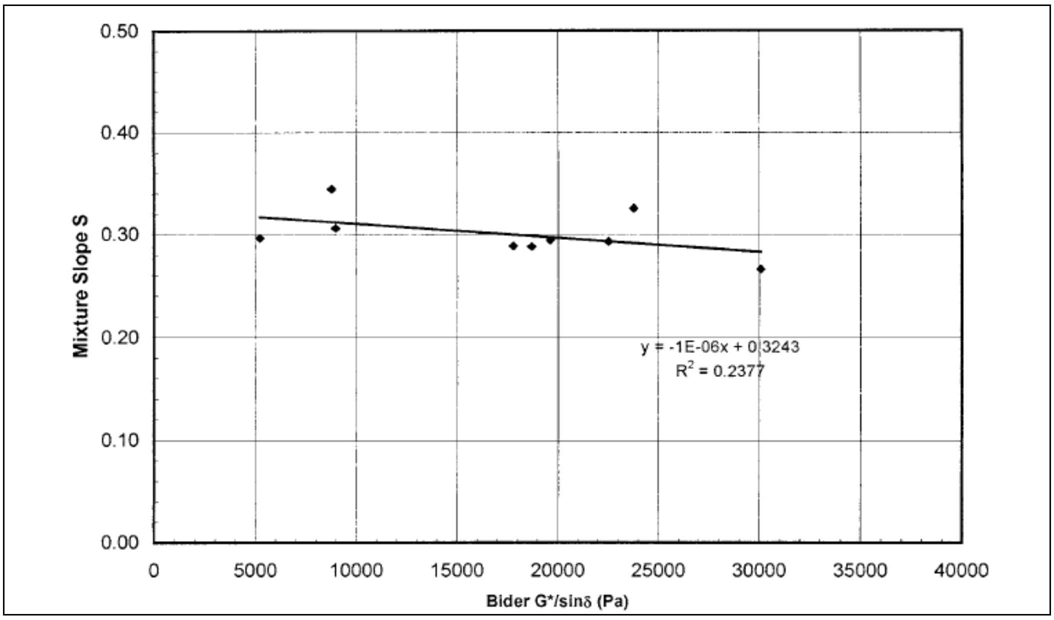


Figure 3.24. The correlation between SHRP binder rutting parameter and the average mixture rutting parameter, by using modified binders . (NCHRP 459, 2001)

The concept of binder damage behaviour was thus introduced as a correct way to separate reversible energy connected with delayed elastic phenomena from energy dissipated in viscous flow. In fact only the dissipated energy correlated with viscous flow can be associated with the non-reversible deformation (damage) of binders.

On the basis of this concept, different rheometrical approaches based on creep analysis were thus developed for asphalt binders characterization during the NCHRP project 9-10 (repeated creep and recovery) and by CEN TC336 (static creep).

Although these two test methods are based on similar theoretical concepts, the rheometrical conditions and the final specification parameters proposed for the standardisation are different. Moreover the reliability in the case of modified binders and the influence of the test conditions on the results are not fully known (Giuliani & Merusi, 2007). Each of the proposed model have given rise to various indicators, for rational and experimental methods, which are described below.

NCHRP parameter: G_v

Aggregate properties and mix design are very important but binders properties certainly play an important role in rutting resistance as was observed, within the NCHRP project, by analysing the mitigation of rutting problems when modified binders are used (Bahia & Anderson, 1995).

Considering that correlation between the mixture rutting indicators and |G*|/sinδ is very poor, when modified binders are used (Fig. 3.24), the repeated creep test was introduced as a better method for estimating binder resistance to permanent strain accumulation under conditions of repeated loading and unloading cycles. The test is conducted at elevated service temperatures, which are significant for rutting. An AASHTO test protocol has been published in NCHRP report 459 (NCHRP 459).

$$J(t) = J_e + J_{de} + J_v = \frac{1}{G_0} + \frac{1}{G_1} \cdot \left(1 - e^{-t\frac{G_1}{\eta_1}} \right) + \frac{1}{\eta_0} t \qquad (3.16)$$

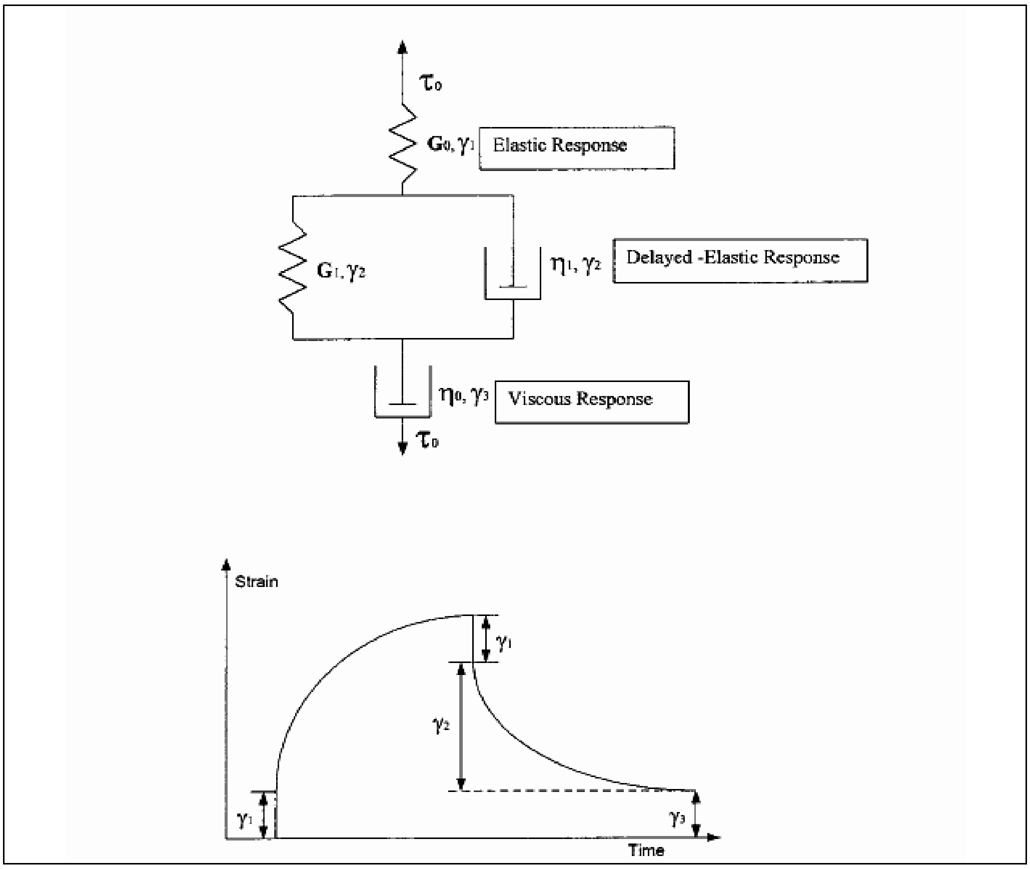


Figure 3.25. Burgers model and its response. (NCHRP 459, 2001)

According to this protocol, the test is performed using a dynamic shear rheometer at low stress level (between 30 and 300 Pa at the outer edge of the plates). The loading time is typically 1 s, but 2 s or 3 s could also be used. The ratio between loading time and unloading time has to be 1:9 (e.g. 9 s unloading for 1 s loading). The sample is subjected to 100 cycles and the strain is measured as a function of time. The test data of cycles 50 and 51 are fitted using the four element Burgers model (eq. 3.16). The advantage of the Burgers model is that the response could be successfully divided to estimate the viscous component, J_v, which is believed to be the cause of permanent deformation, and to estimate its accumulation in paving mixtures. The viscous component is inversely proportional to the viscosity, η_0, and directly proportional to stress and time of loading, t. Based on this separation of the creep response, the compliance could be used as an indicator of the contribution of binders to rutting resistance. Therefore within the NCHRP project, in order to be compatible with the concept of stiffness introduced during SHRP, instead of using the compliance, J_v, the inverse which is the viscous component of the creep stiffness, G_v (Eq. 3.15), was proposed as rutting indicator.

$$G_v = \frac{\eta_0}{t} \rightarrow \gamma_{acc} = \frac{\tau}{G_v} \qquad (3.17)$$

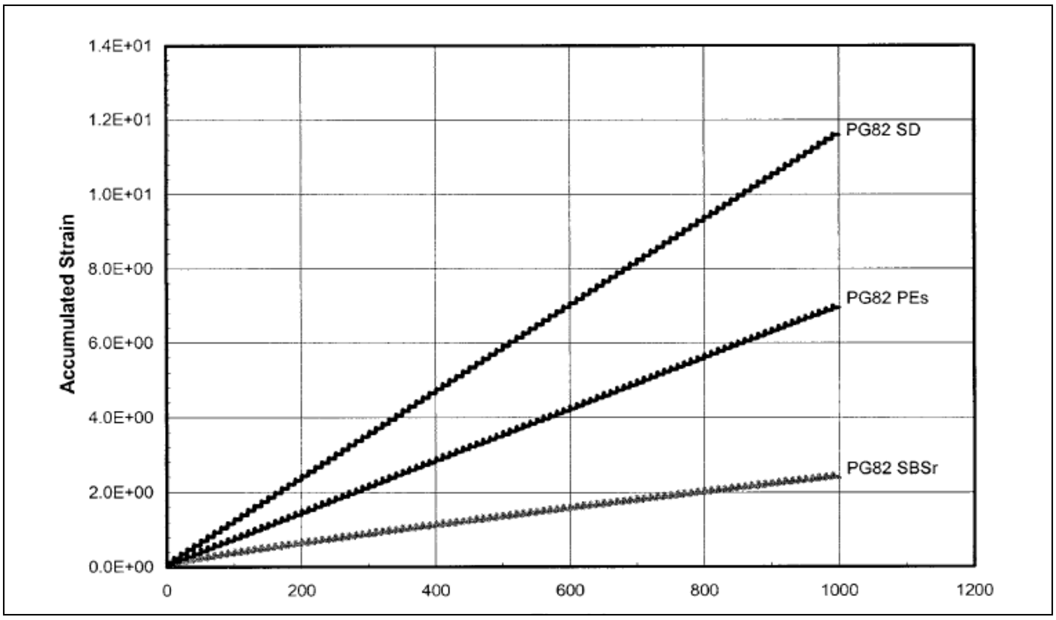


Figure 3.26. Results of the accumulated strain under repeated creep testing for three PG 82 binders at 1 s loading and 9 s recovery (70°C, 300 Pa). (NCHRP 459, 2001)

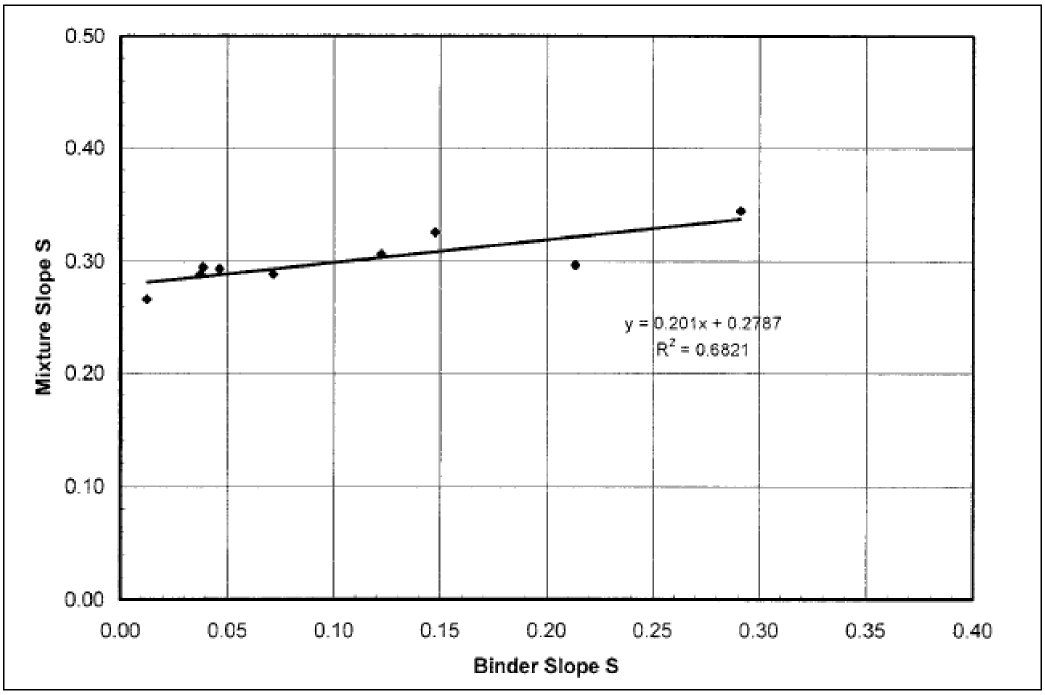


Figure 3.27. The correlation between NCHRP binder rutting parameter and the average mixture rutting parameter, by using modified binders. (NCHRP 459, 2001)

The value of the viscous part of the creep stiffness is estimated at selected loading times related to the expected traffic speed. Longer loading time is used for slower traffic that requires higher levels of G_v (NCHRP 459, 2001).

In order to validate the proposed indicator, researchers of the NCHRP correlated the rate of accumulation of permanent strain of mixtures with the rate of accumulation of permanent strain in the binder , S. Results shown that correlation between the proposed parameter G_v and mixture rutting is good for certain aggregates, but not for others. It appears that the effect of aggregates and the interaction of aggregate characteristics with binder properties are very complex. Isolation of the binder effects to evaluate the validity of G_v or any other binder only property is very difficult (NCHRP 459, 2001).

Nevertheless, if the NCHRP indicator (Fig. 3.27) is compared with the SHRP indicator (Fig. 3.24), the repeated creep test protocol for measuring the accumulated permanent strain of the modified binder represents an improvement in the theoretical and practical concepts for better rating binder properties related to pavement rutting.

Zero Shear Viscosity (ZSV)

The difficulties encountered in fully interpreting the rheological behavior of bitumen has led other European researchers to identify some critical point in the Superpave system. One of the alternative approaches undertaken by Europan researchers, led to the definition of the creep resistance of the binder, interpreted in terms of viscosity and more specifically in the determination of the so-called Zero Shear Viscosity.

ZSV is identified by a flow which is established by subsequent state of nearly equilibrium, in which the internal structure of the material remains unchanged compared to the condition of rest (Giuliani & Merusi, 2006). Therefore, to determine of the Zero-Shear Viscosity, the following must occur:

1. stationary flow ($d\gamma/dt \rightarrow k$)
2. strain rate close to zero value ($d\gamma/dt \rightarrow 0$)

Conditions 1 and 2 ensure that the measure of viscosity occur at the end of delayed elasticity phase (condition 1) and within the linearity region of the flow (condition 2), creating a situation where the elastic and delayed elastic components, J_e, and J_{de}, of the compliance J (t), can be considered negligible. Thus, it is possible to evaluate only the viscous component of the module, J_v, which according to the description of the behavior of linear viscoelastic solid explained by the Burger model (Eq. 3.16), is directly related to the value of ZSV (BitVal, 2006).

The experimental measurement of ZSV can be addressed through two different strategies rheometry: static analysis at low level of flow and dynamic analysis at low frequencies.

Creep ZSV. With respect to Burger's model presented above (Eq. 3.16), it can be observed that zero-shear viscosity can be identified by the parameter η_0. This leads us to think that there is a close correlation between this method and the repeated creep method, but in this case the rheometrical conditions are different: a single cycle of load is performed and the creep time is longer than one hour. When the measurement verifies this time condition and the stress applied is internal to the Newtonian region of flow, only the viscous compliance, $J_{v,}$ increases, according to the theoretical equation of Burger's model (Eq. 3.16). Hence the zero-shear viscosity of the material can be well represented by parameter η_0 of Burger's model, and can consequently be determined by the slope of the compliance curve (Giuliani & Merusi, 2007):

$$t \rightarrow \infty \Rightarrow \qquad {}^{dJ\ \ t}\!\Big/_{dt} = {}^{dJ_v}\!\Big/_{dt} = {}^{1}\!\Big/_{\eta_0} \Rightarrow \qquad \eta_0 = {}^{\Delta J}\!\Big/_{\Delta t} \tag{3.18}$$

A draft test method to measure the ZSV was prepared by CEN TC 336/WG1/TG1, "High Temperature Performance". The test consists in a low shear static creep of the binder at temperatures corresponding to the maximum service of asphalt (45-60°C) and at low shear stress values, which are the conditions unfavorable against the rutting. In this test method, the parallel plate geometry is recommended with a diameter of 20 mm or greater, a 2 mm gap and the conditions given in Table 3.3. The cone and plate geometry is also appropriate. The draft also specifies a range of the viscosity (100 to 50 000 Pa.s) beyond which the test is not applicable (BiTVal, 2006).

Table 3.3. Dynamic Shear Rheometer testing geometry

Type of binder	Stress (Pa)	Time (h)	Temperature (°C)
Non Modified	50	1	60
Polymer modified	10-50	4	60

The average viscosity over the last 15 min (900 s) is derived from the compliance curve according to Equation 3.19.

$$\eta_0 = {}^{\Delta t}\!\Big/_{\Delta J} = {}^{900}\!\Big/_{(J_{end} - J_{15\min beforeend})} \tag{3.19}$$

The reproducibility of the results when following the test protocol was investigated (BiTVal, 2006). It was concluded that the test is suitable for conventional, multigrade and lightly modified binders. For highly modified binders, it was concluded that the steady state creep flow cannot be attained within a reasonable creep period and, hence, ZSV cannot be measured. In these cases, several researchers suggest introducing the concept of Low Shear Viscosity (LSV) for the characterization of the resistance to permanent deformation binders.

Oscillatory ZSV. ZSV is also obtainable in an oscillatory regime, by subjecting the binder to a dynamic rheological analysis with variable frequency (DMA). In fact, as well known, the results from tests conducted at very low frequencies (0.01 Hz) are qualitatively equivalent to results obtained in static tests for a long time to load ($d\gamma/dt$ →k e $d\gamma/dt$ →0). In the frequency domain, ZSV is related to the loss compliance J”(ω) by according to

$$J''(\varpi) - \int_0^\infty \varpi\,[J_{de}(\infty) - J_{de}(t)]\cdot\cos\varpi t\cdot dt = \frac{1}{\omega\eta_0} \qquad (3.20)$$

Consequently, when the oscillation frequency tends to zero, the oscillatory ZSV can be determined by the following expression:

$$\eta_0(\omega)'' = 1/(\omega\cdot J''(\omega)) = G^*(\omega)/\omega\cdot\sin\delta \qquad (3.21)$$

Shenoy’s parameter

The Superpave specification parameter |G*|/sinδ was identified as the term to be used for high temperature performance grading of paving binders in rating the binders for their rutting resistance. The ineffectiveness of |G*|/sinδ in capturing the high temperature performance of paving binders for rating their rutting resistance became a matter of significant concern as more and more polymer-modified bitumen were tested for their performance. The failure of this parameter was demonstrated in several studies and, as seen before, also through laboratory testing during the National Cooperative Highway Research Program (NCHRP) Project 9-10 (NCHRP 459, 2001) in which the repeated creep and recovery test for binders (RCT) was suggested as a possible means to estimate the rate of accumulation of permanent strain in the binders. Though the RCT test gives realistic information, the procedure is time-consuming and not attractive from a specification standpoint. Shenoy, (2001) showed that the information obtained during RCT on the unrecovered strain in a binder that is periodically subjected to an applied stress could be estimated effectively directly from the frequency sweep test data. The following term:

$$|G^*| / (1-(1/\tan\delta\sin\delta) \tag{3.22}$$

was suggested (Shenoy, 2001) as a refinement to the Superpave specification parameter for performance grading of asphalts. Shenoy's parameter was shown (2001) to be more sensitive to the variations in the phase angle δ than the Superpave specification parameter

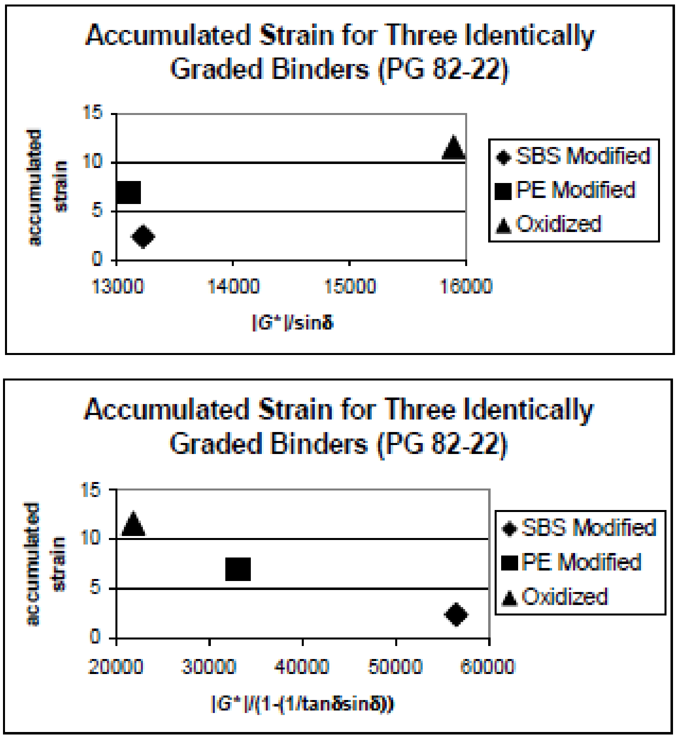


Figure 3.28. Plot of the accumulated strain versus the SHRP and Shenoy's parameter parameter at 70°C for three binders identically graded as PG 82-22 (Bahia et al., 2001)

$|G^*|/\sin\delta$ and thus was found to describe the unrecovered strain in the binders more accurately, especially in the case of polymer-modified bitumens (Shenoy, 2002).

In fact, when the RCT data (Bahia et al., 2001) at the temperature of 70°C for the three binders with the same high temperature performance grade of 82 are compared with the term $|G^*|/(1-(1/\tan\delta\sin\delta))$, the correct trend is obtained as shown in Figure 3.29 (Shenoy, 2002). Despite, the rutting parameter was modified; Shenoy kept on defining the high specification temperature T_{HS} (°C) as that temperature at which the term $|G^*| / (1 - (1/\tan\delta\sin\delta))$ takes a value of 1 kPa for the original unaged binder and a value of 2.2 kPa for the RTFOT aged binder.

Multiple Stress Creep Recovery Test (J_{nr})

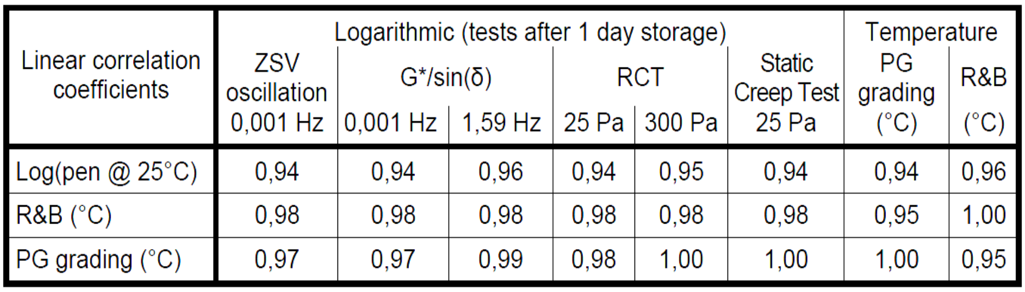
The latest researches have correlated the rutting of the mixture with the Non-recoverable compliance, J_{nr}, of the binders. This parameter has been introduced to identify the elastomeric response of modified bitumens by means of percent recovery obtained in the Multiple Stress Creep Recovery test (MSCR). The MSCR test is conducted using the Dynamic Shear Rheometer (DSR) at the high performance grade (PG Grade) temperature of the asphalt binder. It is intended for use with residue from Test Method AASHTO T240 (ASTM D 2872) (RTFOT) which is designed to simulate plant aging (ASTM D7405 10a). The test is run at the selected temperature using a constant stress creep of 1.0 second duration followed by a zero stress recovery of 9.0 second duration. Two stress levels 100 Pa and 3200 Pa are applied and ten cycles are run at each of the two stress levels for a total of 20 cycles. At the end of any cycle the average un-recovered strain, γ_u, is calculated and by dividing for the applied stress, τ (100 and 3200 Pa):

$$J_{nr} = \gamma_u / \tau \tag{3.23}$$

The tests are conducted at two stress levels to allow evaluation of the shear susceptibility of the binders. The level of 3200 Pa has been chosen because most of the neat binders remain within the linear domain at this stress level. This parameter seems to work very well with modified binders and recently it became a standard: ASTM D7405 -10a

Correlations between rutting parameters

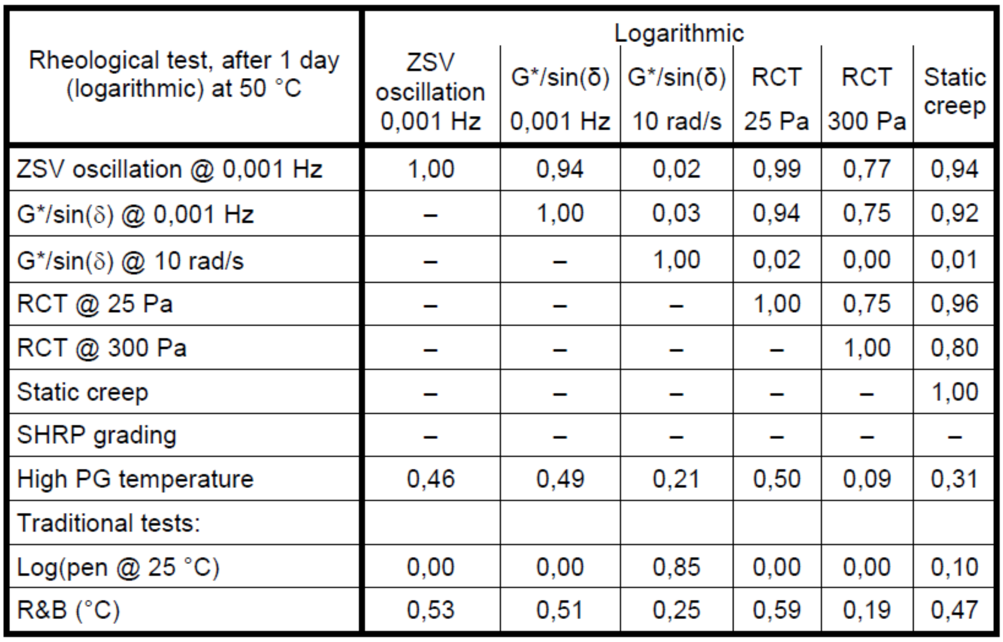
In the phase 1 of the BiTVal project (Bitval, 2006), a set of 15 binders were compared in order to find some correlations between the creep ZSV and the other binder properties related to permanent deformation. The creep period was one hour, regardless of whether or not the creep flow had reached steady state. Figure 3.28 shows the correlations obtained for the unmodified binders and modified binders. By testing unmodified binders, ZSV by the oscillation method, the SHRP parameter of $G^*/\sin\delta$, the repeated creep test, the static creep test (creep ZSV), and also conventional properties such as Sofetning point and penetration, have all been found to correlate closely to the traditional rheological properties of penetration and R&B softening point ($R^2 \approx 1$).



Linear correlation coefficients	Logarithmic (tests after 1 day storage)						Temperature	
	ZSV oscillation 0,001 Hz	G*/sin(δ) 0,001 Hz	G*/sin(δ) 1,59 Hz	RCT 25 Pa	RCT 300 Pa	Static Creep Test 25 Pa	PG grading (°C)	R&B (°C)
Log(pen @ 25°C)	0,94	0,94	0,96	0,94	0,95	0,94	0,94	0,96
R&B (°C)	0,98	0,98	0,98	0,98	0,98	0,98	0,95	1,00
PG grading (°C)	0,97	0,97	0,99	0,98	1,00	1,00	1,00	0,95

Figure 3.29. Correlations between various rutting-related binders tests for unmodified binders (Bitval, 2006)

Instead, correlating the parameters found by testing unmodified binders, creep ZSV has a good correlation only with the oscillation ZSV, with the SHRP parameter of G*/sinδ when measured at a very low oscillation frequency of 0,001 Hz and with the repeated creep test. The only link between the rheological parameters and conventional that deserves to be highlited is between G */sinδ at 10 rad/s and penetration. (R = 0.85).



Rheological test, after 1 day (logarithmic) at 50 °C	Logarithmic					
	ZSV oscillation 0,001 Hz	G*/sin(δ) 0,001 Hz	G*/sin(δ) 10 rad/s	RCT 25 Pa	RCT 300 Pa	Static creep
ZSV oscillation @ 0,001 Hz	1,00	0,94	0,02	0,99	0,77	0,94
G*/sin(δ) @ 0,001 Hz	–	1,00	0,03	0,94	0,75	0,92
G*/sin(δ) @ 10 rad/s	–	–	1,00	0,02	0,00	0,01
RCT @ 25 Pa	–	–	–	1,00	0,75	0,96
RCT @ 300 Pa	–	–	–	–	1,00	0,80
Static creep	–	–	–	–	–	1,00
SHRP grading	–	–	–	–	–	–
High PG temperature	0,46	0,49	0,21	0,50	0,09	0,31
Traditional tests:						
Log(pen @ 25 °C)	0,00	0,00	0,85	0,00	0,00	0,10
R&B (°C)	0,53	0,51	0,25	0,59	0,19	0,47

Figure. 3.30. Correlations between various rutting-related binder tests for modified binders (Bitval, 2006)

Based on the results and analysis of this literature review, the findings may be summarized as follows:

Conventional tests such as the **Penetration** and S**oftening point test**, are good indicator only for unmodified binders. Their usage as rutting indicators for modified binders, stand alone or in terms of Penetration Indecies, can be excluded because the R&B softening temperature is not capable of correctly ranking PMBs in accordance with their rutting sensitivity (Bitval, 2006).

Rheological parameters able to indicate the rutting behaviour of the bituminous binders, can be grouped in two classes: Static parameters and Dymanic parameters.
The first one are obtained thorugh rotational tests:

Creep ZSV can be regarded as an indicator for permanent deformation. However, questions remain concerning:

- The precision of the results for PMBs with a high polymer content. This concern was also the conclusion of the round robin test conducted by CEN TC336 WG1/TG1. It should be further investigated if the reproducibility can be improved by refining the test protocol (e.g.by fixing criteria for stopping the creep test).
- The duration of the creep test. From a practical point of view, a creep period of 8 h or more is not desirable. Shorter creep periods may lead to good correlations with asphalt rutting, but this assumption can only be demonstrated by actually performing asphalt tests and looking at correlations with creep tests after various creep periods.
- The large deformations applied. With creep periods of hours and more, the deformations become very large and outside the range of deformations normally encountered in asphalt mixtures. It is not clear to what extent this difference in range also has an impact on the degree of correlation.

Viscous creep stiffness, G_v, obtained with the repeated creep test is an interesting candidate, for which, as seen before, good correlations with asphalt rutting tests have been reported. However, the validation of this test still requires some work, including the estimation of the precision under conditions of reproducibility.
Nevertheless, it has already been reported in the USA that the reproducibility of the test is not good because the test requires very high standards for the DSR equipment (De

Visscher et al., 2004). Moreover, the correlation between the proposed parameter Gv and mixture rutting is good for certain aggregates, but not for others. It appears that the effect of aggregates and the interaction of aggregate characteristics with binder properties are very complex. Isolation of the binder effects to evaluate the validity of Gv or any other binder only property is very difficult (NCHRP 459, 2001). Therefore, it is questionable to invest more research into following this trail (Bitval, 2006).

Non-recoverable compliance, J_{nr}, is probably the most interesting candidate between the static rutting paramets. Compared with the previous parameters, it is very fast (20 sec) and different researches have already shown its validity as rutting indicator asociated to modifed binders (Giuliane & Merusi, 2007). Recently the MSCR test to asses the J_{nr} became a standard: ASTM D7405 -10a.

The dynamic rutting parameters are obtained from oscillatory tests, therefore they could also be directly extrapolated from the DMA:

SHRP parameter $G^*/\sin\delta$ (at $\omega = 10$ rad/s) is a reliable indicator of rutting resistance only for unmodifed binders. For unmodified binders, only its measurment at very low frequency (0.0001 Hz) can be a good indicator, but this is an hypothesis because in the United States the SHRP indicator is being questioned for PMBs and alternatives are being considered (NCHRP 459, 2001)

Oscillation ZSV is one of the most interesting candidates because good correlations have been reported, coming from three different sources. Moreover, it can be obtained from the same data obtained to characterise the binder with DMA. It has not yet been shown which exact test conditions (temperature and frequency) will give results that correlate best with asphalt rutting. However, the following guidelines generally apply (Bitval, 2006):

- the correlation will be best if the test temperature is as close as possible to the temperature at which rutting occurs; and
- test frequencies from 0,01 Hz to 0,001 Hz lead to a good correlation, while still being practically feasible.

Shenoy's parameter is an other interesting candidate, because as the Oscillation ZSV it can be obtained from the same data obtained to characterise the binder with a DMA.

This performance-based specification term was shown to be more sensitive to the variations in the phase angle δ, than the SHRP parameter and thus it can describe the unrecovered strain in the binders more accurately, especially in the case of modified bitumens (Shenoy, 2002).

4. Modification of bitumen

On the majority of roads, the use of neat bitumens still allows obtaining pavements that perform well. Nevertheless, demands made upon roads increase year by year and it is well known that pavements undergo important distresses due not only to extreme temperatures but also to increasing traffic loads (higher traffic levels, larger and heavier trucks, new axle designs and increased tyre pressure). Moreover, since comfort, high standard of safety, maintenance frequency and service life became key factors on road design, it is of primary importance for pavements applications to enhance the properties of the binder in order to achieve better performance and durability of the asphalt.

The ideal binder should have enhanced cohesion and very low temperature susceptibility throughout the range of temperatures to which it will be subject during service, while keeping a low viscosity at the usual temperatures at which it is placed. Its susceptibility to loading time should be low, whereas its permanent deformation resistance, fracture strength and fatigue characteristics should be high. At the same time, it should have at least the same adhesion qualities (active and passive) as traditional binders. Finally, its aging characteristics should be good, both for laying and in service. Figure 4.1 illustrates these points with respect to temperature susceptibility (Brule', 2007)

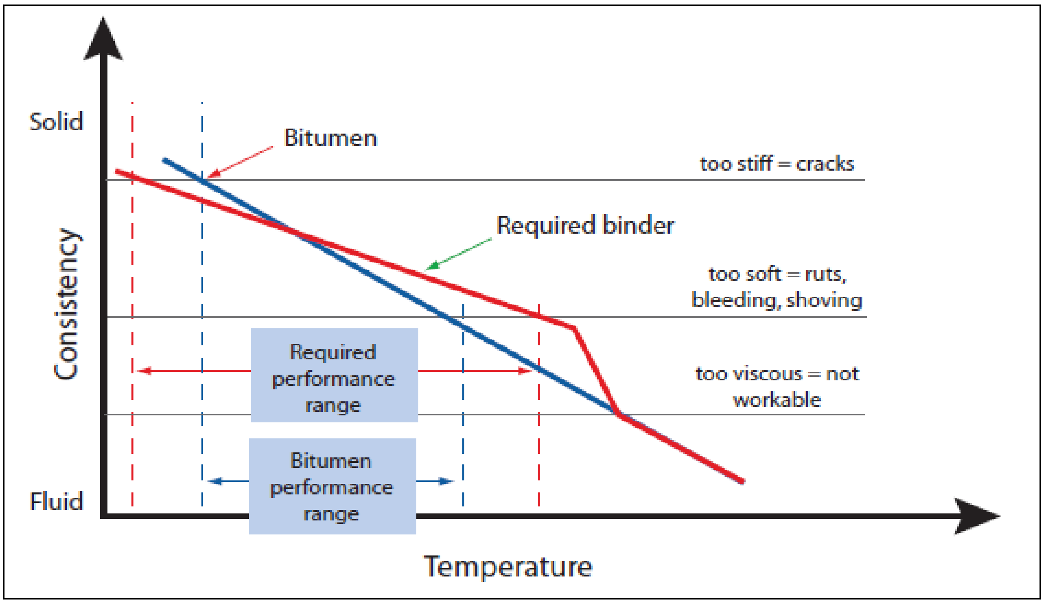


Figure 4.1. Temperature susceptibility of an ideal thermoplastic binder. (Brule', 2007)

Bitumen modification offers one solution to overcome deficiencies of conventional bitumens and to improve the performance of asphalt pavement by various means including (Read & Whiteoak, 2003):

- Obtaining a stiffer asphalt mixture at high service temperatures to minimise rutting
- Obtaining softer mixtures at low temperatures to minimise non-load associated thermal cracking
- Improving fatigue resistance
- Improving bitumen-aggregate bonding to reduce stripping or moisture susceptibility
- Improving abrasion resistance of asphalt mixture to reduce ravelling
- Minimising tender asphalt mixture problems during construction
- Improving workability of the asphalt during compaction
- Reducing costs and fumes by reducing operative temperatures
- Rejuvenating aged bitumens
- Permitting thicker bitumens films on aggregate for increased asphalt mixture durability
- Reducing flushing or bleeding
- Improving resistance to ageing or oxidation

- Reducing structural thickness of pavement layers
- Reducing life cost of asphalt pavements
- Improving overall performance of asphalt pavements

4.1 Principle of bitumen modification

4.1.1 Bitumen modifiers

In the last thirty years, researchers have looked at a wide spectrum of modified materials for bitumen used in road constructions. Many different kinds of additives and modifiers have been tested to improve one property or another of the bituminous binder. As a matter of fact, different substances can potentially give similar benefits to the bitumen, but for modifiers to be effective and for its use to be both practicable and economic, it must (Denning, 1981):

- Be readily available
- Resist degradation at asphalt mixing temperature
- Blend with bitumen
- Improve resistance to flow at high road temperature without making the bitumen too viscous at mixing and laying temperatures or too stiff or too brittle at low road temperatures
- Be cost effective

Moreover, when blended with bitumen the modifier should:

- Maintain its premium properties during storage, application and in service
- Be capable of being processed by conventional equipment
- Be physically and chemically stable during storage, application and in service
- Achieve a coating or spraying viscosity at normal application temperatures.

Obviously, the above listed characteristics cannot be achieved all at the same time and with the same effectiveness, because each one of them depends upon the compatibility between the base bitumen and the type of modifier (source, chemical structure, molecular weight) (Di Mino, 1991). Depending on the various substances that are mixed with the bitumen by using mechanical and/or chemical systems at controlled temperature levels, it is possible to modify the original nature and/or behaviour of the bitumen by several processes including additive modification, polymer modification and chemical reaction modification. (SITEB, 2000b).

Additives

Making asphalt for paving roads requires the achievement of high temperatures to allow the proper mixing of bitumen with stone aggregate and to obtain mixtures of adequate workability. The addition of substances of various kinds to the base bitumen is a technological solution that allows, within narrow range, to vary some characteristics of the binder (mainly physical parameters as penetration, viscosity, etc. ..) and is mainly useful for reducing costs and environmental impact during paving applications (high temprature), but with little influence in improving the mechanical properties of binders at service temperatures. Among the additives used to modify the bitumen, it is appropriate to dwell on the following additives:

Oil extenders (Fluxes). Compounds that provide saturated or unsaturated oils for the base bitumen, which can then be used with various functions. In fact, the increase in the volatiles content, i.e. oils, leads to a reduction in viscosity of the base binder and therefore increasing their workability, but it can be used also for a rejuvenation of the binder (i.e. increasing the oil phase of aged bitumens) or to improve the compatibility of bitumen with polymers during the modification process.

Warm mix additives (WMA). The WMA techniques are technological solutions characterized by the common aim of reducing the temperature required for packing and laying of asphalt without limiting operational performance and durability. Some of these techniques are based on the addition of specific mineral agents (zeolite) able, at certain temperatures, to release water vapour and facilitate asphalt workability through the processes of microfoaming of the binder. (Hurley et. al., 2005).Other techniques are based instead on the addition of organic additives such as synthetic waxes. These products consist of high molecular weight aliphatic hydrocarbons, characterized by a crystalline structure and high melting point (> 90 ° C). (Edwards, 2005). With these characteristics, synthetic waxes favour the decrease of the viscosity of bitumen at high temperatures without compromising the mechanical properties in service and even providing a modest increase in stiffness within the entire range of operating temperatures (Merusi, 2009). In addition to those described above, also the following products belong to the family of additives: inorganic fillers, ebonite powder, chemical additives and various plasticizers.

Chemical reaction

As seen before, additives are mainly used as viscosity reducers, oil sources and to decrease cost and environmental impact of the asphalt production. The main purpose of modification of binders is to obtain a material that allows to get an asphalt mixture that shows better mechanical properties at service temperatures. In order to achieve this point, it is necessary to modify the chemical and physical structure of the base bitumen by deeply influencing its rheological behaviour and thermal susceptibility (SITEB, 2000a).

The first practice of modification of bitumen can take place already during its manufacture by air blowing the residue of crude oil distillation (§ 2.2.1). Air blowing is an industrial application of the chemical reactivity of bitumen, in use for more than a century. The main effect of the air blowing is that it converts some of the relatively low molecular weight “maltenes” into relatively higher molecular weight “asphaltenes”. The major result is the change in some physical properties as the reduction in penetration, a comparatively greater increase in softening point and lower temperature susceptibility. Depending on the level of air blowing, it is possible to distinguish semi-blown or fully blown bitumens (oxidised) (Read & Whiteoak, 2003).

It was early observed that bitumen could be reacted with other compounds such as sulphur, chlorine or various acids (sulphuric, nitric, acid sludge, fatty acids) in normal storage tank (Lesuer, 2009). However this process did not get industrial success because of the corrosion problem involved with manipulating such products and also because similar effect could be obtained by the cheaper air blowing process. In parallel, air blowing was progressively abandoned for paving bitumens, because of the increased fragility of the binders and the higher susceptibility (Lesuer, 2009).

In recent years bitumen chemical modification was rediscovered because it started to make economical sense and seemed to lack the fragility problem of air-blown bitumens (Edwards et al., 2006; Philip et al., 1999). In particular, polyphosporic acid (PPA) modification is currently gaining industrial importance since it permits to significantly harden bitumen in an easily controllable way. The reactivity of bitumen towards acid is still not completely understood. It is known that not all the bitumen show the same reactivity, but the general overall effect is the stiffening of the binder by increasing the asset of the asphaltenes, increasing in turn the solid fraction and hence the viscosity (Orange et al., 2004). Several mechanisms have been proposed and reported in literature (Baumgardner et al., 2005; Orange et al., 2004)

Polymers

The most important family of bitumen modifiers is represented by the polymeric materials. Addition of natural or synthetic polymers to straight asphalts is known to impart enhanced service properties over a wide range of temperatures in road paving applications. As a matter of fact, by blending bitumen with polymers it is possible to deeply influence its rheological behaviour and thermal susceptibility which, due to structural change, tends to assimilate the main characteristics of the modifier (SITEB, 2000a). A large number of research works have been devoted to the study of the effect of these additives on the properties of such modified bitumens and their road performance. Several studies have confirmed the beneficial effects of polymer modification on bituminous binders (Di Mino et al., 1991; Airey, 2003; Brule', 2007, Yildirim, 2007): decreased thermal susceptibility and permanent deformation (rutting), increased fatigue, and low temperature cracking resistance.

Tables 4.1 details the majority of bitumen modifiers and additives that have been examined in the last decades and the benefits of the different modifiers related to pavement distresses (NCHRP 459, 2001).

Table 4.1. Generic types of modifiers currently used for paving applications (NCHRP 459, 2001).

Modifier type	Class	Effect on distress				
		PD	FC	LTD	MD	AG
Fillers	Carbon Black	x				x
	Mineral: Hydrateted lime	x				x
	Fly ash	x				
	Portland cement	x				
	Baghouse fine	x				
Extenders	Sulpur	x	x	x		
	Wood lignin				x	

Polymers-Elastomers	Styrene butadiene di-block SB	x		x	x	
	Styrene butadiene triblock/radial block (SBS)	x	x	x		
	Styrene isoprene (SIS)	x				
	Styrene ethilbutylene (SEBS)					
	Styrene butadiene rubber latex (SBR)	x		x		
	Polycloroprene latex	x	x			
	Natural rubber	x				
	Acrynolite butadiene styrene (ABS)	x				
Polymers-Plastomers	Ethylene vinil acetate (EVA)	x	x			
	Ethylene propylene diene monomer (EDPM)	x				
	Ethilene acrylate (EA)	x				
	Polyisobutylene	x				
	Polyethylene (low density high density)	x		x		
	Polypropylene	x				
Crumb rubber	Different sizes, treatments and process	x	x	x		
Oxydant	Manganese compounds	x				
Hydrocarbons	Aromathics			x		
	Naphtenics					
	Paraffinic/wax			x		
	Vacum gas oil	x		x		
	Asphaltenes: ROSE process resins	x				
	SDA asphaltenes	x				
	DEMEX asphaltenes	x				
	Shale oil				x	x
	Tall oil					
	Natural asphalt: Trinidad	x	x	x	x	
	Natural asphalt: Gelsonite	x			x	
Antistrips	Amines: Amidoamines				x	
	Amines: Polyamines				x	
	Polyamides				x	
	Hydrateted lime				x	
	Organic-metallics				x	
Process based	Air blowing					
	Steam distillation					
	Propane de-asphaltated (PPA)					
Fibers	Polypoprilene	x	x	x		
	Polyester	x		x		
	Fiber glass					
	Steel	x	x	x		
	Reinforcement	x	x	x		
	Natural cellulose					
	Natural mineral					
Antioxydant	Carbanates: Lead			x		x
	Carbanates: Zinc			x		x
	Carbon Black	x				x
	Calcium salts					x
	Hydrateted lime				x	x
	Phenols					x
	Amines				x	x

PD – Permanent deformation
FC – Fatigue cracking
LTC – Low temperature cracking
MD – Moisture damage
AG – Oxidative aging

4.2 Polymer Modified Bitumen (PMB)

Polymer modification of bitumens is not a new phenomenon, but interest of this technique has increased considerably during the past decade due to the increased performance-related requirements on asphalt pavements.

One of the prime roles of a bitumen modifier is to increase the resistance of the asphalt to permanent deformation at high road temperatures without adversely affecting the properties of the bitumen or asphalt at other temperatures. As a matter of fact, adding polymer to bitumen allows to greatly increase the high temperature end of paving grade, leaving the low temperature slightly better. More specifically, a rule of thumb gives that for every 1% of added polymer, 2°C in high temperature PG are typically gained. On the low temperature end, the rule becomes more 1% of added polymer, 1°C in low temperature PG. Since the PG classes are based on 6°C steps, the typical 3% polymer-content modification generally allows gaining one high-temperature class leaving the low temperature sometimes unchanged. (Lesuer, 2009).

The use of a polymer has no value if it does not substantially improve the life cycle cost of the material in which it is used or solve a specific problem. The selection of polymer modification should almost always be based on improved performance related to cost (FHWA, 2011).

Brief history and geography of PMB

Processes of bitumen modification involving natural and synthetic polymers were patented as early as 1843. Test projects were underway in Europe in the 1930s, and neoprene latex began to be used in North America in the 1950s (Yildirim, 2007). Nevertheless, experiences with modified bitumens started seriously in the mid 1970s with the introduction of styrene butadiene styrene (SBS) as a bitumen modifier (Airey, 2002). In the late 1970s Europe (France in particular) was ahead of the US in the use of modified bitumens because the European contractors, who provided warranties, motivated a greater interest in decreased life cycle costs, even at higher initial costs. In the mid 1980s, newer polymers were developed and European technologies began to be used in the US. By 1997 all but three states of US were already using modified binders or intended to use them in the future and federal regulations supported their use (Yildirim, 2007). In Europe, in the late 1990s France and Germany, already used intensly the modified bitumens for road pavement applications (SITEB, 2000b). In Italy from 1995 to 2000, 24 societies, all under a unique trade known as GPM (Gruppo Promozione bitume Modificato), promoted the use of modified bitumen in all countries, putting in evidence how the large use of polymer modified bitumens could help environment, security and quality of road constructions. Nowadays, Italy is one of the top-level European producers of modified bitumen. (SITEB, 2000a).

4.2.1 Polymers for bitumen modification

Polymer is a derived word meaning "of many parts". Polymers can be thought of as long chemical strands that are made up of many smaller chemicals (monomers) that are joined together. Names of polymers are usually based on the names of the monomers used to make the specific polymer. Thus, the polymer that comes from polymerizing ethylene monomers is polyethylene. (Polacco et. al, 2005)

Despite the large number of polymeric products, there are relatively few types which are suitable for bitumen modification. In fact, when used as bitumen modifiers, polymers should be compatible with bitumen, resist degradation at asphalt mixing temperatures and be cost-effective. The degree of modification depends on the characteristics of bitumens, polymer type and content, as well as the process used for preparation of the modified bitumens. (Isacsson & Lu, 1999).

For these reasons, the most popular, because most compatible (§4.2.5), types of polymer used in modifying bitumen for road applications are thermoplastic plastomers and thermoplastic elastomers, which respectively have glassy (stiffness) or rubbery (elastomeric) properties (FHWA, 2011)

A thermoplastic polymer is a polymer that will deform in a plastic or viscous manner at melt temperatures and becomes hard and stiff at low temperatures, i.e. the structure is reversibly broken down with the application of heat. Moreover, by using these materials vulcanization may be avoided because by simply cooling the blend it can maintain the desired shape. The modification with plastomer allows stiffening the bitumen so that the total viscoelastic response of the asphalt is reduced (glassy behaviour). The second option is to increase the elastic component thereby reducing the viscous component; this is the case of modification with elastomers (elastic behaviour). Whereas elastomers can improve the resistance to rutting as well as low temperature and fatigue cracking, plastomers will generally only improve the resistance to rutting (Polacco et al., 2005).

Thermoplastic Plastomers

EVA is the most common plastomer used in modified road binder and acts by increasing the viscosity of the bitumen making the PMB stiffer than conventional bitumen. EVA polymers are easily blended into asphalt by simple low shear mixing.

Polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and various ethylene copolymers (semi-crystalline polymers), such as ethylene methyl acrylate (EMA) and ethylene butyl acrylate (EBA), are the other principal non-rubber thermoplastic plastomer that have been examined in these years (Airey, 2002).

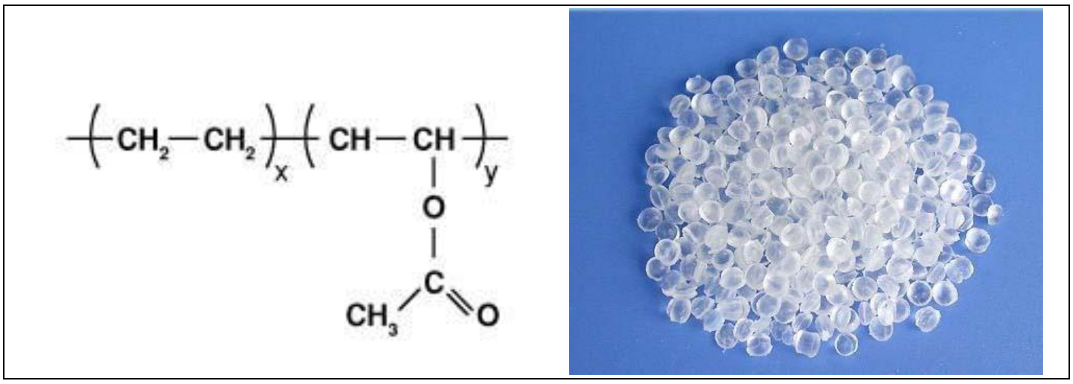


Figure 4.2. EVA – molecular structures and aspect.

Thermoplastic Elastomers

An elastomer is a polymer that has a flexible 'rubber' backbone and large sidechains in its structure. **Styrene Butadiene Styrene (SBS)** is an example of this type. Thermoplastic elastomers derive their strength and elasticity from a physical cross-linking of the molecules into a three dimensional network. SBS is the most common asphalt polymer used in road bitumen modification. SBS is a triblock copolymer incorporating styrene sections attached to a central butadiene section (Fig. 4.3). It is the polystyrene end-blocks that impart strength to the polymer and the mid-block butadiene that gives the material its exceptional elasticity. This combination of strength and elasticity gives SBS modified bitumens the ability to resist permanent deformation and to minimize fatigue and low temperature cracking. At temperatures above the glass transition temperature of polystyrene (100°C), the polystyrene softens and will even dissociate under stress, thus allowing easy processing. Upon cooling, at asphalt service temperatures, the cross linked polymer network is restored, therefore enhancing bitumen rutting resistance (Read & Whiteoak, 2003). The SBS has a temperature behavior similar to vulcanized rubber and the segments act as polybutadiene elastomers while the rigid polystyrene domains are acting as cross-linking points.

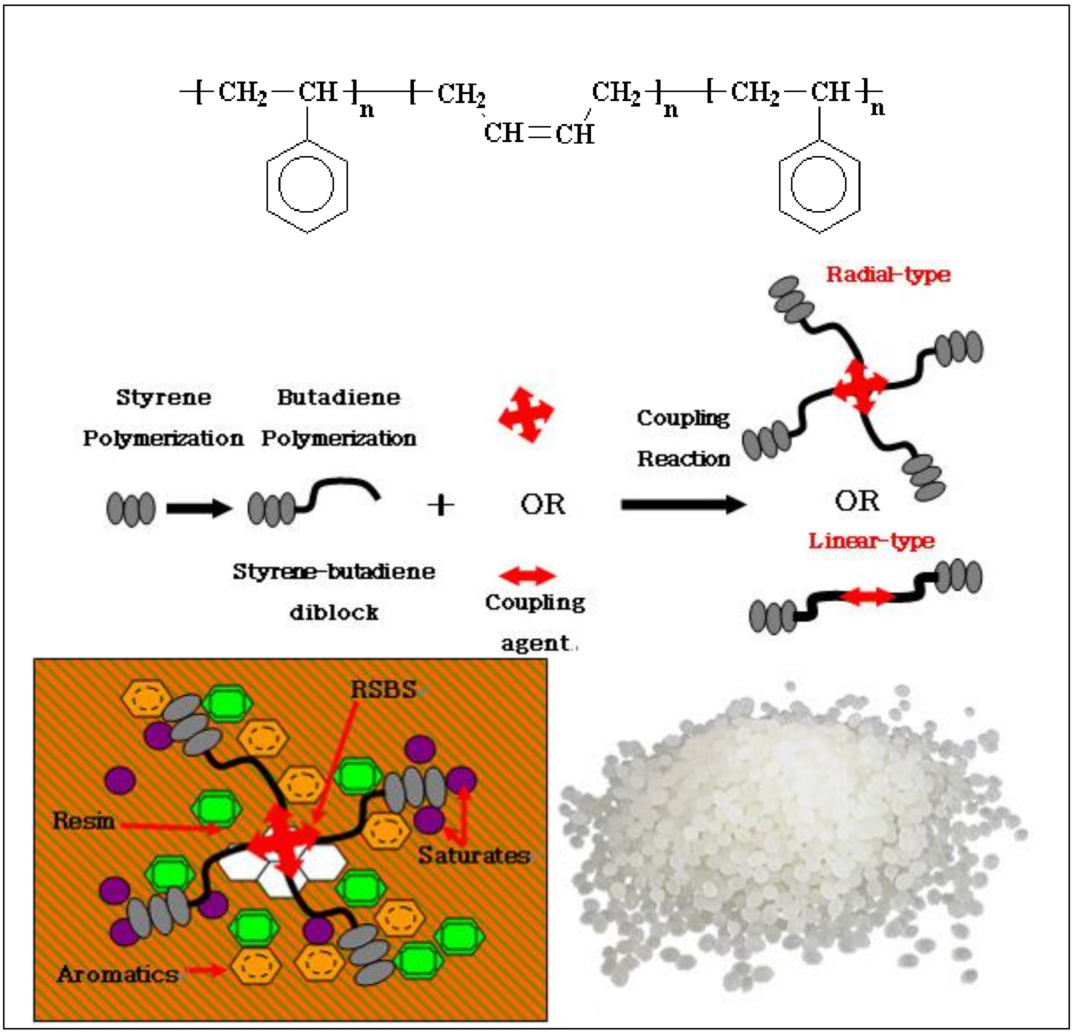


Figure 4.3. SBS – molecular structures, compatibility with bitumen and aspect.
(TradeKorea.com, 2011)

This network (unlike vulcanized rubber) is reversible, so the physical and mechanical properties of the copolymer does not vary after repeated heating and cooling processes, i.e. the material is thermoplastic (Polacco et al., 2005).

As with most polymers, SBS is available in many different forms. The polymer molecules can be different lengths and can have different arrangements of the molecules. These differences can affect the degree of modification provided by the polymer, as well as the ease of blending and the storage stability (Fig. 4.3)

SBS-based PMBs are reasonably easy to manufacture by blending powdered SBS polymer into a bitumen using low to medium shear mixing. Cross-linking additives such as elemental sulfur or other proprietary chemicals, or even high temperatures, can enhance the linking of the asphalt with the polymer structure and can minimise the amount of polymer needed for a given level of performance (Fig. 4.3).

Other common elastomers include SIS, styrene-isoprene-styrene, SB, which is a diblock copolymer of styrene-butadiene, and PBD, which is Polybutadiene, a polymer formed from the polymerization of the monomer 1, 3-butadiene. Styrene-butadiene rubber latex (SBR) is a random copolymer of styrene and butadiene in a water based system. SBR is often used in asphalt emulsions for chip sealing or slurry seals. Ethylene terpolymer, commonly known through its brand name Elvaloy®, consists of an ethylene backbone with copolymers of n-butyl acrylate and glycidyl methacrylate. (the word terpolymer refers to a polymer made from three subunits.) Crumb rubber (CR) is produced from recycled tyres. The method of processing the recycled tyres can have significant effects on the consistency of performance of the mixture as will be shown in next chapter (§ 4.3)

4.2.2 Base bitumen for polymer modification

Bitumen can be processed from a variety of different crude oils and its broad chemical composition can be determined by analytical techniques such as liquid chromatography (§ 2.2.2). As discussed before (§ 2.2.3), the four main components are referred to as saturates, aromatics, resins and asphaltenes. The relative ratios of these components have a major influence on the way a polymer is solubilised or can swell in the base bitumen and therefore greatly influence the end-performance of the PMB. Saturates and aromatics can be viewed as carriers for the polar aromatic, i.e. the resins and asphaltenes. The addition of thermoplastic polymers with molecular weight similar to or higher than that of the asphaltenes disturbs the phase equilibrium (Read & Whiteoak, 2003).

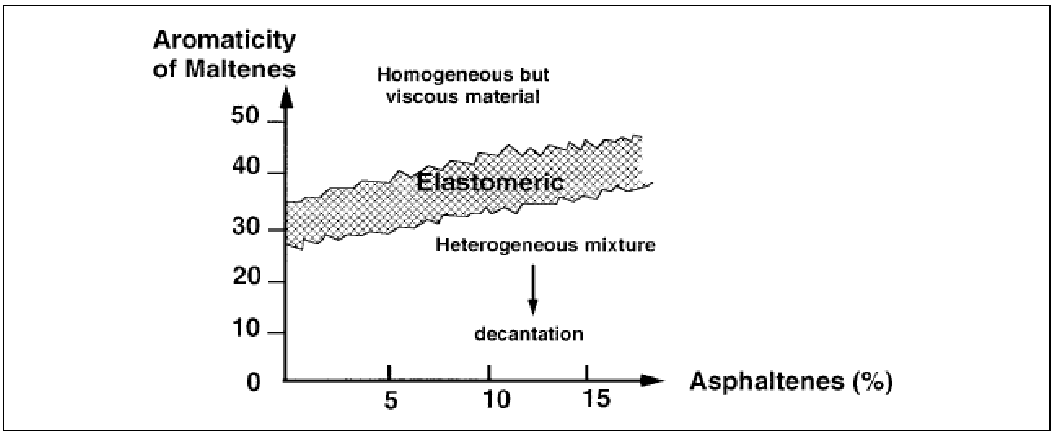


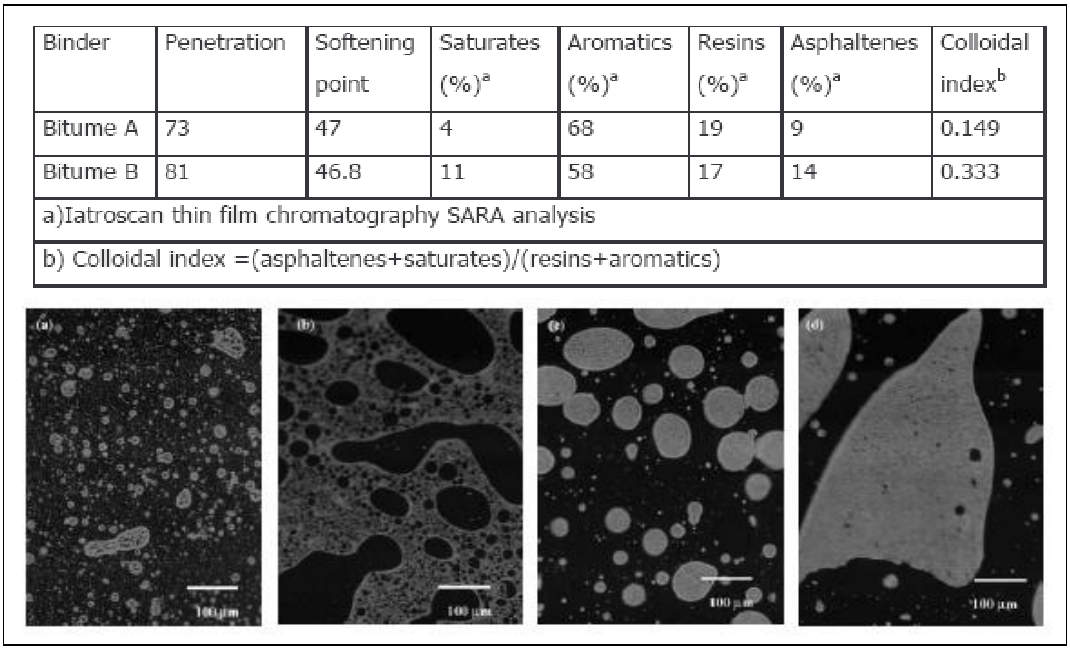
Figure. 4.4a. Effect of aromaticity of maltenes on the characteristics of SBS-modified bitumens. (Van Beem & Brasser, 1973)

For SBS-modified bitumens (Van beem, 1973), it has been indicated that the aromaticity of maltenes plays an important role in compatibility and properties (Fig. 4.4a). Other researchers (Diani & Gargani, 1987) provided details on the effect of the generic composition of bitumens on the properties of SBS-modified bitumen mixes with high SBS contents used in the waterproofing industry. Among other things, they demonstrate the determining effect of the saturated oils content on the physical properties of modified binders (penetration and R&B softening point).

On the other hand, an equivalent study dealing with EVA-modified bitumens with high polymer content (Madella et al., 1991) demonstrated that the effect of the chemical composition of the bitumen is much less marked.

Another interesting example is given by the study undertaken from Airey (Airey, 2003), in which several modified bitumen with SBS, differing from bitumen bases and polymer content, were studied through morphological analyses. Bitumen A is a paraffin base (Russia), while bitumen B is a basic naphthenic (Venezuela); the two bases have very similar softening points and consistency, but differ greatly in their chemical fractional composition SARA. Modification was made with different percentages by weight of copolymer (5% and 7%) for both bases. Figure 4.4b clearly demonstrates the differences in morphology of the PMBs as a function of base bitumen type and polymer content.

In this study, the Colloidal Indexes (CIs) are indicated as potential indicator of compatibility of the base bitumens to polymer modification.



Binder	Penetration	Softening point	Saturates (%)[a]	Aromatics (%)[a]	Resins (%)[a]	Asphaltenes (%)[a]	Colloidal index[b]
Bitume A	73	47	4	68	19	9	0.149
Bitume B	81	46.8	11	58	17	14	0.333

a)Iatroscan thin film chromatography SARA analysis

b) Colloidal index =(asphaltenes+saturates)/(resins+aromatics)

Figure 4.4b. Different morphologies of SBS modified bitumen by changing the base bitumen (Airey, 2003)

In general a lower CI value (greater percentage of polar and non-polar aromatics) will lead to a more compatible system with higher degree of solvency for the polymers (Airey, 2003).

Other researchers (Serfass et.al, 1992; Masson et.al, 2003) are of the opinion that no precise CIs borderline separates “compatible” and “not compatible” to modification bitumen. Masson et. al (2003), in particular affirm that the use of CIs as criteria for selecting an appropriate base bitumen for modification is of dubious value, because it has been shown that both saturates and aromatics contribute to the stability of a bitumen polymer blend. These fractions play against each other in the calculation of CI, so it may be the other fractions, the asphaltenes in particular, that have the greatest influence on the index.

Moreover, the same researchers have shown that necessity for a high aromatics content to enhance stability is also questionable. As a matter of fact, similar results have been obtained by modifying bitumen with 15-30% of aromatics and others with the higher concentration of 50-60%. The poor value of the aromatics content as a guide for bitumen-

polymer stability is also recognized from the instability of blends of SBS and a bitumen with 41% of naphtene aromatics (aromatics) and 50% of polar aromatics (resins).
These researchers suggest, therefore, to assess bitumen-polymer stability taking into account the contributions of the thermodynamical properties ΔH and ΔS affirming that for a blend to be stable the change in Gibbs energy upon mixing has to be less than zero (Olabisi et al., 1979, Kwei & Wang, 1978)

$$\Delta G_{mix} = \Delta H_{mix} - \Delta S_{mix} < 0 \qquad (4.1)$$

Selections based on CI aim to maximise molecular interactions and therefore the favorable contribution of ΔH to ΔG. In contrast, selections based on asphaltenes aim to minimise the content of the highest molecular weight fraction within bitumen, and thus maximise ΔS (Masson et.al, 2003).

On this basis, the colloidal instability index and the content of aromatics or asphaltenes in bitumen lead to discordant stability predictions. These methods effectively emphasises the effect of either ΔH or ΔS but not both. Moreover, it should always be kept in mind that polymer compatibility, with a specific base bitumen, does not necessarily mean that this base asphalt will be compatible with other types of polymers.

4.2.3 Manufacturing of PMBs

There are many types of manufacturing configurations to make polymer-modified bitumens. Manufacturing may be done at high or low shear, on site, or in a factory. The main stages of manufacturing require the following procedures (FHWA, 2011):

- Metering of polymer, bitumen, and additives
- Wetting of the polymer by the bitumen/additive mix
- Dispersion of the polymer
- Allowance for any interaction (reaction) of the polymer with the asphalt
- Storage and transportation

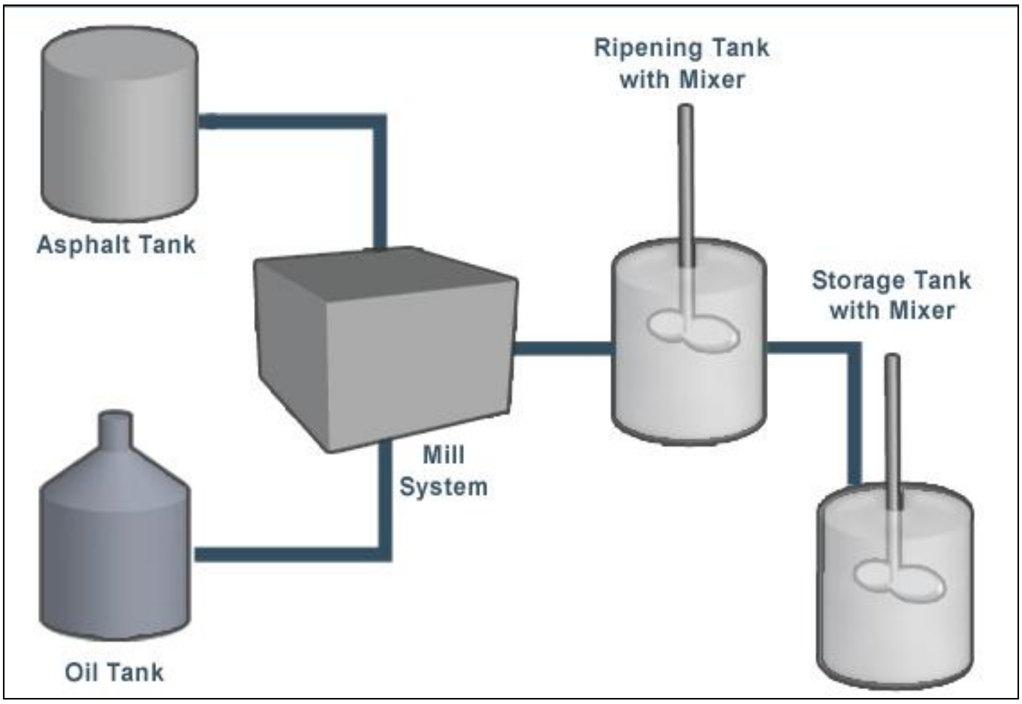


Figure 4.5. Typical Polymer Blending Plant (Holleran et al., 2011)

Most of these are mechanical issues and are achieved by relatively simple techniques. Figure 4.5 illustrates an ideal manufacturing (blending) plant for PMBs. It has to be highlighted that storage tank, to avoid phase separation, is equipped with a mixer to keep the binder under agitation. The most important steps in the manufacturing process are dispersion and reaction. This is what determines the structure (i.e., morphology) of the final binder and hence its properties. These steps also determine the level of polymer required to achieve the desired results. Compatible systems usually have superior rheological, aging, and stability properties to those of incompatible systems at the same polymer level (FHWA, 2011).

4.2.4 Compatibility (Stability) of polymer - bitumen blends

The major restriction encountered in polymer modifications of bitumen remains the incompatibility of the modifying polymer and the bitumen matrix. In general, incorporating a polymer in a bitumen matrix results in a multiphase material with a great tendency to phase separate (Hesp & Woodhams, 1992) (Fig. 4.6).

If, without taking any special precautions, a road bitumen and a given thermoplastic polymer are mixed hot, one of the following three results may occur:

- The mix is heterogeneous: this is the most likely result (i.e.,where the polymer and the bitumen prove to be incompatible). In this case, the constituents in the mix separate and the mix has none of the characteristics of a road binder.

- The mix is totally homogeneous, including at the molecular level: this is the infrequent case of perfect compatibility. In this case, the oils in the bitumen solvate the polymer perfectly and destroy any intermacromolecular interactions. The binder is extremely stable, but the modification of service qualities with respect to those of the initial bitumen is very slight. Only its viscosity increases. This is, therefore, not the desired result.

- The mix is microheterogeneous and is made up of two distinct finely interlocked phases. This is the compatibility sought and gives the bitumen genuinely modified properties. In such a system, the compatible polymer “swells” by absorbing some of the oily fractions of the bitumen to form a polymer phase distinct from the residual bitumen phase comprising the heavy fractions of the binder (the rest of the oils, plus the resins and asphaltenes).

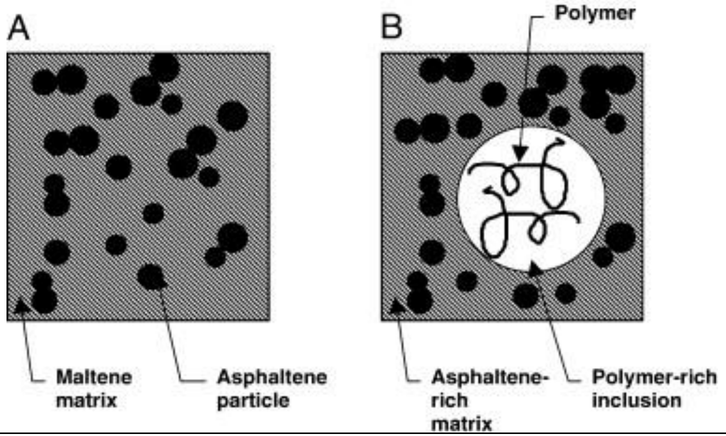


Figure 4.6. Effect of polymer-modification on the colloidal structure of a bitumen: original bitumen (A) and the corresponding PMB with increased asphaltenes content in the matrix (B) (Lesuer, 2009)

A desirable system, therefore, has to be a blend of bitumen with a partial miscible polymer that is homogeneous as judged by eyesight but heterogeneous under the microscope (Pfeiffer, 1950). As a consequence, even for compatible systems, the equilibrium situation is a macroscopic phase separation of the two-phases. The Asphaltenes Rich Phase (ARP) being the denser phase, creaming of the Polymer Rich Phase (PRP) occurs at a rate controlled by Stokes sedimentation rate. Thus the larger the density difference and the larger the particle size, the faster the creaming rate. Polymer/bitumen compatibility is indeed a dynamic concept and compatible system are those with slow creaming rate (Lesuer, 2009).

Usually this equilibrium is reached with a medium-high percentage of polymer, around 5-6% by weight, which create a three-dimensional polymer network that radically changes the properties of bitumen; with lower percentage (<3÷4%) a continuous bitumen phase with a dispersed polymer is obtained, with higher amount (6÷7%) instead is the bitumen that is disperded in a continuous polymer phase (Lesuer, 2009).

Storage stability of modified bitumens

As seen before (§ 2.1.1), the bitumen internal structure is already complex; when a polymer that reacts with the oil fractions is added, the blend may be thermal unstable.

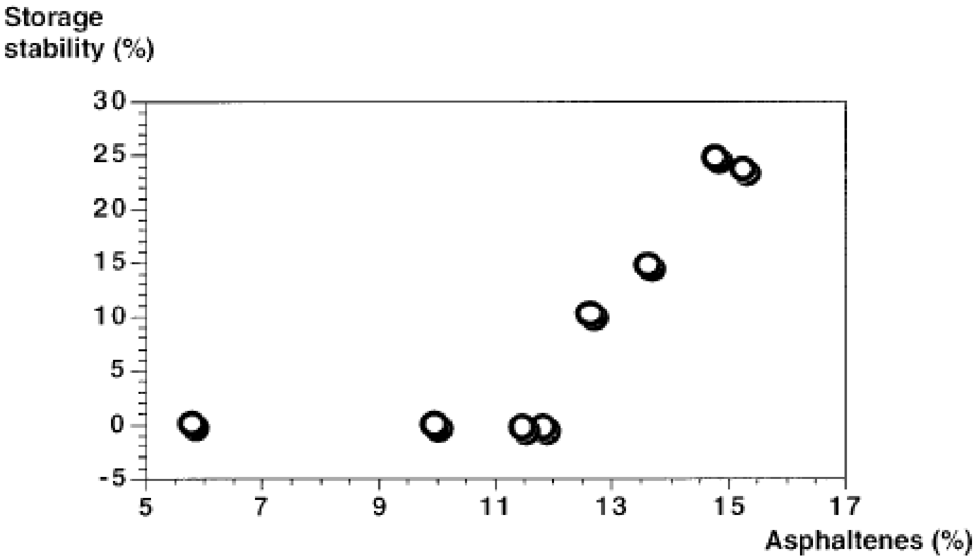


Figure 4.7. Effect of asphaltene content on the storage stability of EVA-modified binders. (Brule', 2007).

The thermoplastic polymer has a molecular weight similar to that of asphaltenes or even higher, therefore polymer and the asphlatenes “compete” for the solvency power of the maltenes phase and when insufficient oils are available, phase separation may occur. (Read & Whiteoak, 2003). This separation is an indication of incompatibility between the bituminous base and the polymer phase.

Due to the tendency of phase separating of modified binders, the storage stability is an extremely important characteristic to be assessed. Since these binders consist of two distinct phases, they are subject to the same physical principles as those governing the separation or sedimentation of bitumen emulsions (Stokes’ law). In other words, the velocity of displacement of dispersed particles (polymer phase in the case of a bitumen matrix and bitumen phase in the case of a polymer matrix) increases as:

- The particle size increases,
- The difference in density between the two phases increases, and
- The viscosity of the continuous phase decreases.

Making polymer-modified bitumens with good storage stability therefore implies micronising the dispersed phase (effect of the process and manufacturing process) or both phases of equal density at the storage temperature (effect of the chemical composition of the bitumen). As an example, Brule’ has shown that for EVA modified asphalt cements, the storage stability of the binder depends strongly on the asphaltene content of the base asphalt cement (0 percent on storage stability test means that there is no separation of the polymer phase) (Fig. 4.7).

Improving compatibility of polymer - bitumen blends

In order to improve compatibility, therefore prevent phase separation, it is fundamental to choose the right materials to blend and optimise all the variables that play an important role in the production of a PMB. The effectiveness of the modification and stability are based on optimization of many parameters such as:

- Composition and amount of modifier
- Composition of bitumen (Fig. 4.5)
- Thermal profile of the mixing process
- Mixing protocol.

Moreover, few stabilization mechanisms were developed to improve polymer blends compatibility. As a matter of fact, it is possible to add aromatic oils to the base bitumen, so to improve the solvency power of the maltenes phase, but taking into account that, for instance in the case of SBS, a too high percentage of oils dissolves polystyrene foam blocks cancelling the benefits of adding the copolymer. In any case the characteristics of the base bitumen are crucial to the final structure of the product. (Polacco, 2005).

The most used method at industrial level is the dynamic vulcanization (Coran, 1987). This consists in adding a cross-link agent under agitation. In this method it is important to allow the PRP to slightly cross-link preventing PRP droplets to coalesce. The freezing of the equilibrium droplet under agitation yields to a very low particle size favoring stability. High cross-link density is not sought after because it would result in a lower swelling extent.

Finally, it has to be underlined that ways to predict whether a particular polymer will be compatible with a given bitumen are not well defined and the formulator has to relies on laboratory experiments rather than on theoretical predictions. In all cases, and even if polymer has potentially compatible chemistry, the formulation of PMBs requires a good selection of the initial bitumen (Lesuer, 2009) and, as a result, without several trials it is really hard to identify a priori compatible bitumen-polymers pairs.

Thermodynamic approach

Thermodynamic approaches regarding polymer bitumen modification do not have comprehensive theoretical treatment unites or criticizes, but some researchers (Masson et. Al, 2003) showed that stability of a polymer blend is indeed governed by thermodynamics. These researchers affirm that thermodynamics of blends provide a general theoretical framework for understanding the complex interrelationship of the various parameters that affect the stability of bitumen-polymer blends. A useful tool to understand the behavior of a binary blend is reflected in its phase diagram (Olabisi et al., 1979; Kwei & Wang, 1978).

In perfectly miscible binary blends, the phase diagram is a continuous 1-phase region (Fig. 4.8a). In blends that segregate, the composition of the phases depends on the spinodal and the temperature; the spinodal being the border between the 1- and 2-phase regions (Fig. 4.8b-e).

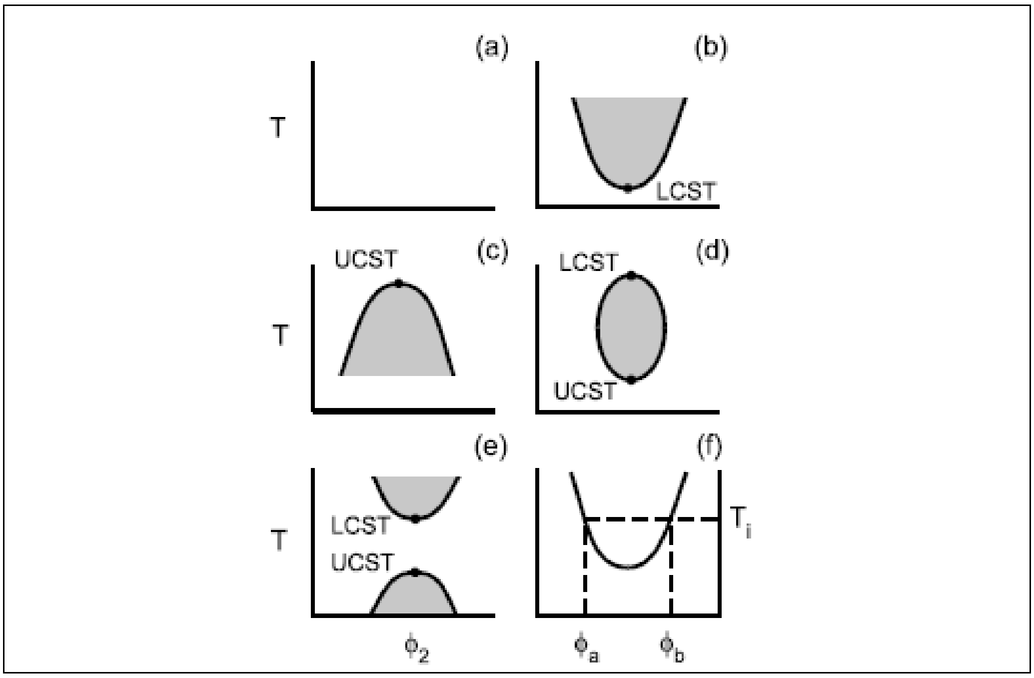


Figure 4.8. Typical phase diagram for binary mixtures miscible in all temperatures (a) that segregate upon heating, (b) that segregate upon cooling, (c) that segregate upon heating and cooling (d,e). The composition of the segregated phases (Φ_a and Φ_b) is governed by the spinoidal curve (f) (Masson et al., 2003)

The blends segregating upon heating have a lower critical solution temperature (LCST, Figure 1b), whereas blends that segregate upon cooling show an upper critical solution temperature (UCST, Figure 1c). Some blends have both a UCST and an LCST (Figs 4.8d and 4.8e). When segregation occurs at T_i, the equilibrium composition of the segregated phases, ϕ_a and ϕ_b, is defined by the spinodal (Fig. 4.8f).

The phase diagram for bitumen polymer blends shows a lower critical solution temperature (LCST) below which the blends are stable, but above which they segregate.

Considering this background, and the fact that for a blend to be stable, as seen before (§ 4.2.2.), the change in Gibbs energy upon mixing (ΔG_{mix}) must be lower than zero, compatibility of polymer-bitumen blends, could be investigated by considering the contribution of the polymer and that of the bitumen to entropy, ΔS, and enthalpy, ΔH that occurs upon mixing (Masson et. Al, 2003).

At the spinodal, $\partial^2 \Delta G_{mix} / \partial \phi_a = 0$ so that a sufficient and necessary condition for stability is $\partial^2 \Delta G_{mix} / \partial \phi_a > 0$. On this basis, it is possible to affirm that the stability of blends of bitumen with polymers is governed by the entropy (ΔS) and enthalpy (ΔH) of mixing or, in other words, by molecular weights and intermolecular interactions. The molecular weights of both bitumen and polymer will affect ΔS, but given the higher molecular weight of polymer, the polymer will have a dominant effect. Similarly, a change in bitumen or polymer composition will affect intermolecular interactions between the pair; as a matter of fact when the blend components have an attractive interaction, heat is released and ΔH is negative, which favors mixing and thus ΔH.

Therefore, whatever the component that leads to an higher value of ΔG (i.e decrease in ΔS due to increase in polymer content, or higher molecular weight) the result is the downward translation of the spinodal that means, a lower LCST and reduced blend stability (e.g. Fig. 4.9).

The phase diagram helps explaining the effect of the blend components on stability, including concentrations, molecular weights, and compositions.

This theoretical framework of thermodynamics can be applied to the general behavior of bitumen-polymer blends. On this basis, it is understandable how having precise phase diagram of a blend is a fundamental tool to assess the blend compatibility and to know the LCST. In practical terms, it would help to determine the temperature at which hot storage of PMBs without segregation of polymer is possible, and the quench temperatures to use in an attempt to control dispersion size and blend morphology. The result would be improved control over macroscopic properties. (Masson et. Al, 2003).

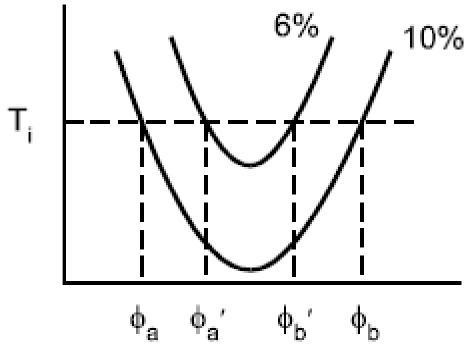


Figure 4.9. Translation of the spinoidal along the temperature axis due to a change in SBS content and its effect on equilibrium concentration (Masson et al., 2003)

4.2.5 Rheological characteristics of PMBs

Research into the rheological performance of bitumens has led to the development and implementation of dynamic mechanical analysis (DMA), performed with DSRs, as a useful means of studying the fundamental performance of bitumens and polymer modified bitumens (PMBs).

Thanks to DMA it is possible to understand the role of a polymer within a PMB in a better way than using empirical tests such as penetration and softening point, and to provide a more detailed explanation of the modification associated with PMBs containing plastomers (EVA) or elastomers (SBS).

The combination of the different data representation methods (§ 3.4.2) provide a comprehensive explanation of the rheological changes associated with polymer modification. (Airey, 2002). In the Figures below, DSR rheological data for a base bitumen, SBS PMB and EVA PMB are presented in the form of Black diagrams (Fig. 4.10), master curves of complex modulus (Fig. 4.11) and phase angle (Fig. 4.12) at a reference temperature of 25°C and isochronal plots of complex modulus and phase angle versus temperature (Fig. 4.13).

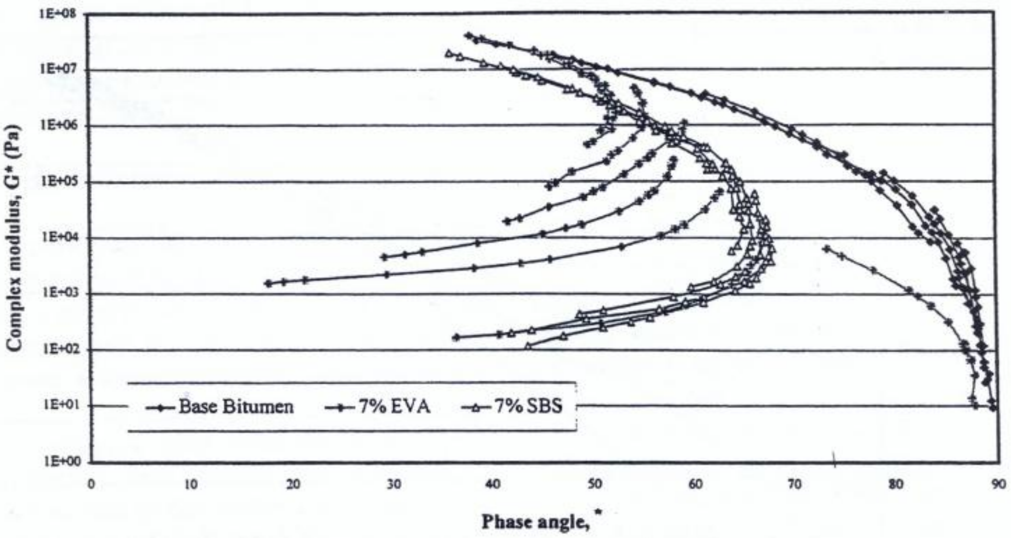


Figure 4.10. Black diagrams for base bitumen, EVA and SBS PMBs (Airey, 2002)

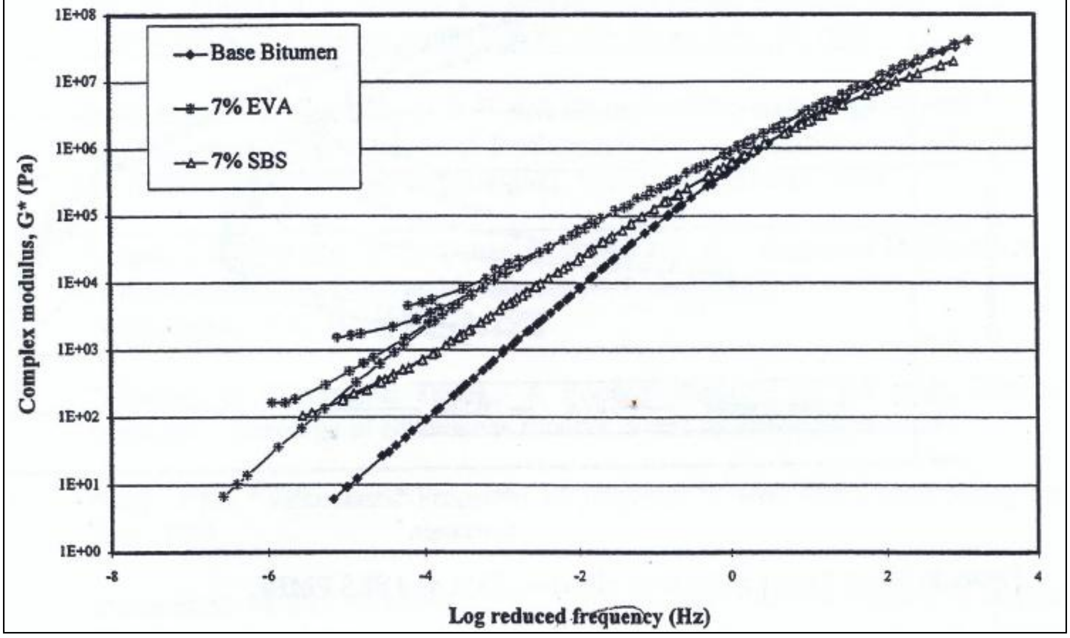


Figure 4.11. Complex modulus master curve at 25ºC for base bitumen, EVA and SBS PMBs (Airey, 2002)

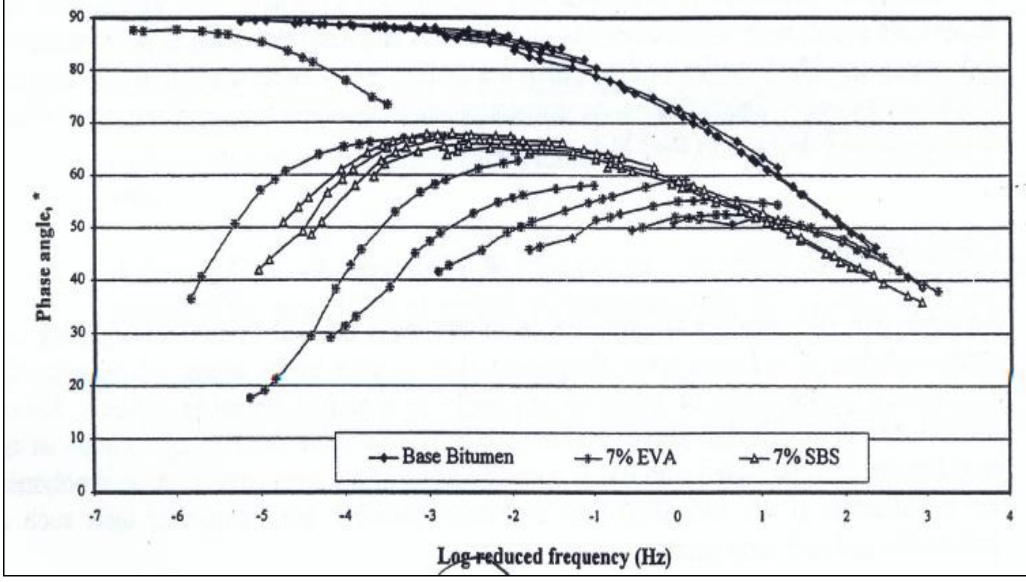


Figure 4.12. Phase angle master curve at 25ºC for base bitumen, EVA and SBS PMBs (Airey, 2002)

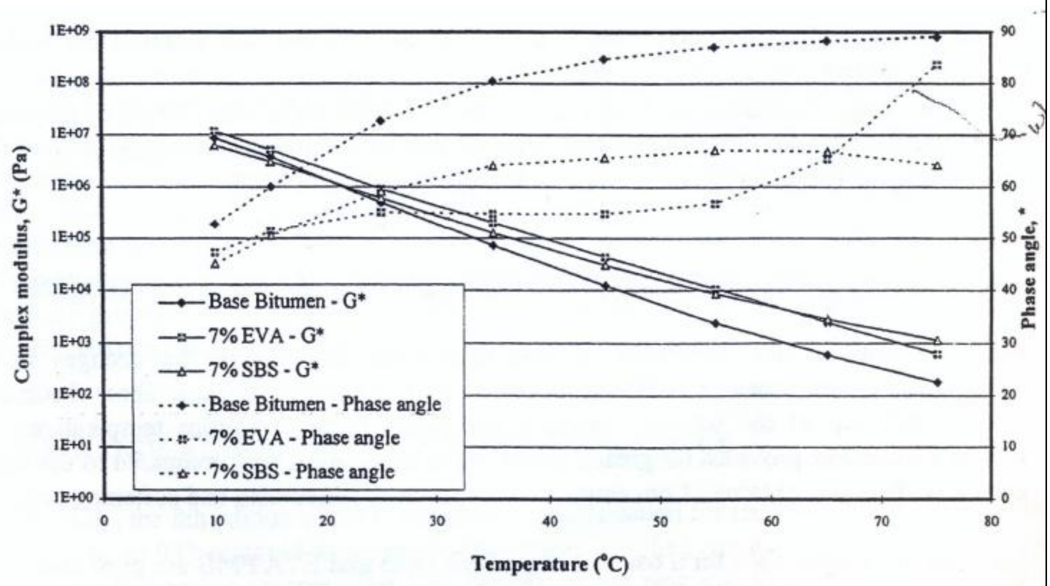


Figure 4.13. Isochronal plot at 1 Hz for base bitumen, EVA and SBS PMBs (Airey, 2002)

As it is possible to see in Figures 4.11 and 4.13, at low temperatures (≤ 10 °C), or high frequency, the complex moduli for a pure bitumen and PMBs are very similar and that most binders tend towards the same complex modulus at these low temperatures irrespective of the polymer and the bitumen grade. At temperatures above 10 °C, the influence of the polymer begins to appear and PMBs tend to show superior thermal susceptibility compared to pure bitumen. These findings are, however, dependent on the rheological characteristics of the polymer and the compatibility of the PMB system.

Plastomeric PMBs

In general a binder should have high values of G* and G′ at high temperatures for deformation resistance. The semi-crystalline EVA copolymer provides the modification of bitumen through the crystallisation of rigid three-dimensional networks within the bitumen. These EVA networks result in an increased "stiffness" of the EVA PMB compared to the unmodified base bitumen (Figures 4.12 and 4.14).The isochronal plots of G* (Fig. 4.14) indicates that the degree of EVA modification is most significant within the temperature range of 45–65 °C. Coupled with the increased complex modulus is an increased elastic behaviour after modification as depicted by lower phase angles (Figs 4.10, 4.12 and 4.13).

The rheological data obtained from the DSR allows a more detailed explanation of modification than simply the hardening or stiffening effect discussed above. The discontinuities of the master curves and Black diagram curve for the EVA PMB represents the formation of different EVA copolymer crystalline structures at different temperatures within the PMB. These discontinuities are termed "branches" or "waves" and correspond to unique crystalline structures within the EVA PMB which result in the loss of the equivalency between temperature and loading time found for penetration grade bitumens (Airey, 2002).

Elastomeric PMBs

The thermoplastic rubber SBS copolymer provides polymeric modification by means of a highly elastic network within the bitumen. The result of SBS modification is to increase the stiffness of the PMB at high temperatures and/or low loading frequencies and reduce it at low temperatures and/or high loading frequencies when compared to the base bitumen (Figs. 4.11 and 4.13). The highly elastic network also increases the elastic behaviour of the modified bitumen as shown in Figures 4.10, 4.12 and 4.13.

Particularly with elastomers, as the temperature exceeds about 20°C the polymers begin to significantly improve the elasticity of the modified binders, expecially at high temperatures (Fig. 4.13). This can be attributed to the viscosity of the mobile bitumen components, which is low enough to allow the elastic network of the polymer to influence the mechanical properties of the modified binders. With increasing temperature, the phase angle generally passes through trend inversions (Fig. 4.13), corresponding to the transition and plateau regions, respectively, which may be indicative of a polymer network. This is a desirable phenomenon as it is an indication of the improvement in elasticity, which would result in an improved resistance to the deformation of an asphalt (Lu & Isacsson, 1997).

Unlike the EVA PMB, the elastic network within the SBS PMB is not crystalline but amorphous in structure, therefore producing smooth continuous master curves and Black diagram curves. The fundamental rheological investigation of the EVA and SBS PMBs has shown that there is considerable difference in behaviour and modification associated with plastomeric and elastomeric copolymers which cannot be quantified by empirical tests such as penetration and softening point. The behaviour of the PMBs are dominated by either the polymer or the base bitumen components depending on the temperature and/or loading frequency regime at which the rheological behaviour of the PMB is measured.

4.3 Tyre Rubber Modified Bitumen (TR-MB)

Rubber in asphalt has been in use in the USA since at least the early 1960s by the Arizona Department of Transport. Since then the material has been used more widely in four states in the US and elsewhere, including South Africa, Europe and Australasia. There are two main processes of using rubber in asphalt, i.e. the dry and the wet process; this study focuses upon the use of rubber in asphalt by the wet process, i.e. to produce rubberised bitumen. Rubberised bitumen can be used in four different areas of applications: spray seal, stress alleviating membrane, stress alleviating membrane interlayer and asphalt mixture. The latter (rubberised asphalt mixture) is discussed in more detail in this work.

Brief history and geography of TR-MB

The use of recycled rubber in asphalt pavements started 170 years ago, with an experiment involving natural rubber with bitumen in the 1840s (Heitzman, 1992), attempting to capture the flexible nature of rubber in a longer lasting paving surface. The early bitumen-rubber formula provided little or no benefit, the result being a modified asphalt pavement that cost more and had a shorter service life than conventional asphalt. It was not until the 1960s that a successful formulation was discovered by Charles H. MacDonald, who worked with the City of Phoenix after retiring from the U.S. Bureau of Public Roads (now FHWA, Federal Highways Agency). While devising methods to repair potholes on the streets of Phoenix, Arizona, MacDonald experimented with adding ground tyre rubber to hot liquid bitumen. He found that after thoroughly mixing crumb rubber with bitumen and allowing it to react for periods of forty-five minutes to an hour, new material properties were obtained. This material captured beneficial engineering characteristics of both base ingredients; he called it asphalt-rubber. In this report it will be called tyre rubber modified bitumen. By 1975, crumb rubber was successfully incorporated into asphalt mixtures and in 1988 a definition for rubberised bitumen was included in the American Society for Testing and Materials (ASTM) D8 and later specified in ASTM D6114-97. The preference for using this particular modifier was due to the fact that not only does the utilisation of end o life tyres solve environmental problems but it also offers other benefits such as increased skid resistance, improved flexibility and crack resistance, and reduced traffic noise (Terrel and Walter, 1986; Takallou and Hicks, 1988).

South Africa and Australia started introducing bitumen-rubber as a binder for asphalt and for seals from the early 1980s and mid 1970s respectively. In South Africa, both wet and dry processes were reported to have been used successfully although the dry process was mainly used in asphalt (Visser and Verhaege 2000). Two states in Australia (New South Wales and Victoria) adopted the wet process for limited application of rubberised asphalt, mainly as a crack resisting layer, but otherwise its usage has been predominantly for sprayed seal applications (Widyatmoko & Elliot, 2007).

Taiwan was reported to have adopted the Arizona DOT gap-graded and open-graded rubberised asphalt mixtures for flexible pavement rehabilitation (Widyatmoko & Elliot, 2007). There were concerns about moisture damage on asphalt surfacing in Taiwan since it has a relatively moderate climate i.e. generally high temperatures, no frost but with significant summer rain. The rubberised asphalt mixture, having air voids around 4%, contained 1 percent Portland cement as mineral filler. The overall material cost was reported to be 30 percent higher than that of conventional asphalt concrete. After 42 to 46 months, the rubberised asphalts were reported to have been performing well with insignificant fretting for the gap graded and some binder richness (bleeding) for the open graded mixture.

It has been reported that rubberised asphalt has been trialled in Beijing and for use in new and maintenance work as part of the preparation for the 2008 Olympics in China. The material has also been used in EcoPark Project in Hong Kong (Widyatmoko & Elliot, 2007).

In Europe, rubberised asphalt has been used since 1981 in Belgium, as well as in France, Austria, Netherlands, Italy, Germany and Sweden, and more intensively since 1999 in Portugal and Spain (Sousa, 2005).

In Italy AR technology is quite new. One of the first applications was made in 2006 (Santagata et al., 2008), followed by other application studies (Santagata et.al, 2009; Canestrari et. al 2009) which have demonstrated positive results, particularly in terms of noise reduction and water sensivity. Higher number of applications and longer time are necessary to have results also in terms of mechanical properties and durability of the AR mixtures.

4.3.1 The material "Tyre Rubber"

The tyre is a complex and high-tech safety product representing a century of manufacturing innovation, which is still on-going. The tyre comprises many materials, the very best the metallurgical, textile and chemical industries can produce. There is no room for even the slightest defect and it is an extremely complex process to develop and manufacture the product.

From a materials point of view, the tyre is a mixture of synthetic and natural rubber, to which are added a range of specific substances to ensure performance, durability and safety. In fact, natural rubber is sticky in nature and can easily deform when heated up and it is brittle when cooled down. (Tab. 4.2). In this state it cannot be used to make articles with a good level of elasticity. The reason for inelastic deformation of unvulcanised rubber can be found in the chemical nature as rubber is made of long polymer chains. These polymer chains can move independently relative to each other, and this will result in a change of shape. By the process of vulcanisation cross-links are formed between the polymer chains, so the chains cannot move independently anymore.

Table 4.2. Effect of temperature on natural rubber (Rahman, 2004)

-10 ºC	Brittle and opaque
20 ºC	Soft, resilient and translucent
50 ºC	Plastic and sticky
120 ºC -160 ºC	Vulcanised when agents e.g., sulphur are added
180 ºC	Break down as in the masticator
200 ºC	Decomposes

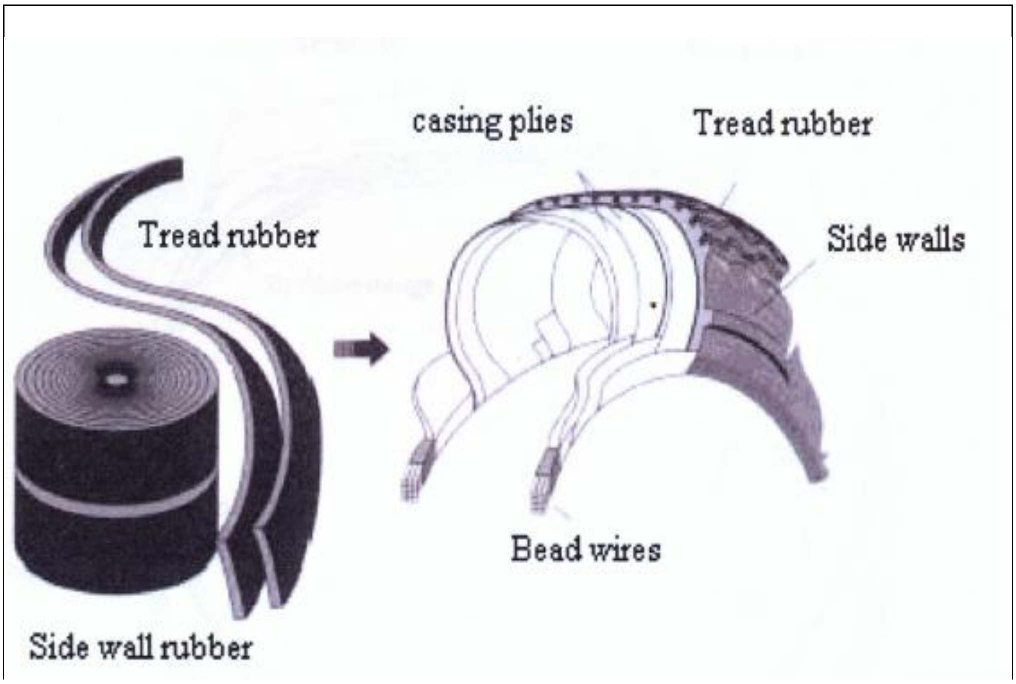


Figure 4.14. Raw material used in tyre

As a result, when stress is applied the vulcanised rubber will deform, but upon release of the stress the rubber article will go back to its original shape. Compounding is finally used to improve the physical properties of rubber by incorporating the ingredients and ancillary substances necessary for vulcanisation, but also to adjust the hardness and modulus of the vulcanised product to meet the end requirement. Different substances can be added according to the different tyre mixtures; these include mineral oil and reinforcing fillers as carbon black and silica.

The main components of a tyre are the tread, the body, side walls and the beads. The tread is the raised pattern in contact with the road. The body supports the tread and gives the tyre its specific shape. Beads are metal-wire bundles covered with rubber, which holds the tyre on the wheel. The composition of a tyre is illustrated in Figure 4.14. The inherent characteristics of the tyre are the same worldwide. They include: the resistance to mould, mildew, heat and humidity, retardation of bacterial development, resistance to sunlight, ultraviolet rays, some oils, many solvents, acids and other chemicals. Other physical characteristics include their non-biodegradability, non-toxicity, weight, shape and elasticity However, many of the characteristics, which are beneficial during their on-road life as consumer products, are disadvantageous in their post-consumer life and can

Table 4.3. Comparison of passenger car and truck tyres in the EV (ETRA, 2004)

Material (contents)	Car (%)	Truck /Buses (%)
RubberlElastomers	48	43
Carbon Black	22	21
Metal	15	27
Textile	5	--
Zinc oxide	1	2
Sulphur	1	1
Additives	8	6

create problems for collection, storage and/or disposal. Table 4.3, which summarises the general tyre composition of tyres used in cars and trucks in the EU (Shulman, 2000).

ELTs recycling process

The tyre life cycle traditionally comprises five main stages, which includes extraction, production, consumption, collection of used tyres and waste management. A simplified version of the tyre cycle is illustrated in the figure below. After the collection of ELTs, the next stage includes landfilling and recovery. In Europe, since 1996, there has been a continuous decline in landfilling used tyres from 32% of used tyres arising to 4% in 2009, while the combined recycling, recovery (material & energy recovery), reuse and retreading routes now contribute to a substantial 96% of the total amount of used tyres (Tab 1.2). The major markets in 2009 were energy recovery 45% and material recovery 41% (ETRMA, 2010). After sorting used tyres for retreading and reuse/export (which in total represents about 581,000 tonnes of used tyres), there remains a flow of end-of-life tyres of 2.6 million tonnes which enter the multiple recovery routes. These recovery routes include different options such as: “energy recovery”, in which the end of life tyres having a calorific value equivalent to that of good quality coal, are used as an alternative to fossil fuels, or “chemical processing” such as pyrolysis, thermolysis and gasification, (the economic viability of these options has yet to be proved) or also “granulate recovery” in which large machinery is used to cut up tyres into small pieces of different sizes. At this stage, after the removal of the steel and fabric components, tyre rubber can be used for a variety of civil engineering projects (i.e.flooring for playgrounds and sports stadiums, as shock absorbing mats, paving blocks, roofing materials, etc.)

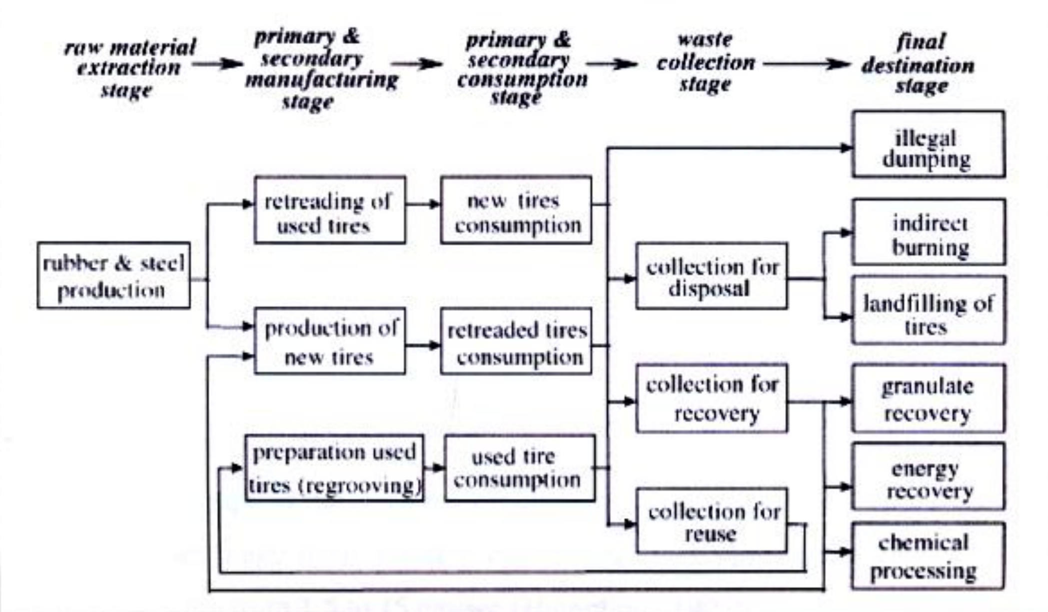


Figure. 4.15a Life cycle of End of Life Tyres (Rahman, 2004)

TR grinding processes

After the collection of end of life tyres, the next stage of the tyre recycling process is shredding and chipping of scrap tyres. The tyre shredding and chipping processes involve the use of large machinery that cuts up tyres into smaller pieces (Fig. 4.15b). The size of the tyre shreds may range from as large as 460 mm to as small as 25 mm, with most particles within the 100 mm to 200 mm range, while the tyre chips range from 76 mm down to approximately 13 mm. By further reducing the size of shreds and chips, it is possible to produce Ground and Crumb Rubber, also known as size-reduced rubber, which are suitable to be re-used in the asphalt industry.

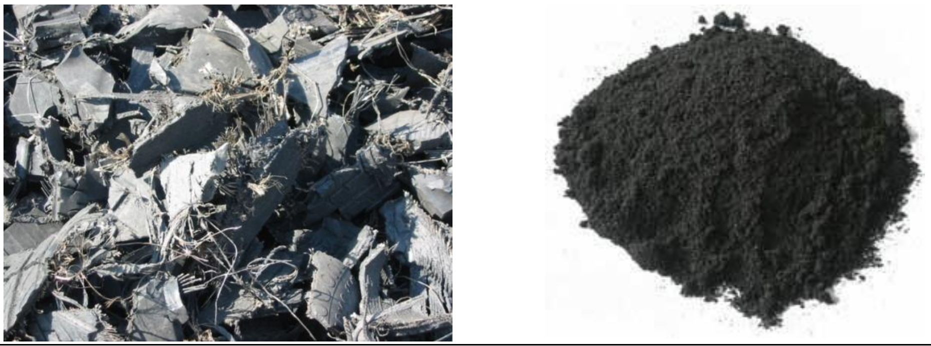


Figure 4.15b. Shredded tyre (left) and crumb rubber (right)

Crumb Rubber Modifer (CRM) is the common name used to identify the rubber particles used to modify bitumen. There are several processes that can be used to produce ground rubber crumbs, two of the most common are listed below.

Ambient grinding. This is a method of processing where scrap tyre rubber is ground or processed at or above ordinary room temperature. Ambient processing is typically required to provide irregularly shaped, torn particles with relatively large surface areas to promote interaction with the paving bitumen. This is a mechanical grinding, performed by means of rotating blades and knives, in which the critical step is the separation of the fibers, amongst which are generally included steel fibers. Once separated from the metallic material, ambient grinding is able to produce rubber crumbs with grain size ranging from 5 to 0.5 mm.

Ambient grinding is the most commonly used and probably the most cost effective method of processing end of life tyres in the Europe.

Cryogenic grinding. This process uses liquid nitrogen to freeze the reclaimed tyre rubber (typically between -87 to -198ºC) until it becomes brittle, and then uses a hammer mill to shatter the frozen rubber into smooth particles with relatively lower surface area than those obtained by ambient grinding (Rahman, 2004)

Oliver (1981) showed that several characteristics of the rubber granulate determine the elastic properties of the crumb rubber (Fig. 4.16) and those conferred on the final mix: they enhance with the decrease of specific gravity and particle size, and increase with the higher surface porosity of the granules. In fact, in wet process, rubber particles with a smooth surface, showed reduced reaction with the bitumen and worst the elastic properties of the mixture, if compared with those obtained by using granules with bigger porous surfaces and less specific weight. As a results, the use of granulated rubber from cryogenic process in bituminous mixtures is discouraged (Roberts, 1989).

A comparison between the properties of cryogenic and ambient ground rubber is summarised in Table 4.4

Table 4.4 Comparison between Ambient and Cryogenic Ground Rubber

Physical property	Ambient	Cryogenic
Specific gravity	same	same
Particle shape	irregular	regular
Fibre content	0.5%	Nil
Steel content	0.1%	Nil
Cost	Comparable	Comparable

4.3.2 Tyre Rubber technologies in asphalt pavements

Use of tyre rubber in bituminous paving materials generally has two distinct approaches. One is to dissolve crumb rubber in the bitumen as binder modifier, the other to replace a portion of fine aggregates with ground rubber that is not fully reacted with the bitumen. These are referred to as the 'wet process' and the 'dry process', respectively. In the Wet Process, rubber and bitumen are made to react together at high temperatures, so that the blend obtained is suitable for making bituminous mixtures. By contrast, in the Dry Process, CRM is added to the mineral aggregate before mixing with bitumen.

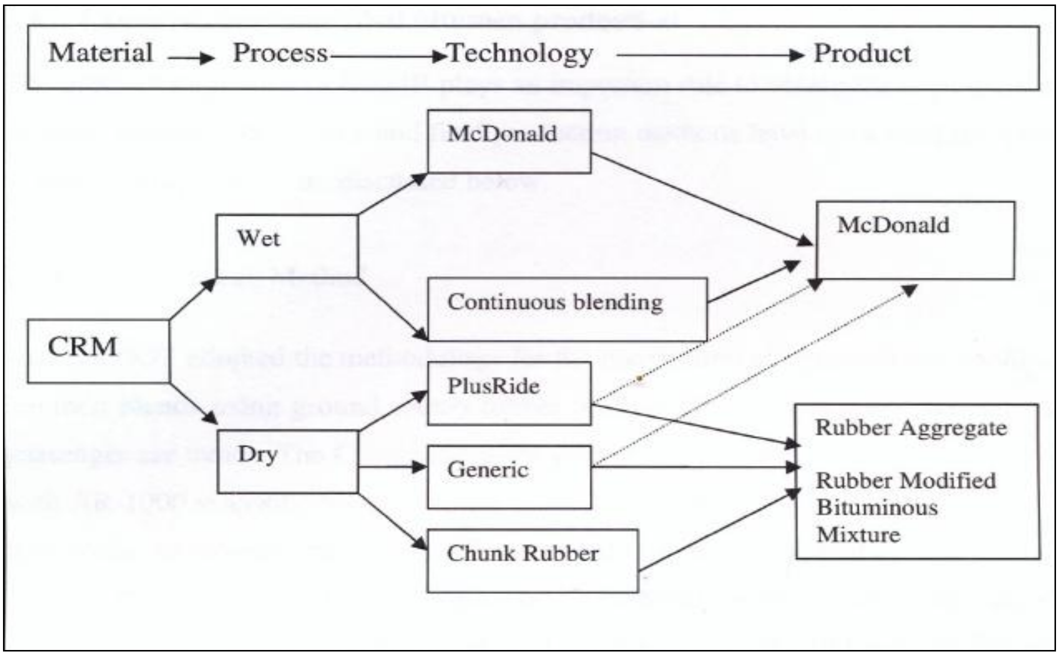


Figure 4.15c. Different processes and technologies in application of tyre rubber in asphalt (Heitzman, 1992)

This way the rubber introduced acts both as an inert charge and as a modifying agent, in that during the mixing phase it reacts, though only partially, with the bitumen (Rahman et al., 2006). The two processes differ not only in the quantity and gradation of the rubber used, but also in the quantity of the components (bitumen, in particular), as well as in the equipment required for production; the fact is that Wet Process involves the need for specific equipment (high shear mixers and special storage tanks), which are not necessary for the Dry Process (Celauro et al, 2004).

To promote clear understanding, definitions of the processes and technologies linked to application of tyre rubber in asphalt are explained below.

Wet Process. The method of modifying bitumen with CRM produced from scrap tyre rubber and other components as required before incorporating the binder into the bitumen paving materials. Although most wet process tyre rubber modified bitumens require agitation to keep the CRM evenly distributed throughout the binder, some TR bitumen binders may be formulated so as not to require agitation (see Wet process-no agitation). The wet process requires thorough mixing of the CRM in hot bitumen (176ºC to 226ºC) and holding the resulting blend at elevated temperatures (150ºC to 218ºC) for a

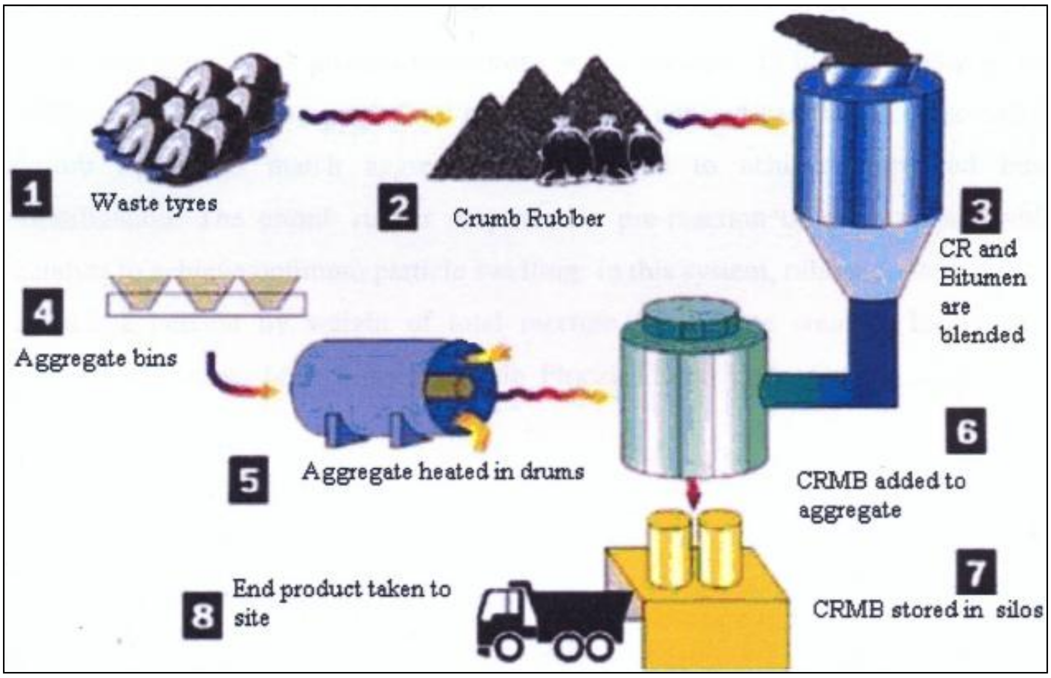


Figure 4.16. Schematic diagram of wet process (Airey, 2002)

designated period of time (typically 45 to 60 minutes, shorter for some variations) to permit an interaction between the rubber and bitumen. The percentage of the rubber used in the blend is usually in the range of 18-22% bitumen weight (Hicks, 2002). Other components (e.g. oil extenders, higher amount of natural rubber, etc.) may be included, depending on applicable specifications. The interaction (also referred to as reaction) includes swelling of the rubber particles and development of specified physical properties of the bitumen and CRM blend to meet requirements. Typical specification requirements, in the US (e.g. DOTs in Arizona, California,Florida, and Texas or South Africa, Australia, etc.) include an operating range for rotational viscosity, and minimum values of softening point, resilience, and penetration (needle or cone, at cold and/or room temperature), (Caltrans, 2006).

The wet process can be used to produce a wide variety of TR modified binders with a range of physical properties. The most important distinctions among the various blends seem to be related to the rotational viscosity of the resulting TR modified bitumen blend at high temperature. According to Caltrans (2006), Tyre Rubber Modified Binders with viscosities ≥ 1,500 cPs at 177ºC or 190ºC should be assumed to require agitation.

It is possible to divide the wet process into two families linked to two very different types of TR modification currently in use. The terminology presented is intended to provide a better description and understanding of the subject products and is related to definitions being considered by ASTM Subcommittees D04.45 (Modified Asphalt) and D04.95 (Quality Control, Inspection and Testing Agencies),(Caltrans, 2006).

Wet Process-No Agitation (Terminal blend process). The term “terminal blend” is often used to describe rubber-modified binders that do not require constant agitation to keep discrete rubber particles uniformly distributed in the hot asphalt cement. However such binders may be produced in the field or at an asphalt concrete plant as well, such that calling them terminal blends may be misleading and is unnecessarily restrictive.

The preferred description for this type of binder is, therefore, “wet process-no agitation”. (Caltrans, 2006). In this process, the crumb rubber is digested into the bitumen at the refinery and delivered to the plant in the same manner as conventional bitumen without rubber. No modifications to the asphalt plant are required in this process.

These binders are typically modified with TR particles passing the 300 μm (No. 50 sieve) that can be digested (broken down and melted in) relatively quickly and/or can be kept dispersed by normal circulation within the storage tank rather than with agitation by special augers or paddles. Polymers and other additives may also be included.

In the past, rubber contents for such blends have generally been ≤ 10% by weight of bitumen or total binder, but some products now include 15% or more TRM. Although such binders may develop a considerable level of rubber modification, rotational viscosity values rarely approach the minimum threshold of 1,500 cPs (1.5 Pa.s) at 177ºC, that is necessary to significantly increase binder contents above those of conventional AC mixes without excessive draindown. (Caltrans, 2006)

Wet Process-High Viscosity (McDonald process). Tyre Rubber modified binders that maintain or exceed the minimum rotational viscosity threshold of 1,500 cPs at 177ºC (or 190ºC) over the interaction period should be described as "wet process–high viscosity" binders to distinguish their physical properties from those of wet processing agitation materials. These materials require continue agitation, with special equipment, to keep the TR particles uniformly distributed. They may be manufactured in large stationary tanks or in mobile blending units that pump into agitated stationary or mobile storage tanks. Wet process-high viscosity binders include asphalt rubber materials that meet the requirements of ASTM D6114. Wet process-high viscosity binders typically require at least 15% scrap tire rubber to achieve the threshold viscosity. However, for some specifications (Caltrans) the viscosity requirements are meet also with less than 15% of tyre rubber content (Caltrans, 2006).

McDonald process. This terminology is related to the system of producing tyre rubber modified bitumen with the original wet process proposed by Charles McDonald in the 1960s. The McDonald blend is a bitumen rubber blend produced in a blending tank by blending crumb rubber and bitumen. This modified binder is then passed to an holding tank, provided with augers to ensure circulation, to allow the reaction of the blend for a sufficient period (generally 45 – 60 minutes). The reacted binder is then used for mix production (McDonald mix). It is possible to produce McDonald's blends in the field only after incorporating some modifications to the existing bitumen plant.

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These binders are typically modified with TR particles passing the 300 µm (No. 50 sieve) that can be digested (broken down and melted in) relatively quickly and/or can be kept dispersed by normal circulation within the storage tank rather than with agitation by special augers or paddles. Polymers and other additives may also be included.
In the past, rubber contents for such blends have generally been ≤ 10% by weight of bitumen or total binder, but some products now include 15% or more TRM. Although such binders may develop a considerable level of rubber modification, rotational viscosity values rarely approach the minimum threshold of 1,500 cPs (1.5 Pa.s) at 177ºC, that is necessary to significantly increase binder contents above those of conventional AC mixes without excessive draindown. (Caltrans, 2006)

Wet Process-High Viscosity (McDonald process). Tyre Rubber modified binders that maintain or exceed the minimum rotational viscosity threshold of 1,500 cPs at 177ºC (or 190ºC) over the interaction period should be described as “wet process–high viscosity” binders to distinguish their physical properties from those of wet processing agitation materials.

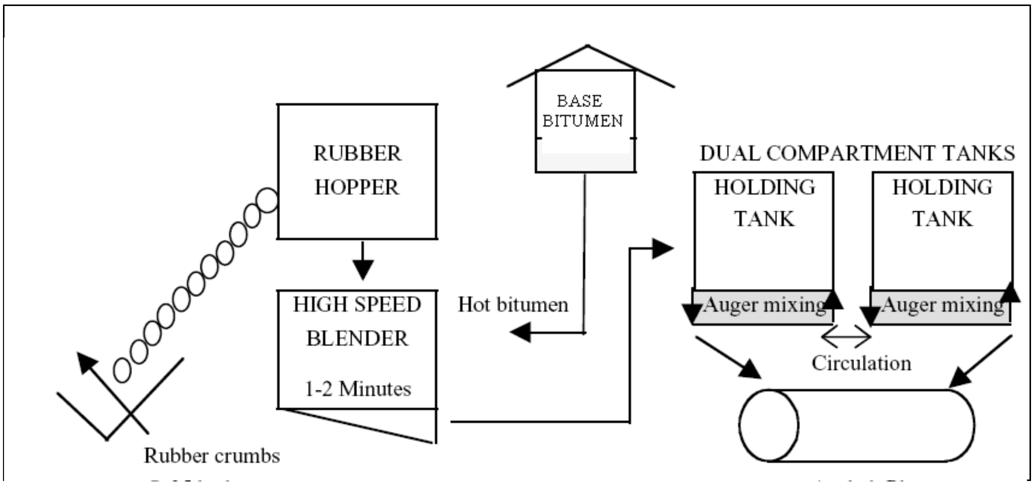


Figure 4.17. Schematic diagram of McDonald's wet process

These materials require continue agitation, with special equipment, to keep the TR particles uniformly distributed. They may be manufactured in large stationary tanks or in mobile blending units that pump into agitated stationary or mobile storage tanks. Wet process-high viscosity binders include asphalt rubber materials that meet the requirements of ASTM D6114. Wet process-high viscosity binders typically require at least 15% scrap tire rubber to achieve the threshold viscosity. However, for some specifications (Caltrans) the viscosity requirements are meet also with less than 15% of tyre rubber content (Caltrans, 2006).

McDonald process. This terminology is related to the system of producing tyre rubber modified bitumen with the original wet process proposed by Charles McDonald in the 1960s. The McDonald blend is a bitumen rubber blend produced in a blending tank by blending crumb rubber and bitumen. This modified binder is then passed to an holding tank, provided with augers to ensure circulation, to allow the reaction of the blend for a sufficient period (generally 45 – 60 minutes). The reacted binder is then used for mix production (McDonald mix). It is possible to produce McDonald's blends in the field only after incorporating some modifications to the existing bitumen plant.

These modifications includes blending equipments, combination of blending and reaction tanks, rubber storage, rubber feed, heated blending tanks and a heated reaction tank (Heitzman, 1992). Hence, nowadays the equipment used to blend bitumen and rubber, through the wet process, requires less drastic modification to a standard hot mix asphalt plant. In fact, in the market is it possible to find the so called “Asphalt rubber production unit” (Fig. 4.18), which are portable equipment base on the McDonald system. The equipment is typically trailer mounted and is transported into the asphalt plant site. The Mixing Unit receives ground rubber in the hopper, the rubber then moves to the mixing chamber to be blended with virgin liquid bitumen; the resulting rubberized bitumen is stored in the Portable Reaction Tank. Once reacted, binder is moved to a second compartment where it is fed to the hot-mix plant to be included in the HMA production. At the end, conventional paving equipment without modifications is used to place the material.

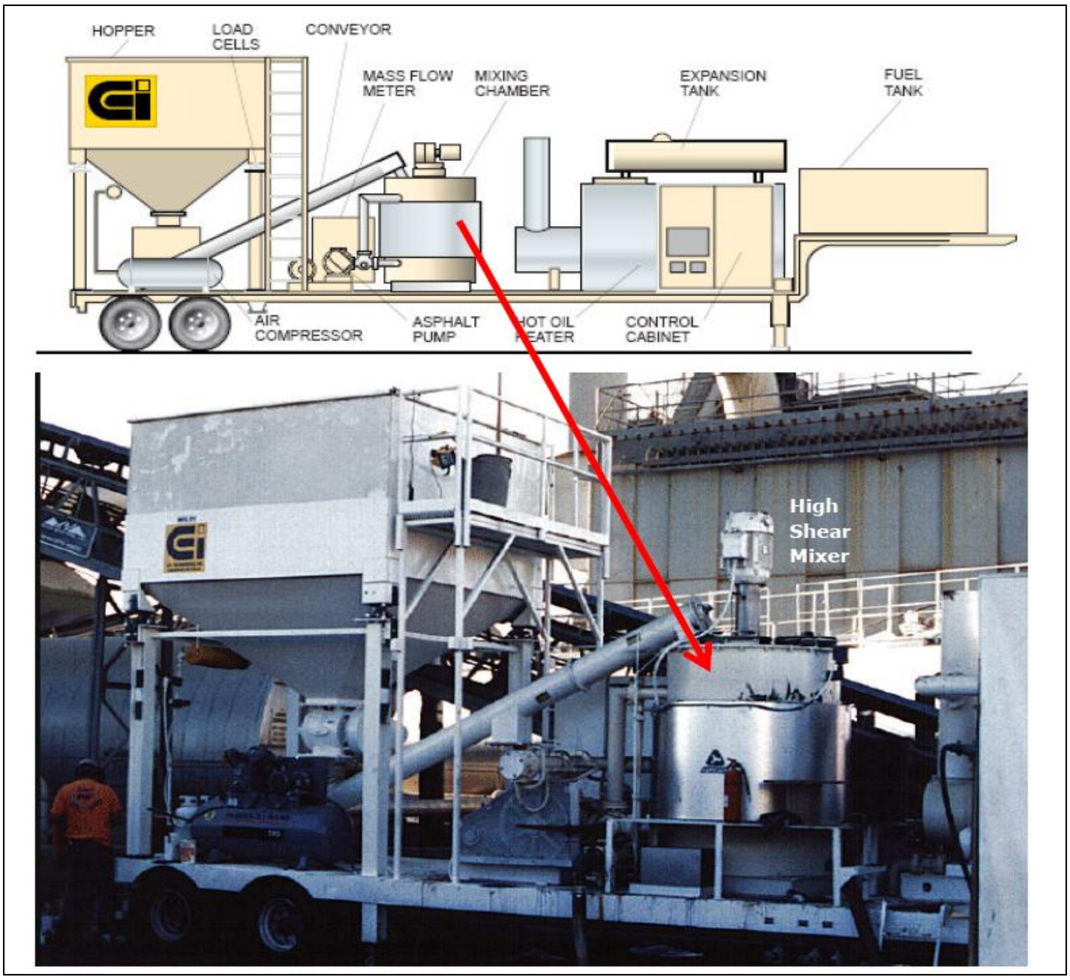


Figure 4.18. Example of Portable Asphalt Rubber production unit: 1) Mixing unit

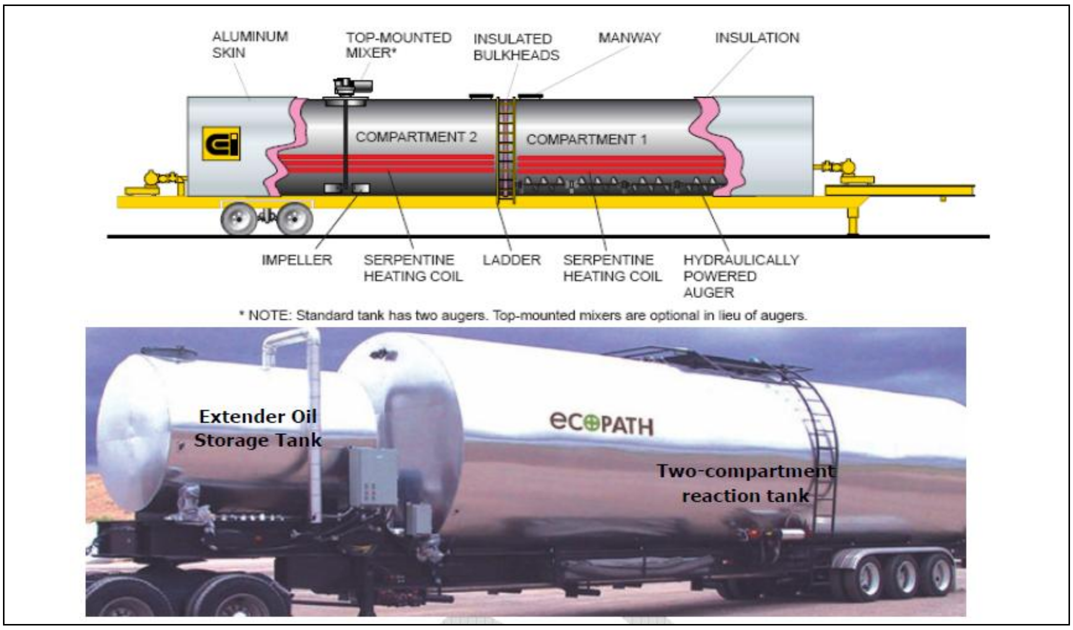


Figure 4.19. Example of Portable Asphalt Rubber production unit: 2) Reaction tank

Continuous Blending-Reaction Systems. This system is similar to the McDonald process of blending, the difference is that CRM and bitumen are continuously blended during the mix production or prepared by hand and then stored in storage tanks for later use (Heitzman, 1992 and Paul Krugler, 1993). Therefore, it consists of a unique unit with agitators, in which the reaction occurs during the blending. (Heitzman, 1992).

Dry Process. The dry process includes CRM as a substitute for 1 to 3 % of the aggregate in the Asphalt mixes. This concept uses both coarse and fine crumb rubber to match aggregate grading and to achieve improved binder modification.

In the dry process, the crumb rubber from the high shear mixer is added to the aggregate about ten seconds before the hot bitumen is added. Specialized blending equipment is not required in the process.

The Dry Process can be used for hot mix asphalt paving in dense-graded, open-graded, or gap-graded mixtures, but it cannot be used in other asphalt paving applications, such as cold mix and chip seals or surface treatments. Hence, the Dry Process is less difficult to run, while the Wet Process, though more complex, has several more applications and has got the advantage to better govern the rheological properties of the binder.

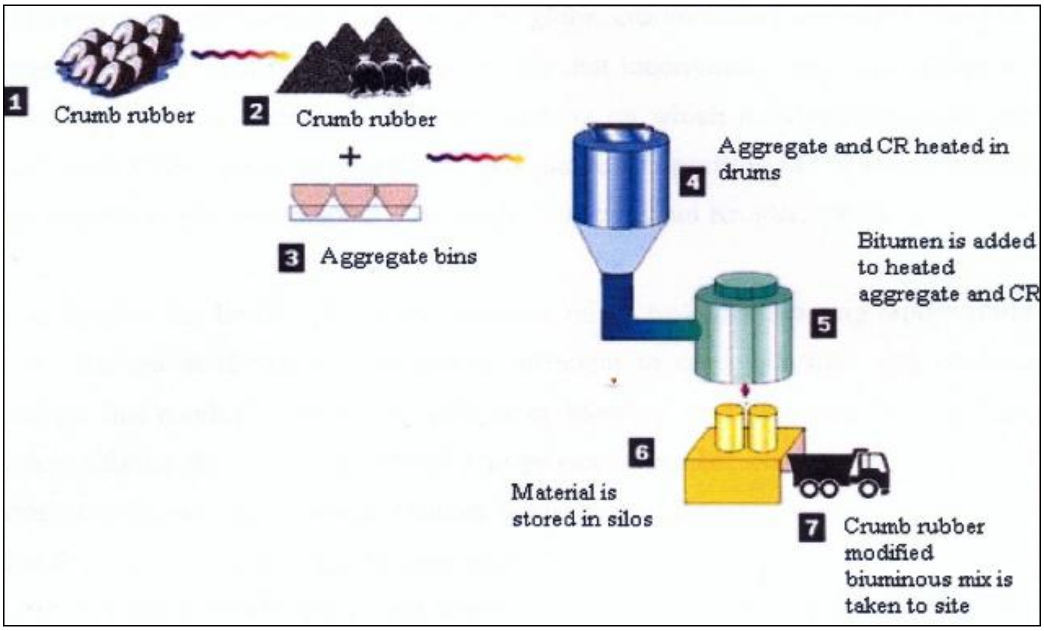


Figure 4.20. Schematic diagram of the dry process

This study focuses upon the use of rubber in asphalt by the wet process, therefore Dry process is not going to be described with further details.

4.3.3 *Wet Process: Overview of processing conditions*

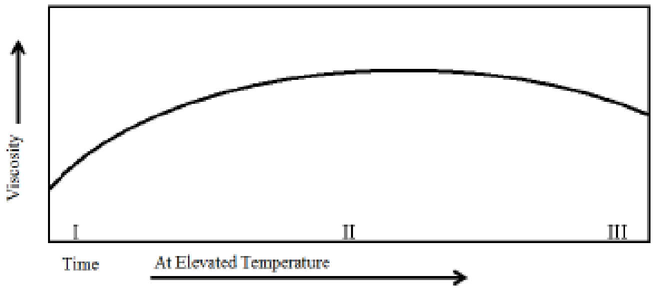
Tyre rubber modified binders are extremely dependent on the processing conditions, particularly to what concerns the temperature and time of reaction. Morevoer, Tyre Rubber modified binders must be properly designed and, where necessary, produced to comply with specifications and provide a quality product suitable for the expected climate and traffic conditions. In fact, it has been experienced that individual components (e.g. rubber, bitumen, etc.) that comply with specifications may be combined and interacted in proportions that also fully comply, but may yield a binder that is not usable.

As seen previously (§ 4.3.3), Caltrans (2006) as well as Sabita (AsAc, 2007) and Autostrads (AP-T42, 2006) are fully aware of the primary importance of governing modification process; for this reason all of them specifies compulsory prior laboratory testing.

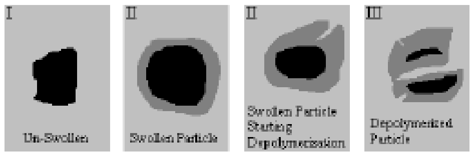
Bitumen-rubber interactions

The nature of the mechanism by which the interaction between bitumen and CRM takes place has not been fully characterized. Traditionally it is reported that Bitumen-Rubber interaction is not chemical in nature (Heitzman 1992), but other studies claim that the increase in binder viscosity can not be accounted for only by existence of the rubber swelling particles (Bahia & Davis, 2004).

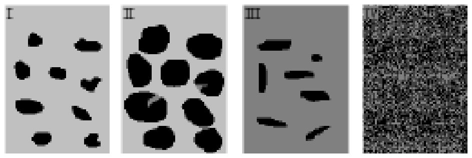
The reaction itself is made up of two simultaneous processes: partial digestion of the rubber into the bitumen on one hand and, on the other, adsorption of the aromatic oils available in this latter within the polymeric chains that are the main components of the rubber, both natural and synthetic, contained in the TR. The absorption of aromatic oils from the bitumen into the rubber's polymer chains causes the rubber to swell and soften (Chehovits et al, 1982; Oliver, 1982).



(a) Change of Binder Viscosity over Time at Elevated Temperature



(b) Change of Particle Size over Time at Elevated Temperature



(c) Change of Binder Matrix over Time at Elevated Temperature

Figure. 4.21. Bitumen rubber interaction phenomenon (Abdelrahaman, 2006)

Rubber particles are swollen by the absorption of the bitumen oily phase at high temperatures (160–220ºC) into the polymer chains, which are the key components of the Tyre Rubber binder to form a gel-like material. Therefore, during the reaction there is a contemporaneous reduction in the oily fraction and an increase of rubber particle sizes with a consequent reduction of the inter-particle distance. This implies the formation of gel structures that produce a viscosity increase up to a factor of 10 (Oliver 1981, Heitzman 1992, Bahia and Davies 1994).

Rubber reacts in a time-temperature dependent manner. If the temperature is too high or the time is too long, the swelling will continue to the point where swellin is replaced by, due to long exposure to the high temperatures, depolymerisation/devulcanisation which cause dispersion of the rubber into the bitumen. Depolymerisation starts releasing rubber components back to the liquid phase causing a decrease in the stiffness (G*) while the elastic properties (δ) continues to modify (Fig. 4.21 a,b). If temperature is high or time is long enough, depolymerisation will continue causing more destruction of the binder networking and so δ modification is lost (Abdelrahman and Carpenter 1998).

The interaction between bitumen and CRM materials is material-specific and depends on a number of basic factors, including:

1. Processing Temperature
2. Processing Time
3. Processing Device (applied shear stress)
4. Bitumen Source (physical and chemical properties)
5. Rubber Type
6. Rubber Source (processing methos)
7. Rubber Gradation
8. Rubber Amount

All these variables represent therefore the processing/interaction conditions that are necessary to monitor during the mixing of rubber within bitumen in order to govern the modification process. The aim of this section is to perform a literature review in order to assess the role of any single factors affecting the processing conditions, thus the Tyre

Rubber Modified Binders. To better explain it the factors were divided in three groups, namely: Processing variables, Base binder, Crumb Rubber Modifier,

Processing variables

Due to the variety of materials utilized in tyre rubber paving materials, there are numerous issues relating to selection and design. Physical and engineering properties of modified binders are highly dependent on the unique interactions between the component materials: bitumen and tyre rubber. These interactions depend primarily on their respective chemical but processing conditions such as:

- temperature,
- interaction time,
- shear stress and
- pressure

have a primary importance during any mixing process (Chung, 2000). In the bitumen modification process the temperature plays the major role.

Processing Temperature. The final properties of TR-MBs are largely dependent on processing temperature. As reported by Navarro et al. 2006, the rubber solubilized in the bitumen phase remains constant and equal to the initial value for processing temperatures comprised between 90 and 120ºC, and consequently, these conditions are not severe enough to break up the chemically crosslinked network. Thus, the observed rheological behavior would be a consequence of the presence of rubber particles swollen by light components of the maltenic fraction. Higher processing temperatures (160-180ºC) lead to partial depolymerization/devucalization of the rubber network, increasing the amount of components that are incorporated to the bitumen phase (bitumen matrix) and, consequently, reducing both solid concentration and rubber particle size (Navarro et al. 2006). Various experiences (Navarro et al. 2007, Austroads, 2006) showed that when 15% of rubber is added only a percentage ranging from 2 to 4 of rubber is dissolved or dispersed in the bitumen. By increasing processing temperature, the dissolution/dispersion of rubber into the bitumen is clearly enhanced due to faster rates of breaking crosslink bonds.

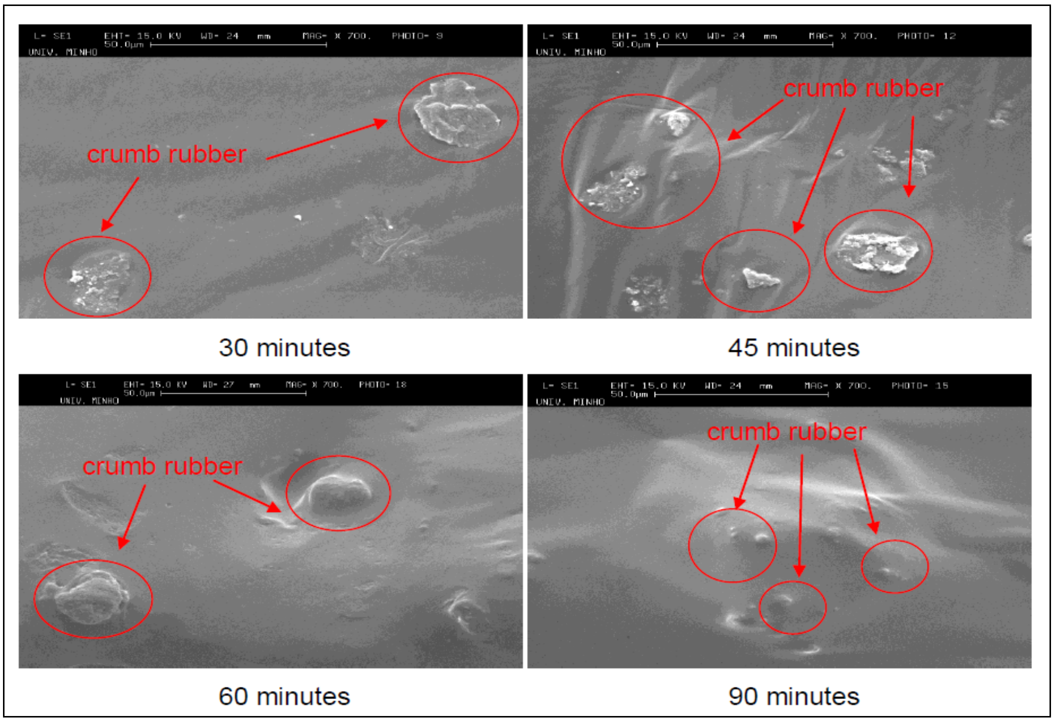
Lalwani et al. (1982) concluded that because of the depolymerization/devucalization of the rubber network, the binder elasticity was drastically reduced by as much as three times when the temperature was increased from 200 to 300ºC, while no significant differences occurred due to changing the temperature from 150 to 200ºC.

As regards to the physical interaction process, Green and Tolonen (1977) concluded that processing temperature has two effects. The first effect is on the rate of swelling of rubber particles. As the temperature increases, for example from 160 to 200ºC, the rate of swelling increases. The second effect is on the extent of swelling. As the temperature increases, the extent of swelling decreases.

Processing time. Rubber reacts in a time-temperature dependent manner, so the two processing conditions are strongly correlated (Fig. 4.22). The effect of interaction time on the developed properties is a function of the interaction temperature. Two main phases of the property development are considered: an initial phase or short term phase that last for 30 to 40 minutes and a second long-term phase that last for few hours. Most of the changes occur in the initial phase. Property stabilise in the second phase (Abdelrahman and Carpenter 1998).

In general, the longer reaction time for digestion of the rubber-modified binder seemed to lead to an increase in the viscosity, which is related to the increase in the rubber mass through binder absorption. Oliver (1981, 1997a, 1997b) indicated that increased digestion time (up to 2 hours over a temperature range of 180°C to 200°C) improved the rubberised binder properties.

Lee et al. (2006) showed with DSR tests that the reaction time ranging from 0 to 480 minutes in a control binder had little effect on the increase of the high failure temperature, and with respect to the rubber-modified binder the difference in the high failure temperature after the reaction times of 60, 90, 120, 240, and 480 minutes was not significant. However, various sources demonstrated that prolonged digestion up to 24 hours was reported to have caused reduction in viscosity and elastic response, suggesting some undesirable rubber degradation. Moreover, rubber degradation is suspected to take place more rapidly at higher digestion temperatures (Oliver, 1981). In fact depolymerisation cracks the binder networking into lower molecular weight molecules.



30 minutes 45 minutes

60 minutes 90 minutes

Figure 4.22. Micrographs of tyre rubber modifed bitumen morphology changing over time (Pereira et al., 2008)

Depolymerisation starts very early at high interaction temperature and continues up to full destruction of the polymer network, if the binder is exposed to very high temperature for enough time (>210ºC), (Abdelrahman and Carpenter 1998, 1999).

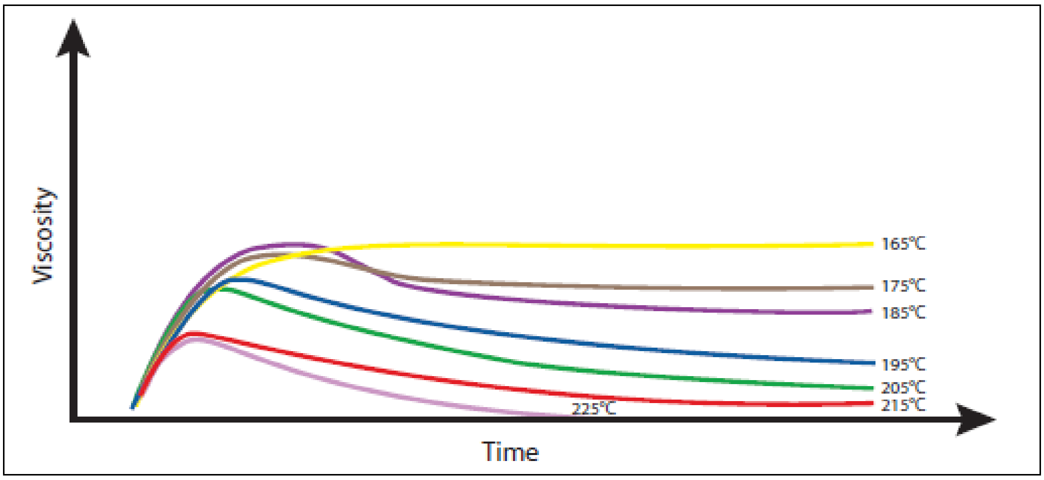


Figure 4.23. Typical changes in viscosity alues fro bitumen rubber at different temperatures over time (AsAc, 2007)

Processing Devices (applied shear stress). As reported by Navarro et al. (2004) the rheological behavior of TR-MBs is not influenced by the processing device and impeller geometry used for their manufacture. Conversely, other authors have found a clear dependence of binder properties from the mixer speed the applied shear rate.

In fact, there are two type of mixing: (1) distributive mixing and (2) dispersive mixing (Fig. 4.24.). Distributive mixing refer to uniform distribution of different components in space, and it does not require a high stress. Dispersive mixing refers to reduction of component size, and it occurs only when the stress in the melt exceeds the coherent strength of the component. In reality, distributive mixing involves some dispersive mixing and viceversa.

Therefore, by producing Tyre Rubber modified binders with high shear stress (> 1000-2000 RPM) implies a dispersive mixing which reduces the particle size of coarse crumb rubber, allowing the interaction process to progress with greater speed (Abdelrahman and Carpenter 1999). Agglomeration is a mechanism that can contribute to the increase of stiffness/viscosity during the modification process (Shenoy, 1999).

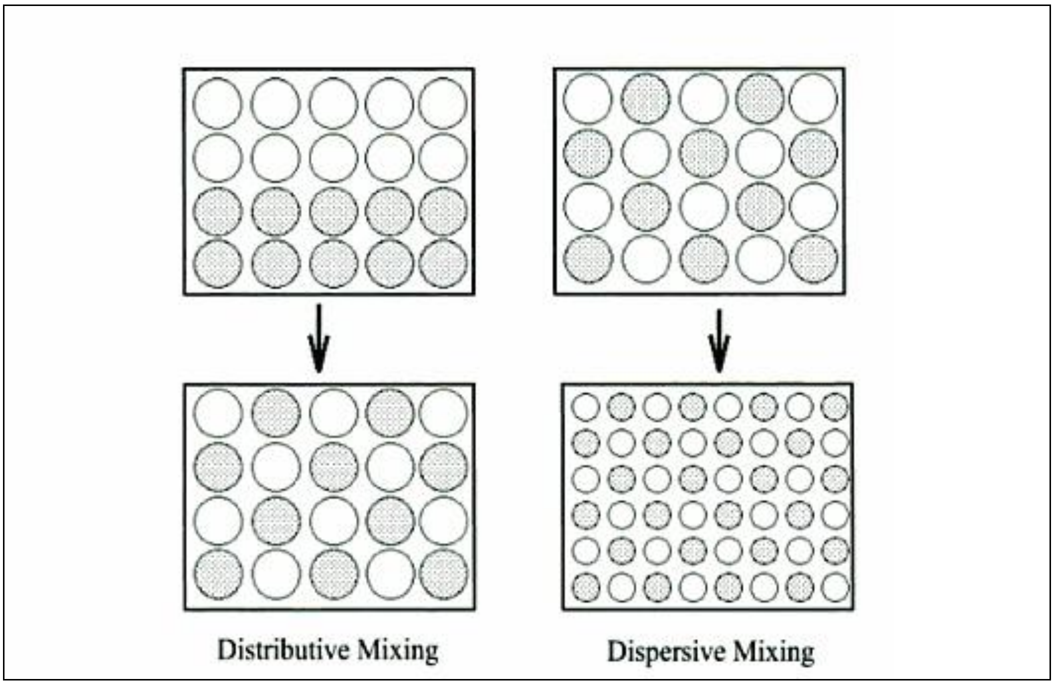


Figure 4.24. Distributive mixing and Dispersive mixing (Chung, 2000)

Shenoy (1999) stated that high shear mixing provides the energy to break particle-particle bonds and helps reducing agglomeration. Once the polymer wets the particle, the bond fails to re-form, leading to better dispersion of the filler in the polymer matrix (Attia & Abdelrahman, 2008).

High shear rate are fundamental to ensure proper dispersion of the rubber within the bitumen matrix and it has been demonstrated that this helps the storage stability of the final blend (Attia & Abdelrahman, 2008)). However, the processing device is secondary to the processing temperature; if the temperature is not high enough to produce rubber depolyimerisation/devulcanization to a great extent, the influence of processing device is not significant (Navarro et al. 2007)

Base binder

It is evident that the preparation of bitumen-rubber blends is strongly related to the nature and the overall properties of the raw components. However, the base bitumen composition is considered as a key factor influencing the final rheological properties of asphalt rubber binder (Abdelrahaman & Carpenter, 1998 and 1999). In fact, both bitumen and rubber are said to affect the properties of the modified bitumen and hence those of the mixes. However, for TR-MBs, the properties of the base binder typically have a greater influence on the rutting susceptibility and viscosity of the binder than the properties of the crumb rubber used in the matrix (Thoedesen et al., 2008).

Bitumen source (physical and chemical properties). Regarding the compatibility between base bitumen and the tyre rubber crumbs, the evolution of the bitumen composition during the curing process indicates that aromatic fractions of bitumen are the major cause of rubber swelling through a migration phenomenon. Viscoelastic properties measurements demonstrate that base bitumen composition should be selected carefully to achieve a good compromise between a sufficient rubber swelling and a reasonable viscosity of the final binder. (Ould Henia et al. 2008)

Thus, in order to optimize the modification process it is suggested to use as base bitumen those that are particularly rich in aromatics and resins or, if necessary, to add naftenic oils in order to favor swelling of the rubber granulate. For this reason, all the mentioned specifications prescribe pretty soft base bitumen with penetration grade usually within a range of 80/100, but also till 200 (Asphalt Rubber Type III).

Oil extenders. The production of TR-MB can have an undesirable side effect, i.e. the absorption of aromatic oils from the bitumen into the rubber's polymer chains could require an increase in the binder content, which may lead to potential problems of flushing or bleeding, increase the paving material's cost, and may cause tracking.

In this case an external source of light fractions (extender oils) can be used to eliminate issues of compatibility. However, extender oils are expensive and typically increase emissions of aromatic and volatile compounds at high temperatures (Caltrans, 2006).

The type and amount of aromatic oil in the bitumen also plays a major role in determining the compatibility of bitumen-rubber blends (Chehovits et al, 1982; Oliver, 1982).

Crumb Rubber Modifier

Depending upon the type of CRM, rubber processing method and rubber particle size used, the blending method is said to vary with the variation in the results of the end product (Pavlovich, 1979). Moreover, Viscosity is strongly related to the size of the CRM particles and relative tire rubber content of the CRM modified blend (Caltrans, 2006)

Rubber type. Generally it is assumed that the mixes made from automobile tyres differ from those made with truck tyres. It states that the difference in terms of the viscosity, ring and ball softening point and ductility can in part be related to the chemical balance of rubber in the two tyre types. The constituent of tyre rubber known to affect the blend behaviour is the natural rubber component. Glenn & Tolonen (1977), indicate that whole truck tyres contain approximately 18 percent natural rubber compared with 9% for whole automobile tyres and 2% for automobile tyre treads.

Therefore, when combinations of bitumen and CRM materials cannot produce a satisfactory blend, it is possible to enhance the content of natural rubber to eliminate issues of compatibility.

Huff and Vallerga (1981), indicate that bitumen-rubber prepared with vulcanised synthetic rubber (scrap tyres) indicated better weather and heat resistant properties when compared to the non-vulcanised rubber. The vulcanised rubber is said to form a bitumen-rubber sheet due to the swelling of rubber after absorbing the oils in bitumen. This is said

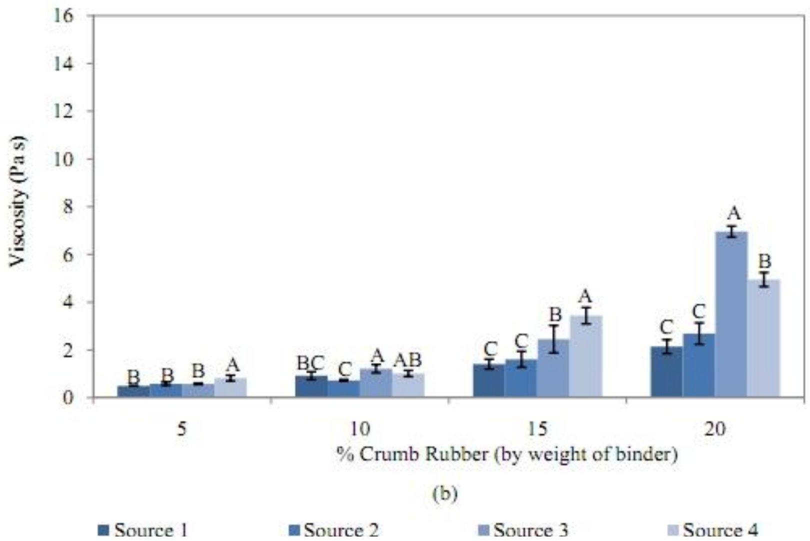


Figure 4.25. Viscosity of four TR-MBs differing by CRM source and content: Source 1 cryogenic/passenger; Source 4 ambient/truck (Thoedesen et al., 2008).

to impart better resistance to fracture under traffic. The bitumen-rubber prepared with dev vulcanised rubber indicated better dispersion and dissolution in bitumen and better binder properties (adhesion and cohesion). However, these blends are reported to lack the toughness and resilience achieved with the vulcanised bitumen-rubber blends.

Rubber Source (Processing method). The method adopted to process the scrap rubber significantly affects the digestion of rubber and the intermediate to high temperature proeprties properties of bitumen-rubber and its mixes (Abdelrahman and Carpenter 1998, 1999). Oliver, (1981) reports that an electron micrograph study on the rubber particles indicated that the rubber processing method affects the rubber size and shape of rubber particles (Fig. 4.26).

The processing method, therefore, affects the surface area of the rubber particles, which in turn affects the rate of reaction and viscosity of the bitumen-rubber binder. A study conducted by Texas Transportation Institute theorised that the increased surface area per volume or weight of the fine particles enhances the ability of the particles to be swollen by, and thus bond with, the binder (Billiter et al. 1995).

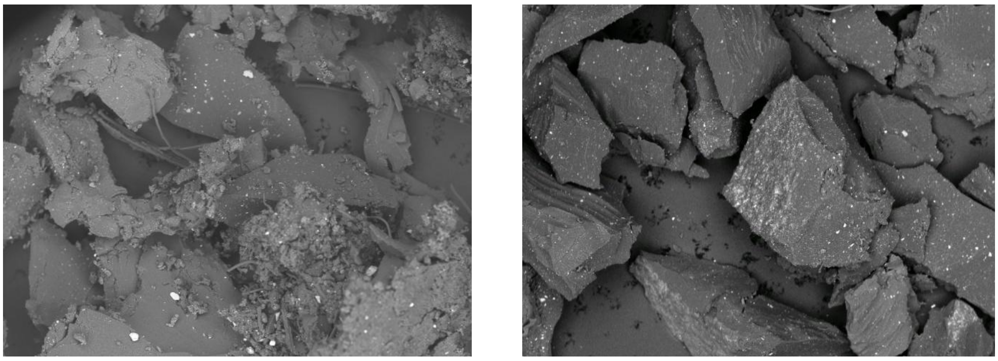


Figure 4.26 SEM micrographs of Ambient CRM (left) and Cryogenic CRM at 30x magnification (Thoedesen et al., 2008).

Rubber particle size. Crumb rubber particle size controls the swelling mechanism over time and affects the binder matrix. Buckly and Berger (1962) showed that time required for swelling increases with the particle radius squared.

Fine rubber swells faster and depolymerises faster, affecting the liquid phase more than the matrix of the binder. Fine particle sizes may require almost no time to react. Coarse rubber has more effect on the binder matrix but has less effect on the liquid phase than fine rubber. Liquid-phase modifications are more stable than matrix modifications (Abdelrahman and Carpenter 1998, 1999).

(Putman & Amirkhanian, 2006). Another study stated that the coarser the particle size the higher the G* value and the lower the δ under the same interaction conditions (Attia & Abdelrahman, 2008).

Rubber amount. A bitumen modified with 15 percent rubber can increase the high temperature viscosity of the blend by a factor of 10 or more (Fig. 4.25). There is evidence to suggest that increasing crumb rubber concentrations, regardless of crumb rubber source or binder type, results in increasing viscosities, failure temperatures, and G*/sinδ values. This confirms that as crumb rubber is added to the binder, the mechanical properties and viscosity are increased; however, the extent of this increase is dependent on the type of binder and crumb rubber properties (Thoedesen et al., 2008).

4.3.4 Wet Process-High Viscosity: Technologies and Specifications

On the grounds of research done around the globe, rubberised bitumen is used as a general term to identify a group of concepts that incorporate tyre rubber into bituminous binders for paving applications. These terms refer to the uses of rubber, as modifying agent in bitumen, that are different in their mix composition, method of production or preparation and in their physical and structural properties. Based on the area, processing types and techniques used, a number of tyre rubber modified binder and mix specifications have been published and each of them is related to a specific technology. Among those, the following are the most commonly used technologies/specifications in the field of tyre rubber modified bitumen.

Table 4.5 Comparison between Ambient and Cryogenic Ground Rubber

Technologies	Specifications	Country
Asphalt Rubber binder	▪ ASTM D6114-97, 2009 ▪ Caltrans' Asphalt Rubber User Guide, 2006	USA
Bitumen Rubber binder	▪ SABITA Manual 19, 2007 ▪ AsAc Technical Guideline, 2007	RSA
Crumb Rubber binder	▪ Austroads, 2006	AUS & NZ

<u>*Asphalt Rubber binder (USA)*</u>

According to the ASTM definition, asphalt rubber (AR) is “a blend of asphalt cement, reclaimed tire rubber, and certain additives in which the rubber component is at least 15 percent by weight of the total blend and has reacted in the hot asphalt cement sufficiently to cause swelling of the rubber particles.”

Rubber requirements. According to ASTM D6114, in order to produce Asphalt Rubber, the rubber should have the following characteristics:

- Less than 0.75% moisture and free flowing
- Specific gravity of 1.15 ± 0.05

- No visible nonferrous metal particles
- No more than 0.01% ferrous metal particles by weight
- Fibre content shall not exceed 0.5% by weight (for hot mix binder applications)
- Recommends all rubber particles pass the No.8 (2.36mm) sieve
- (Note that Rubber gradation may affect the physical properties and performance
- of bitumen rubber hot mix).

The California Department of Transportation (Caltrans, 2006) specifies that CRM must include 25 ± 2 percent by mass of high natural rubber CRM and 75 ± 2 percent scrap tyre CRM. Both types of rubber must meet specific chemical and physical requirements including gradation and limits on fabric and wire contaminants. The scrap tyre CRM consists primarily of 2 mm to 600 urn sized particles (No. 10 to No. 30 sieve sizes). The high natural rubber CRM is somewhat finer, mostly 1.18 mm to 300 urn sieve sizes.

Table 4.6. Typical gradation of the CRM to be used in the Wet Process (Hicks, 2002)

Sieve #	Nominal size (mm)	% Passing
10	2.36	100
16	1.18	75-100
30	600 µm	25-100
50	300 µm	0-45
100	150 µm	0-10
300	75 µm	0

Base bitumen requirements. ASTM D6114 specifies three different types of Asphalt Rubber. Each of them is associated to a suitable bitumen to be used as base of modification

- Type-I binders typically include stiffer base bitumen and are generally recommended for hot climates, such as: AC-20, AR-8000 and PG64-16.
- Type-Il binders typically include base bitumen softer than Type-I and are generally recommended for moderate climates, such as: AC-10, AR-4000 and PG58-22.
- Type-Ill binders typically include the softest grade base bitumen and are generally recommended for cold climates, such as: AC-5, AR-2000 and PG52-28.

where AC (Asphalt Cement) and AR (Aged Residue) are referred to the American grading systems based on viscosity. For example, an AC 20 asphalt has a viscosity of

2,000 poise (+ 20%) at 60ºC, whilst an AR 4000 bitumen has a viscosity of 4,000 poise (+ 25%) at 60ºC after aging. A rough comparison between penetration and viscosity (AC and AR) bitumen grades is shown in Figure 4.27.

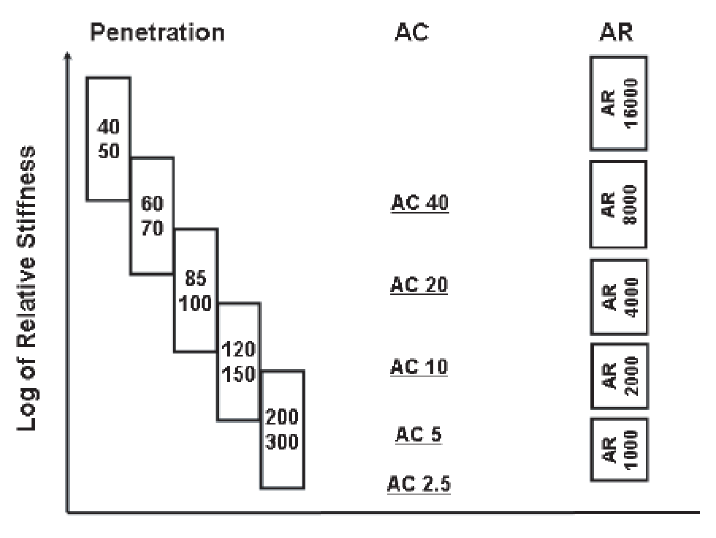


Figure 4.27. Comparison of Penetration and American Viscosity bitumen grades

It is worth to highlight that Caltrans (2006) defines as "Rubberized asphalts" all bitumens modified with CRM that may include less than 15 percent CRM by mass and thus may not comply with the ASTM definition of asphalt rubber (ASTM D8). In the past, terminal blends, or better the "wet process-no agitation CRM modified binders" have typically fallen in this category. Moreover, Caltrans specifies that wet process-no agitation CRM modified binders may be manufactured by different methods and are governed by different specifications and tested with different equipment than the high viscosity asphalt rubber binders.

Asphalt Rubber production. By definition, Asphalt Rubber is prepared using the "wet process – High Viscosity" system (§4.3.2). Physical property requirements are listed in ASTM D 6114, "Standard Specification for Asphalt Rubber Binder". The Asphalt Rubber is produced at elevated temperatures (≥ 350°F, 177°C) in low shear (Shatnawi, 2010) to promote the physical interaction of the asphalt binder and rubber constituents, and to keep the rubber particles suspended in the blend. Various petroleum distillates or extender oil may be added, at a rate of 2.5 to 6 percent by mass of the bitumen binder, to reduce viscosity, facilitate spray applications, and promote workability. Field production of high viscosity Asphalt Rubber binders is a relatively straightforward process and it is still based on the McDonald process (Fig. 4.17). Equipment for feeding and blending may differ among asphalt rubber types and manufacturers, but the processes are similar. The component materials are metered into high shear blending units to incorporate the correct proportions of extender oil and CRM into the paving grade asphalt. The blending units thoroughly mix the CRM into the hot asphalt cement and extender oil, and the blend is pumped into a heated tank where the asphalt rubber interaction proceeds.

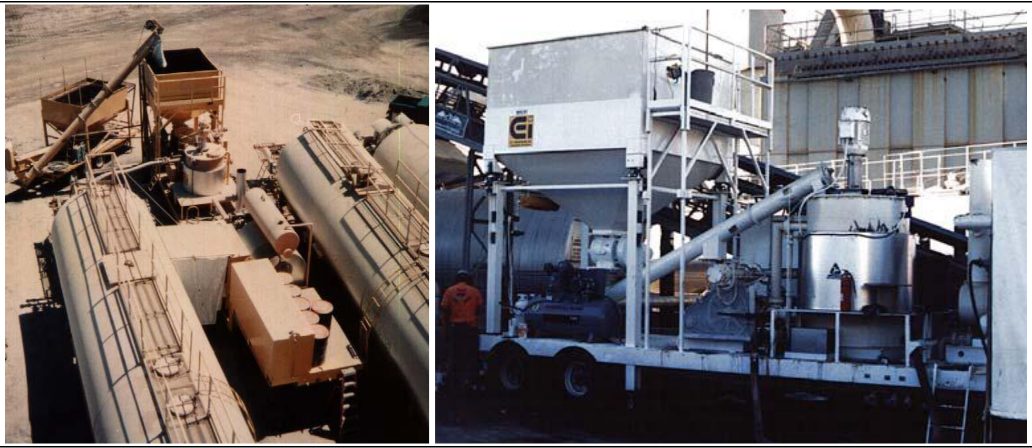


Figure 4.28. Asphalt Rubber Production plant (left) and Weigh Hopper for CRM proportioning. (Caltrans, 2006)

CRM is usually supplied in one ton (0.91 tonne) super sacks that are fed into a weigh hopper for proportioning (Fig. 4.28). Augers are needed to agitate the asphalt rubber inside the tanks to keep the CRM particles well dispersed, otherwise the particles tend either to settle to the bottom or float near the surface. Agitation can be verified by periodic observation through the top hatch or the port where the auger control is inserted.

The asphalt rubber binder must be interacted with agitation for a minimum of 45 minutes at temperatures from 190 to 218°C to achieve the desired interaction between asphalt and rubber. In order to maintain the reaction temperature within the specified range, the bitumen must be hot, 204 to 224°C before the design proportions of scrap tire and high natural CRM are added. This is because the CRM is added at ambient temperature (not heated) and reduces the temperature of the blend.

The component materials are metered into blending units to incorporate the correct proportions of CRM into the bitumen, and are thoroughly mixed. The asphalt rubber producer is allowed to add the extender oil while adding the rubber, although in some cases the base binder may be supplied with the extender included. If the asphalt rubber producer adds the extender oil, use of a second meter is recommended to best control the proportioning. The meter for the extender oil should be linked to that for the bitumen.

An Asphalt Rubber binder interactedat lower temperatures will never achieve the same physical properties as the laboratory design, although it may achieve the minimum specification values for use. Hand held rotational viscometers (e.g. Haak) are used to monitor the viscosity of the asphalt rubber interaction over time for quality control and assurance. Before any asphalt rubber binder can be used, compliance with the minimum

Table 4.7. Specification for Asphalt Rubber (ASTM D6114)

Binder specification	ASTM D6114 (2002)		
	Type I	Type II	Type III
Apparent Viscosity 177.5°C (ASTM D 2196): cp	1500-5000	1500-5000	1500-5000
Penetration at 25°C (ASTM D5): dmm	25-75	25-75	50-100
Penetration at 4°C (ASTM D5): dmm	min 10	min 15	min 25
Softening point (ASTM D36): °C	min 57.2	min 54.4	min 51.7
Resilience at 25°C (ASTM D5329): %	min 25	min 20	min 10
Flash point (ASTM D93): °C	min 232.2	min 232.2	min 232.2
After TFOT (ASTM D1754), residual penetration at 4°C (ASTM D5) : %	min 75	min 75	min 75
Climatic region	hot	moderate	cold
Average minimum monthly temperature: °C	min -1	min -9	min -9
Average maximum monthly temperature: °C	min 43	max 43	max 27

Table 4.8. Caltrans Specification for Rubberised bitumen (Caltrans, 2006)

Test parameter	Specification limits
Apparent Viscosity, Haake, 190°C: cp	1500-4000
Cone Penetration at 25°C (ASTM D217):dmm	25-70
Softening point (ASTM D36): °C	52-74
Resilience at 25°C (ASTM D3407): %	minimum 18

viscosity requirement must be verified using an approved rotational viscometer (e.g. Brookfield). As long as the viscosity is in compliance and the interaction has proceeded for at least 45 minutes, the asphalt rubber may be used (Caltrans, 2006)

Caltrans (2006) recognize that before starting the production an appropriate asphalt rubber binder design must be developed. Caltrans Standard Special Provisions (SSPs), specifes that at least 2 weeks prior to start of construction the Contractor must supply to the Engineer, for approval, an asphalt rubber binder formulation (design or “recipe”) that includes results of specified physical property tests, along with samples of all of the component materials. Samples of the prepared asphalt rubber binder must also be submitted to the Engineer at least 2 weeks before it is scheduled for use on the project.

Asphalt Rubber storage. Caltrans requires that heating be discontinued if Asphalt Rubber material is not used within 4 hours after the 45-minute reaction period. The rate of cooling in an insulated tank varies, but reheating is required if the temperature drops below 190°C. A reheat cycle is defined as any time an asphalt rubber binder cools below and is reheated to 190 to 218°C. Caltrans allows two reheat cycles, but the asphalt rubber binder must continue to meet all requirements, including the minimum viscosity.

Sometimes the binder must be held overnight. The bitumen and rubber will continue to interact at least as long as the asphalt rubber remains liquid. The rubber breaks down (is digested) over time, which reduces viscosity. Up to 10 percent more CRM by binder mass can be added to restore the viscosity to specified levels. The resulting asphalt rubber blend must be interacted at 190 to 218°C for 45 minutes and must meet the minimum viscosity requirement before it can be used.

Bitumen Rubber binder (RSA)

Bitumen rubber binder is a terminology used when modified binder is obtained by the wet process in South Africa. Bitumen Rubber binders combine rubber crumbs (with a specific, grading, morphology and composition) with bitumen at high temperatures to achieve a complex two phase product, named non-homogeneous binder. In the Technical Guideline of the South African Asphalt Acadamey (AsAc, 2007), is also reported that that properties of the modified binder used in hot mix asphalt will influence the engineering properties of the resultant mix, therefore the substitution of a conventional bitumen with a modified binder can result in higher air voids due to reduced workability of the higher viscosity modified binders. For this reason, it is important that split samples of the modified binder are sent to all the participating laboratories (eg: supplier, site and control laboratories) and tested before commencement of a project to ensure that the results are within the reproducible limits as prescribed by the test methods.

Rubber requirements. In South Africa, the Committee of Land Transport Officials (COLTO)'s specification requires the reclaimed rubber to have not less than 30 percent natural rubber by mass of hydrocarbon content (Potgieter, 2004), whilst the SABITA Manual and the Technical Guideline of the South African Asphalt Acadamey (AsAc, 2007) specifies 60 to 75 percent natural rubber by mass of hydrocarbon content, with all rubber particles passing the 1.18mm sieve. The rubber crumb is produced by a mechanical size reduction process. Crumb produced by cryogenic-mechanical techniques are not permitted in South Africa. The tyre rubber must be pulverized, free of fabric, steel cords and other contaminants.

Table 4.9. SABITA requirements for rubber crumbs for modifying bitumen (AsAc, 2007)

Property	Requirement	Test method
Sieve analysis (% mass)		
Passing screen (mm)		
1.180	100	
0.600	40-70	MB-14
0.075	0-5	
Poly-isoprene content (%m/m total hydrocarbon)	25 min	Thermo gravimetric Analysis
Fibre length (mm)	6 max	
Bulk density (g/cm^3)	1.10 – 1.25	MB-16

Base bitumen requirements. The binder used in the production of the bitumen-rubber must be SABITA B12 or B8 road-grade bitumen (60/70 or 80/100 penetration-grade bitumen respectively) or a blend of these grades to provide a product with a particular viscosity and other prescribed properties.

Bitumen Rubber production. The binder is manufactured from blending penetration grade bitumen (72 – 82% by mass), plus extender oil (0-4%) plus rubber crumbs (18 - 24 %) in a patented high shear mixer with a speed of 3000 r.p.m, at a temperature in exces of 180 ºC but not more than 220ºC and for short periods before the introduction of rubber. During the addition of the rubber component, the blend cools down considerably and has to be re-heated to a temperature of 190 to 200ºC to ensure proper digestion of the rubber in the bitumen.

Special manufacturing equipment is required to manufacture this highly viscous material. The product has a limited useable life of 4 to 6 hours and, therefore, manufacture usually takes place onsite or very close to the construction site. Bitumen rubber binder can be used for surface dressing operations, in which case it is applied with binder distributors specially designed to handle this highly viscous binder. For surface dressing applications, the bitumen-rubber binder is manufactured using the "wet process", which is also the most used for the manufacture of bitumen-rubber hot-mix asphalt. The blending unit consists of a small tank equipped with a high speed stirring device that ensures proper "wetting" of the rubber by the binder and prevents the formation of rubber lumps in the final product. From the blending tank the product is transferred to a digestion tank which could also be a specialised binder distributor. In the digestion tank the product is continually agitated while being heated to the final temperature.

The ratio of components varies depending on the bitumen source, the climatic conditions and the application. The more reliable manufacturers in South Africa nowadays prefer to standardise on 20% rubber content and also to preselect the type of tyres for the modification process. Following the addition of the rubber, a digestion period is required for the rubber to swell and partially dissolve in the bitumen/extender oil blend. The rubber never completely dissolves in the bitumen and the product is thus classed as a non-

Table 4.10. SABITA Properties of bitumen rubber surfacing seals and asphalt (AsAc, 2007)

Property		Unit	Test method	Class	
				S-R1	A-R1
Softening Point[1]		°C	MB-17	55-62	55-65
Dynamic Viscosity @ 190 °C		dPa.s	MB-13	20-40	20-50
Compression & Recovery	5 mins	%	MB-11	>70	>80
	1 hour			>70	>80
	4 days			>25	n/a
Resilience @ 25		%	MB-10	13-35	13-40
Flow		min	MB-12	15-70	10-50

homogenous binder. The bitumen rubber blend is then circulated in a holding tank and heated at high temperatures (190 - 210°C) to facilitate the chemical digestion process.

The extender oil could either be added to the penetration grade bitumen before delivery or to the bitumen on site. The requirements of the extender oil are such that it should have a flash point of greater than 180°C and the percentage by mass of aromatic unsaturated hydrocarbons be greater than 55. To prevent sticking of rubber particles, also an addition of calcium carbonate or talc up to 4% by mass of rubber is permitted.

On completion of the digestion period, a hand-held Haake viscometer is used to perform a viscosity test on the product to confirm that sufficient digestion has taken place. If approved, the product is ready for application. (AsAc, 2007)

Bitumen Rubber storage. Bitumen rubber degrades rapidly at application temperatures which are in excess of 200°C. Therefore the blending of bitumen rubber generally takes place in close proximity to the spray site or asphalt mixing plant. On completion of the digestion period, the product generally has a further useable life at the application temperature of approximately 4 hours. The rate of degradation will vary depending mainly on the application temperature and can be monitored on-site with a hand held Haake viscometer. The manufacturer of the bitumen rubber should supply temperature curves showing the changes in the properties over time. Figure 10 shows typical changes in the viscosity properties of a bitumen rubber at different temperatures over time.

Only sufficient quantities of bitumen rubber should be blended at any time in accordance with what can be sprayed or mixed within the application viscosity window of the product. Allowance must be made for changing weather conditions and construction delays. Proper planning and close cooperation between the supplier and contractor is essential to limit the over production of bitumen rubber which may result in unnecessary degradation of the bitumen rubber over prolonged periods of heating. Product must not be superheated if it is not going to be used. This will enable the product to be superheated at a later stage for reuse if it is still within specification. If it is out of specification then up to 25% can be reblended with new bitumen and rubber crumb.

Table below shows the recommended temperatures and time limits for the short-term handling, storing, spraying, mixing and application binders modified with bitumen rubber. S-R1 is a Surface Seal, A-R1 is for hot mix while C-R1 is a Crack sealant, all of them are bitumen rubber binders

Table 4.11. SABITA Typical temperature/time limits for bitumen rubber (AsAc, 2007)

Binder class	Short term handling		Storage		Spraying/Asphalt mixing/Application		
	Max Temp (°C)	Max Holding time (hrs)	Max Temp (°C)	Max Holding time (hrs)	Max Temp (°C)	Min Temp (°C)	Max Holding time (hrs)
S-R1	165	24	150	240	210	195	Refer to time/viscosity curve
A-R1	165	24	150	240	210	190	
C-R1	165	24	-	-	190	180	-

Crumb Rubber Modified binder (AUS & NZ)

Bitumen technologists in Australia have been looking into using rubber in bitumen since the early 1950s, when a surface dressing trial utilising 5% vulcanised reclaimed rubber in R90 bitumen (100 pen) with 10 mm aggregate was applied on the Prince Highway at St. Peters in New South Wales. However, there was not much development until the mid 1970s, when VicRoads in conjunction with the Australian Road Research Board (ARRB) started using crumb rubber modified bitumen in spray seal in urban and rural applications. It has been used extensively as a bitumen modifier in sprayed bituminous seals and occasionally in bitumen applications in Victoria. Thanks to this experience VicRoads, in collaboration with the Roads and Traffic Authority (RTA), New South Wales and the Main roads by Western Australia, have prepared the “Scrap rubber bitumen guide”.

Since 1986, success has been reported using rubberised bitumen in Australia, mainly in the states of New South Wales (RTA, Road and Traffic Authority) and Victoria (VicRoads), specifically when used as a crack resisting layer, e.g. thin bitumen overlay over concrete, SAM or SAMI.

In 2006, Austroads published technical specifications framework (AP-T41, 2006) coupled with a guide to the selection and use of Polymer Modified Binders (AP-T42, 2006) including the use of rubberised bitumen, identified as Crumb Rubber Modifed binder. The reports suggest a wide usage of rubber into asphalt with both wet and dry process.

The AP-T42 guide includes also a “Crumb Rubber Protocol” in which Constituent Specification, Binder Design, Field Blending, Binder Specification Limits and other restrictions regarding and Sampling and Testing to check requirements are indicated. An important component of this crumb rubber specification is the role of laboratory testing as explained later.

Rubber requirements. In Austroads (2006), two levels of rubber content, nominally 15 and 18 are specified for Crumb Rubber Modified binder obtained through the wet process. Another level, from 25 to 30 percent, is designed for the dry process. Crumbs have only 2 sizes, namely 16 (coarse) and 30 (fine). Bulk density (max 350 Kg/mc), grading, maximum particle size, steel content (<0.1%), moisture (< 1%) and other properties must be specified by the contractor. All crumb rubber shall be less than 3mm in length and the rubber shall not contain any foreign material such as sand, fibre or aggregate. All this info is summarised in the table below.

Base bitumen requirements. The only requirements related to the most suitable bitumen to be used as base for the Crumb rubber Modified binders, is indicated in the “Crumb Rubber Protocol” of the technical guide of Austroads (AP-T42, 2006), which specifies to use Bitumen Class 170 (AS2008) corresponding to a Penetration grade of 85/100.

Table 4.12. Austroads Specification for Crumb Rubber for bitumen modification (Austroads, 2006)

Test	Methods	Size 16	Size 30
Grading			
passing 2.36 mm	AG/PT 1:43	100	100
passing 1.18 mm	AG/PT 1:43	80 (min)	100
passing 0.60 mm	AG/PT 1:43	10 (max)	40 (max)
passing 0.15 mm	AG/PT 1:43		5 (max)
Bulk density	AG/PT 1:44	350 kg/m^3	350 kg/m^3
Water content	AG/PT 1:43	< 1 %	< 1 %
Steel content	AG/PT 1:43	< 0.1 %	< 0.1 %

Crumb Rubber Modified binder production. As mentioned previously, the Austroads guide for Selection and use of Polymer Modfied Binders (AP-T42, 2006), gives a major importance to the a priori laboratory testing. In fact, the design process requires a laboratory exercise to be undertaken using the following procedure:

1. A trial mix is prepared for each of an appropriate series of rubber concentrations such that the specification limits for the selected binder grade are met in at least one of the mixes (mixing temperature 195ºC, digestion period 45 minutes for Size 16 rubber and 30 minutes for Size 30).
2. The measured properties are plotted against rubber concentration and the concentration at which the specification limits are complied with is identified. This rubber concentration is deemed to be the design concentration.
3. A rubber extraction is performed on the design mix using AG:PT/T1 42 Laboratory method for determining crumb rubber concentration. The determined concentration of rubber is used as a check for the analysis of field collected samples.

The diagram in the figure below illustrates the key steps. This procedure is based on the one included in the previous Austroads 2000. In the Austroads 2006 specifications, S40R, S45R/S50R and S55R were replaced by S15RF, S18RF, for asphalt application, and S55R was kept for sprayed sealing.

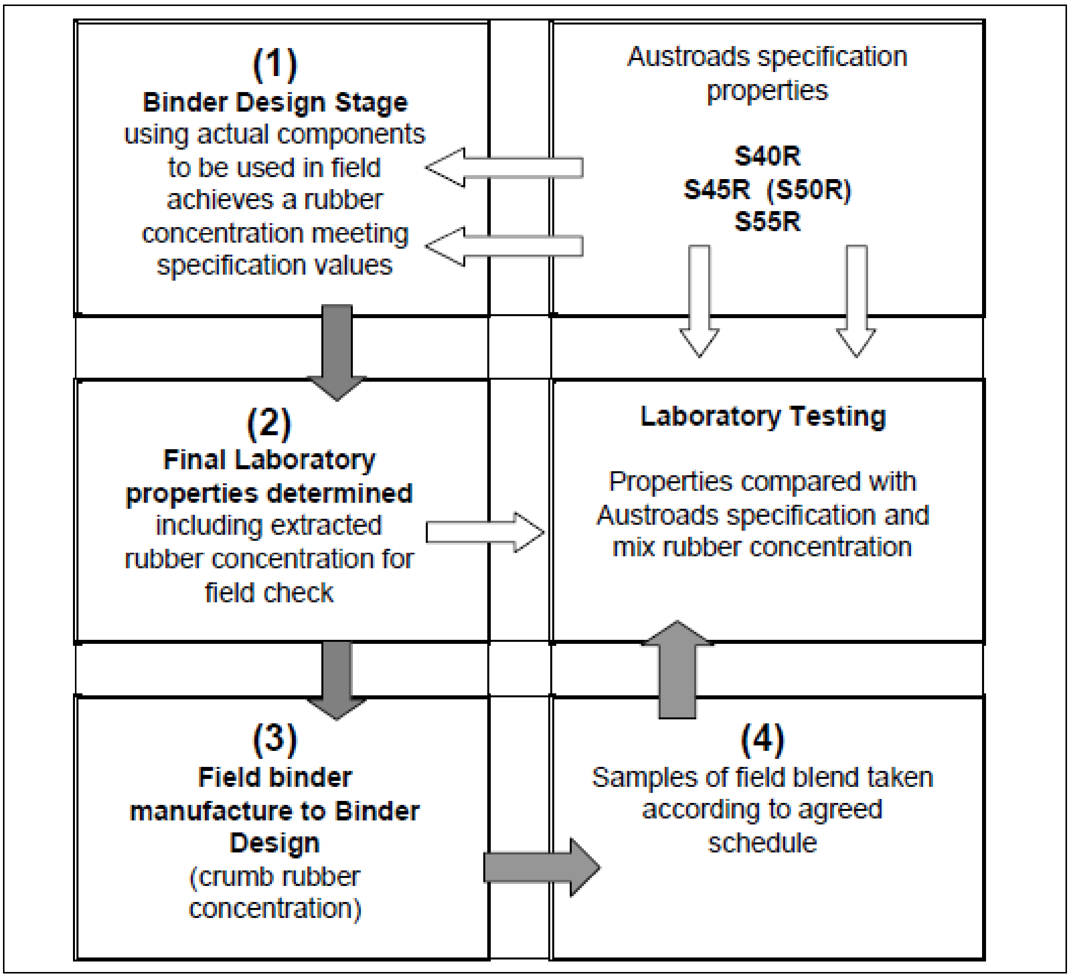


Figure 4.29. Austroads laboratory procedure for Crumb rubber modified binders (AP-T42, 2006)

Plant protocols may require different procedures to the field defined system and the contractor will be responsible for the binder design.

Crumb Rubber Modified binders are produced with production routes: factory and field produced rubberised bitumen.

<u>Factory produced Crumb Rubber Modified binders</u>: usually include a combining oil and lower concentrations of rubber than their field produced counterpart. Factory produced crumb rubber modified binder are used for hot mix asphalt by using the wet process. This has been shown to improve the mix properties but requires relatively high binder contents. Since the concentration of rubber is an important performance controlling

factor, generally the higher the volumetric concentration, the more effective will be the binder in more demanding applications.

Flux oil should only be added to the crumb rubber classes and the manufacturer's recommendations should be followed. It is important to use the finer crumb rubber in order to achieve a reasonable level of digestion in the binder in the short time that the material remains hot.

Field produced crumb rubber modified binders: are produced for sprayed sealing. They are a high temperature blend of bitumen and crumb rubber without combining oils, and may contain up to 25 percent by mass of rubber; these formulations are not suitable for long distance transportation or extended storage but represent the highest performing materials within their class when optimally digested.

The properties of the field produced rubberised bitumen are generally controlled by their softening point, elastic recovery and/or torsional recovery (Austroads, 2006).

Crumb Rubber Modified binder storage. When field mixing crumb rubber binders, the material must be continually circulated to minimise settling out of any rubber particles. Failure to do this will most likely result in blockages of the spraying jets and/or pipework. Do not store field produced crumb rubber mixtures in bitumen sprayers, road tankers or bulk storage because of the potential problem of segregation and settling out of the rubber particles resulting in blocked pipework etc.

It is worth to highlight that current work in Australia is focussing on the use of crumb rubber as a substitute for other modified binders in more conventional applications while using similar design criteria, with particular interest in the use of pre-blended products which behave much more like other pre-blended modified binders. Laboratory investigations with pre-blended crumb rubber modified binders indicate satisfactory performance but at higher binder contents (> 8%).

Table 4.13 summarise some of the most important specifications requirements for the TR-MB production around the world.

Table 4.13. Summary of the most important Specification requirements for TR-MBs

Properties	ASTM 2002			Caltrans 2006	SABITA 2007	Austroads 2007
	Type I	Type II	Type III			
Base bitumen requirements						
Penetration: dmm	85-100	120-150	200-300	120-150	60-100	85-100
Crumb rubber requirements						
Passing sieve: mm	2.36			2.36	1.18	2.36
Rubber content: %	≥15			18-22	18-24	15-18
Additives						
Extender oils: %	-			2.5 - 6	0 - 4	-
Caclium carbonate / Talc: %	0 - 4			-	0 - 4	-
Processing conditions						
Temperature: °C	177			190-220	180-220	195
Mixing speed: rpm	-			-	3000 rpm	-
Mixing time: min	45 + reaction			45-60	-	30-45

4.3.5 Wet Process-High Viscosity: Benefits, Issues and Limitations

Extensive literature (§ 4.3.5) clearly shows the numerous successes obtained using Tyre Rubber bituminous mixtures produced with the Wet Process (Airey et al., 2004; Amirkhanian, 2001; Bahia & Davis, 1994). However, Asphalt rubber is not a panacea, therefore this section was thought to explain the main benefits provided by the usage of this technology and the issues that still exist and, in some cases, limitate its extensive application.

Benefits

The primary reason for using tyre rubber binders is that it provides significantly improved engineering properties over conventional paving grade bitumen. As for Asphalt Rubber binders, they can be engineered to perform in any type of climate as indicated in ASTM

D 6114. At intermediate and high temperatures, that TR-MB show physical and rheological properties significantly different than those of neat paving grade bitumens. The rubber stiffens the binder and increases elasticity (proportion of deformation that is recoverable) over these pavement operating temperature ranges, which decreases pavement temperature susceptibility and improves resistance to permanent deformation (rutting) and fatigue with little effect on cold temperature properties (Caltrans, 2006).

As demonstrated by various researchers, Tyre Rubber Modifed binders obtained through the wet process have reduced fatigue and reflection cracking, greater resistance to rutting, improved aging and oxidation resistance and better chip retention due to thicker binder films (Santagata et al., 2007; Souza et al., 2005; Zborowski et al., 2004; Potgieter et al.,2002; Kaloush et al., 2003; Cook et al., 2006; Bertollo et al.,2004).

Also Asphalt Rubber pavements have been demonstrated to have lower maintenance costs (Way, 2000; Jung et al., 2002), lower noise generation (Pasquini, 2009; Antunes et al., 2006a; Leung et al., 2006), higher skid resistance and better night-time visibility due to contrast in the pavement and stripping (Antunes et al.,2005). (Antunes state of art in Italy) The benefits of Tyre Rubber Modifed binders obtained thorugh the original wet process are summarised below (Caltrans, 2006):

Tyre Rubber Binders have:

- Increased viscosity that allows greater film thickness in paving mixes without excessive drain down or bleeding.
- Increased elasticity and resilience at high temperatures.

Tyre Rubber pavements have:

- Improved durability.
- Improved resistance to surface initiated and fatigue/reflection cracking due to higher binder contents and elasticity.
- Reduced temperature susceptibility.
- Improved aging and oxidation resistance due to higher binder contents, thicker binder films, and anti-oxidants in the tire rubber.
- Improved resistance to rutting (permanent deformation) due to higher viscosity, softening points and resilience (stiffer, more elastic binder at high temperatures).

- Lower pavement maintenance costs due to improved pavement durability and performance.

In addition, Tyre Rubber pavements and binders can result in:

- Reduced construction times due to thinner lifts.
- Reduced traffic noise (primarily tyre noise)
- Better chip retention in chip seals due to thick films of highly modified asphalt.
- Improved safety due to better long-term color contrast for pavement markings because carbon black in the rubber acts as a pigment that keeps the pavement blacker longer.
- Savings in energy and natural resources by using waste products and not contributing to the stockpiles.

Limitations

Asphalt rubber materials are useful, but they are not the solution to all pavement problems. The asphalt rubber materials must be properly selected, designed, produced, and constructed to provide the desired improvements to pavement performance. Pavement structure and drainage must also be adequate. Limitations on the use of asphalt rubber include (Caltrans, 2006):

- Asphalt rubber is not best suited for use in dense-graded HMA. There is not enough void space in the dense-graded aggregate matrix to accommodate sufficient Asphalt Rubber binder content to enhance performance of dense-graded mixes enough to justify the added cost of the binder.
- Construction may be more challenging, as temperature requirements are more critical. Asphalt rubber materials must be compacted at higher temperatures than dense-graded HMA because, like polymers, rubber stiffens the binders at high temperatures. Also, coarse gap-graded mixtures may be more resistant to compaction due to the stone-onstone nature of the aggregate structure.
- Potential odour, also if it seems to not be harmful (see environtmetal issues)
- If work is delayed more than 48 hours after blending the asphalt rubber, some binders may not be usable. The reason is that the CRM has been digested to such an extent that it is not possible to achieve the minimum specified viscosity even if more CRM is added in accordance with specified limits.

- It is not possible to store High Viscosity TR-MB at elevated temperatures without special equipment. Moreover, those binders cannot be stored for prolonged period; it was reported that "the rubberised binder must be used within hours of its production" (Takallou and Sainton, 1992).

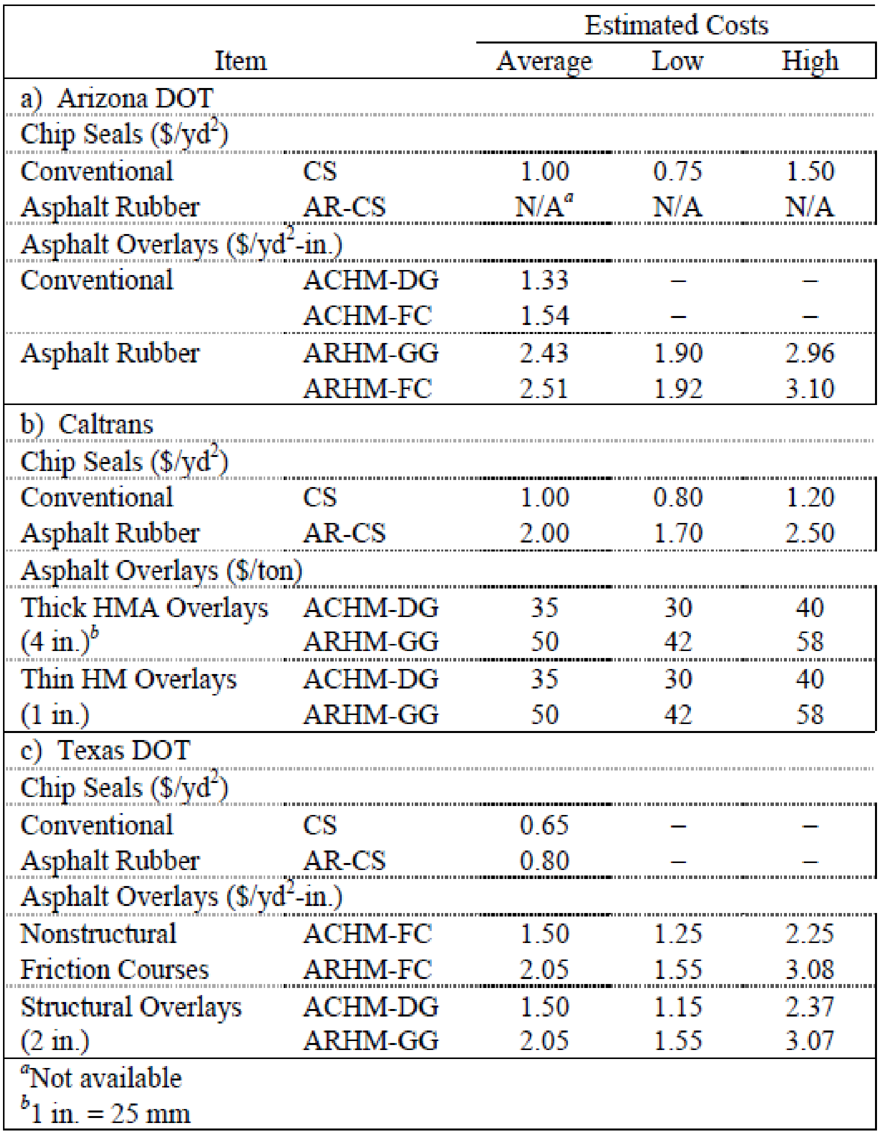
In addition to the above, some of the post-construction problems that have been documented typically relate to issues with construction in cold temperature paving or late season construction and use of thin layer systems. Rubberised asphalt mixture materials should not be placed in conditions where it is likely that the minimum temperature for completion of compaction of 143°C is unlikely to be complied with. For
example:

- during rainy weather;
- during cold weather with ambient or surface temperatures <13°C;
- over pavements with severe cracks more than 12.5 mm wide where traffic and deflection data are not available;
- areas where considerable handwork is required;
- where haul distances between asphalt mixing plant and job site are too long to maintain the mixture temperature required for placement and compaction.

Economical Issues

Issues related to the usage of TR-MBs have been adequately addressed by a large number of research projects and reports and also through long standing construction evaluation. For the sake of brevity, the most notable are discussed below:

Higher initial costs. Costs are higher than conventional asphalt per unit ton until economies of scale are in place. From a study conducted in the USA by Hicks & Epps (2003), it has been experienced that the Asphalt Rubber hot mix could costs almost double than conventional mixes. Another example is given by Caltrans (2006) which stated that in 2000 the Asphalt Rubber hot mix could costs almost double than conventional mixes, but since the year 2000 a falling cost difference trend has been registered, also because costs of construction materials and petroleum products have increased.



Item		Estimated Costs		
		Average	Low	High
a) Arizona DOT				
Chip Seals ($\$/yd^2$)				
Conventional	CS	1.00	0.75	1.50
Asphalt Rubber	AR-CS	N/A[a]	N/A	N/A
Asphalt Overlays ($\$/yd^2$-in.)				
Conventional	ACHM-DG	1.33	–	–
	ACHM-FC	1.54	–	–
Asphalt Rubber	ARHM-GG	2.43	1.90	2.96
	ARHM-FC	2.51	1.92	3.10
b) Caltrans				
Chip Seals ($\$/yd^2$)				
Conventional	CS	1.00	0.80	1.20
Asphalt Rubber	AR-CS	2.00	1.70	2.50
Asphalt Overlays ($/ton)				
Thick HMA Overlays	ACHM-DG	35	30	40
(4 in.)[b]	ARHM-GG	50	42	58
Thin HM Overlays	ACHM-DG	35	30	40
(1 in.)	ARHM-GG	50	42	58
c) Texas DOT				
Chip Seals ($\$/yd^2$)				
Conventional	CS	0.65	–	–
Asphalt Rubber	AR-CS	0.80	–	–
Asphalt Overlays ($\$/yd^2$-in.)				
Nonstructural	ACHM-FC	1.50	1.25	2.25
Friction Courses	ARHM-FC	2.05	1.55	3.08
Structural Overlays	ACHM-DG	1.50	1.15	2.37
(2 in.)	ARHM-GG	2.05	1.55	3.07

[a] Not available

[b] 1 in. = 25 mm

ACHM-DG: conventional hot mix – dense graded

ACHM-FC: conventional hot mix – friction course

ARHM-DG: asphalt rubber hot mix – gap graded

ARHM-OG: asphalt rubber hot mix – open graded

ARHM-FC: asphalt rubber hot mix – friction course

CS: chip seal

AR-CS: asphalt rubber chip seal

Figure 4.30. Typical costs for scenario used by USA state highway agencies (Hicks & Epps, 2003)

Lifecycle economics. As in any economical evaluation, cost effectiveness should be evaluated using Life Cycle Cost Analysis (LCCA). Hicks & Epps, (2003) showed that evaluating different scenarios, in terms of pavement design, maintenance and rehabilitation strategies, the following was concluded:

- Asphalt rubber is a cost effective alternate for many highway pavement applications.
- When variability is considered in the inputs (cost, expected life, etc.), the asphalt rubber alternates would be the best choice in most of the applications considered. But also that,
- Asphalt rubber was not cost effective in all applications. LCCA allows one to determine when and where Asphalt Rubber will be cost effective. Further,
- The cost-effectiveness of rubberised asphalt is dependent in many cases on the ability to reduce thickness when using rubberised asphalt. Without a reduction in thickness, or longer lives for equal thicknesses, the rubberised asphalt alternates would not be cost effective.

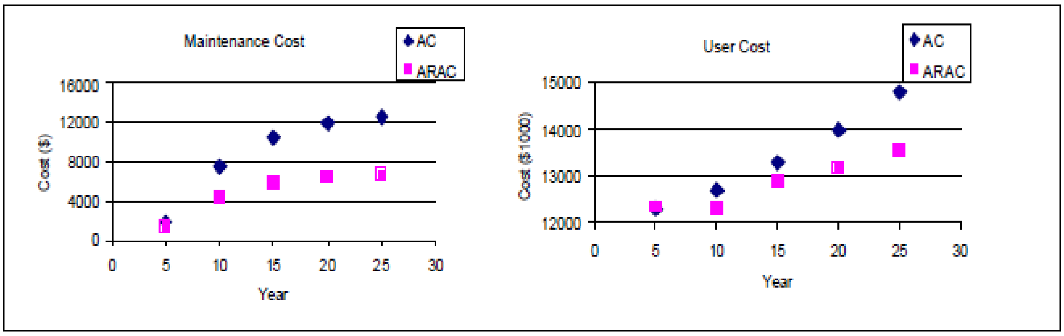


Figure 4.31. Maintainance cost (left) and User cost comparison betwen conventional bituminous mixes (AC) and Asphalt Rubber mixes (ARAC) (Suk Jung et al., 2002)

Other studies conducted at the Arizona State University (Suk Jung et al., 2002) compared maintenance and user costs trends for the conventional bituminous pavements and Asphalt Rubber pavements. Results showed that after 5 years the maintenance and user costs are not much different, after 10 years the maintenance cost begins to substantially be different, as higher maintenance costs will be anticipated for the conventional pavement. This difference for user costs starts at about 15 years Based on the data analysis presented for the two pavements, an asphalt-rubber pavement would be more cost-effective than a conventional pavement with respect to agency costs as well as user costs.

Plant modifications. Another issue that contribute to higher initial cost of the wet process are plant modifications. The equipment used to blend bitumen and rubber requires some, modification to a standard hot mix asphalt plant, which could be also a portable unit as illustrated in section 4.3.2. and depicted in Figures 4.18 and 4.19. Additionally, conventional paving equipment without modifications is used to place the material. The capital investment required for a fully operational tyre rubber modifed plant is anywhere from 500,000 to 750,000 USD (350.000 – 550.000 €) (1999). To put this into perspective, a used bulldozer (1998), can be purchased for about 800,000 USD (600.000€) (Carlson & Zhu, 1999). From an investigation made in 2007 in UK by the Waste & Resources Action Programme (Widyatmoko & Elliot, 2007), in order to study a possible adoption of this technology, resulted that the approximate cost for importing/hiring and running the blending plant for 5 to 7 days of rubberised bitumen production is estimated to be between £60,000 and £90,000 (70.000 – 105.000€). This is because none special mixing units described above is currently available in the UK, and therefore requires importing/hiring from either the US or mainland Europe. Morevoer, for the installation of a Portable rubberised bitumen mixing plant, an area of not less than 150m^2 will be required, depending upon the model and make of the mobile plant. (Widyatmoko & Elliot, 2007)

It is worth highlighting that mobilization and set up of the asphalt rubber binder production equipment cost as much for small jobs as for big ones, but large projects spread mobilisation costs over more asphalt tonnage. The memo suggests that smaller projects may not be cost effective with respect to initial cost. Although the break point for project size may have changed since then, unit costs of small projects (three days Asphalt Rubber paving or less) should be evaluated by LCCA during the design phase (Caltrans, 2006).

From this finding, it is therefore possible to conclude that initial costs are still an issue, which is an important limitation when a technology has to be imported, but the quality of the final product demonstrated to be so good that long term economical analysis indicate tyre rubber asphalt is usually an economically convenient option. However, LCCA is a fundamental tool that, particularly in this case, must be used to assess the most convenient option.

Environmental Issues

Hazardous Emissions. Fume emissions have been studied extensively in a number of Asphalt Rubber projects in USA since 1989. Different studies, performed also by the National Institute for Occupational Safety and Health (NIOSH), Federal Highways Admistration (FHWA), determined that use of asphalt rubber does not appear to increase health risks to paving personnel. In these studies the following is reported: "...risks associated with the use of asphalt rubber products were negligible" and also "Emission exposures in asphalt rubber operations did not differ from those of conventional asphalt operations" and also "…the effect of CRM on emissions may be relatively small in comparison to the effects of other variables." (Caltrans, 2006; Crockford et al., 1995) Those variables include the fueling rate of the dryer, mix temperature, asphalt throughput rate and asphalt binder content.

However, some agencies also concluded that the rubber modified mix had an objectionable odor (Hicks et al., 2010). Moreover, in Colorado while researching and developing specifications for the use of tire rubber asphalt for the 2006 paving season, local contractors expressed concerns about using the "wet or dry methods", due to the excessive smoke and smell that would be expelled into the atmosphere during the manufacturing process of this material at their asphalt plants. The contractors were so concerned about losing their state environmental certifications that they indicated they would not use the "wet or dry methods" without some assurances that their operating permits would not be jeopardized (Khattak & syme, 2010).

Therefore, despite the findings reported above, environmental concerns upon the widespread usage of the wet process still exists.

Recyclability. Before 1992, Asphalt Rubber pavements had been performing well and the replacement/recycling of them was not necessary. As some sections of asphalt rubber pavements have met their service life span, recyclability became an issue. Carlson & Zhu (1999) report of two jobs occurred in the USA where Asphalt Rubber mixes were successfully recycled. One example is the recycling job occurred in the City of Los Angeles, California (Youssef & Hovasapian, 1995), where the initial placement of the asphalt rubber pavement occurred in 1982. In 1994 the pavement was milled and stockpiled at a nearby asphalt plant. The asphalt rubber grindings were added to the virgin rock and oil so that the grindings composed 15% of the final mix. At another location, the grindings were put through a microwave process where nearly 100% of the output was composed of recycled asphalt rubber. This project demonstrated that asphalt rubber can be recycled using either microwave technology or conventional mix design technology. Air sampling during paving and recycling determined that employee exposures to air contaminates were well below the Occupational Safety and Health Administration (OSHA) permissible exposure limits (PEL), and in most cases below the detection limits.

4.3.6 Wet process-NO agitation: The new option

NO-Agitation Tyre Rubber Modifed Bitumen (NO agitation TR-MB), technology was first used in Florida and Texas in the mid-1980s and till nowadays it seem to have been used only in other states of the USA, namely California, Colorado, Louisiana, Arizona, and Nevada.

The idea with Tyre Rubber binders produced with the NO agitation-wet process, also famous as Terminal Blend binders, is to produce a material in which the tire rubber is fully digested, or better dissolved, into the asphalt without leaving visibly discrete particles. The characteristic swelling process of the previously mentioned TR-MB technologies is replaced by the depolymerisation/devulcanization and optimised dispersion of the rubber into the bitumen by using high processing temperature (210-220 ºC) and high shear stress during the mixing, resulting in a smooth, homogeneous product.

Production and Storage. In terms of processing conditions, in the wet process-NO agitation crumb rubber and bitumen are blended at high temperature (200-220ºC) through the Continuous blending-Reaction Systems (§4.3.2). No reaction tanks are provided. The amount of rubber used in this process may vary anywhere between 5 to 18 percent (Hicks et al, 2010). Often also small percentage of other polymers (e.g. SBS), or other additives, are used to produce a combined homogeneous material that exhibits excellent storage stability and compatibility with the finished binder formulation.

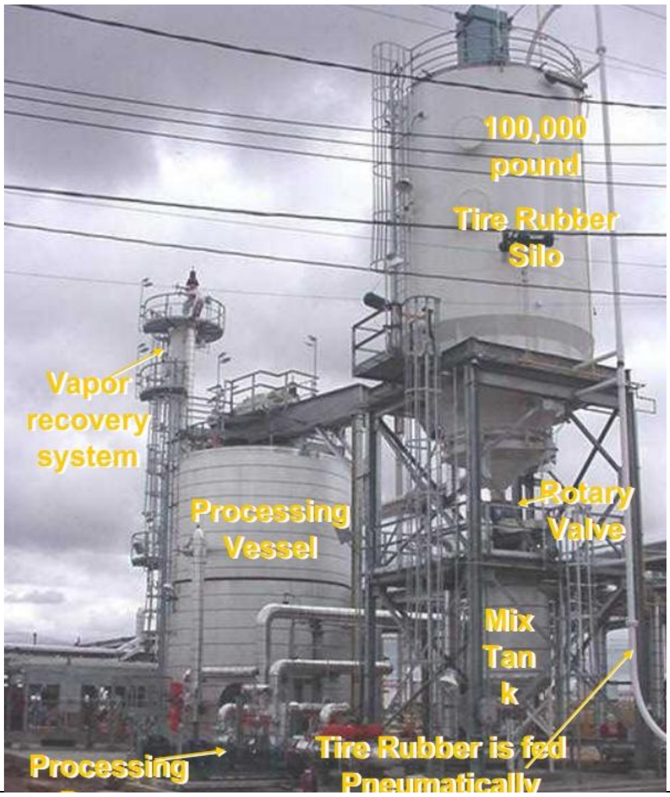
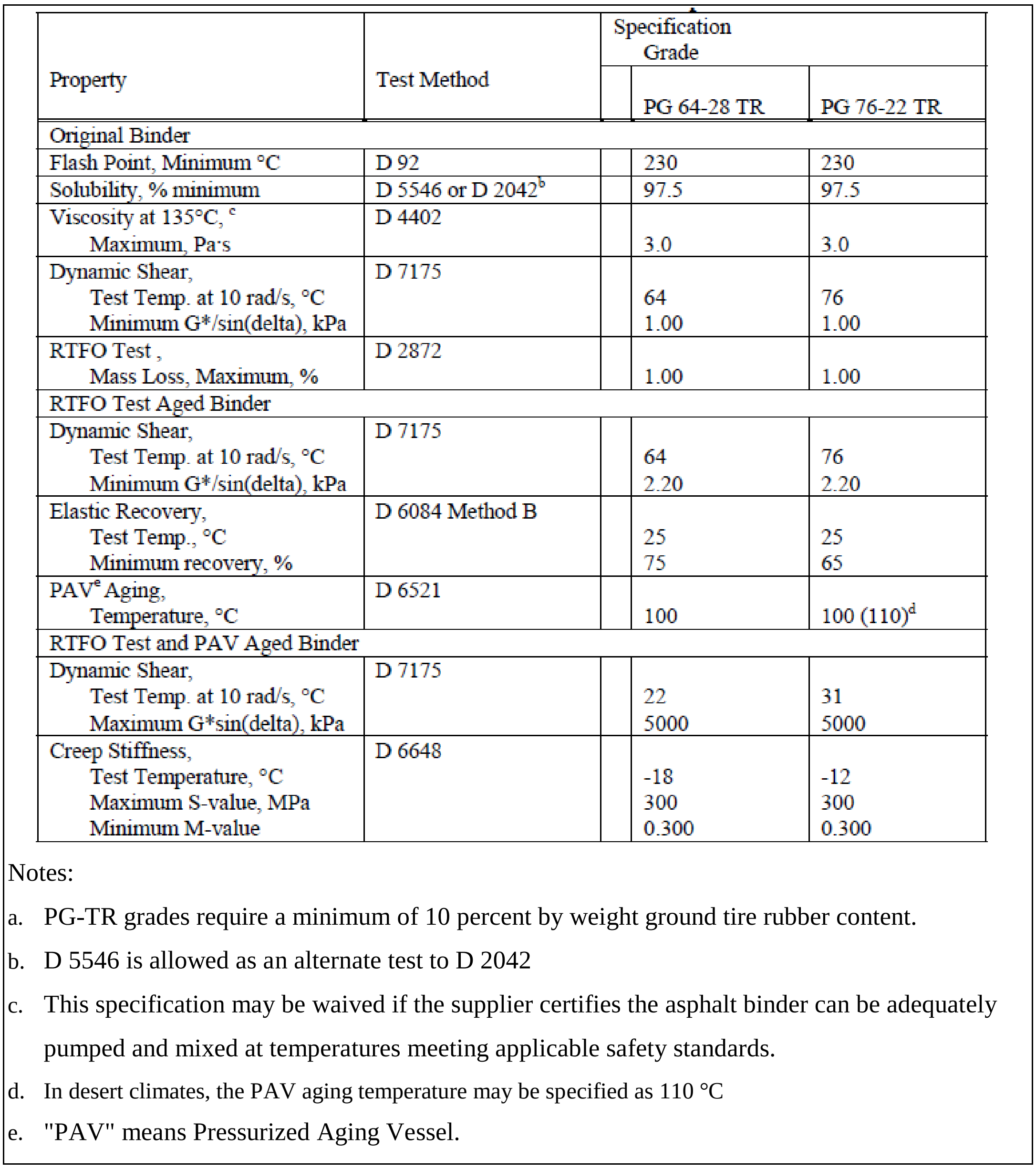


Figure 4.32. Terminal blend Tyre Rubber system

There are some proprietary and other non-proprietary processes used, but in most of them tyre rubber is blended into the bitumen at the bitumen terminal or refinery (that's why is named also terminal blend) with specific pressure, temperature, time and agitation requirements (Fig. 4.32). During this process, the operator takes samples and runs a solubility test to ensure the rubber is completely digested. Most manufacturers used a high shear process to make sure the tire rubber is completed digested. The solubility of the finished product is generally above 97.5 %.

The binder is then delivered to the hot mix plant by truck as a finished product with no additional handling or processing. After mixing with aggregate material is shipped to the job and no special equipment is required for paving, or odor/fume control. Moreover, the TR mix is compacted like regular hot mix asphalt (Asphalt Institute online magazine, 2008).



Property	Test Method	Specification Grade		
			PG 64-28 TR	PG 76-22 TR
Original Binder				
Flash Point, Minimum °C	D 92		230	230
Solubility, % minimum	D 5546 or D 2042[b]		97.5	97.5
Viscosity at 135°C, [c]	D 4402			
Maximum, Pa·s			3.0	3.0
Dynamic Shear,	D 7175			
Test Temp. at 10 rad/s, °C			64	76
Minimum G*/sin(delta), kPa			1.00	1.00
RTFO Test ,	D 2872			
Mass Loss, Maximum, %			1.00	1.00
RTFO Test Aged Binder				
Dynamic Shear,	D 7175			
Test Temp. at 10 rad/s, °C			64	76
Minimum G*/sin(delta), kPa			2.20	2.20
Elastic Recovery,	D 6084 Method B			
Test Temp., °C			25	25
Minimum recovery, %			75	65
PAV[e] Aging,	D 6521			
Temperature, °C			100	100 (110)[d]
RTFO Test and PAV Aged Binder				
Dynamic Shear,	D 7175			
Test Temp. at 10 rad/s, °C			22	31
Maximum G*sin(delta), kPa			5000	5000
Creep Stiffness,	D 6648			
Test Temperature, °C			-18	-12
Maximum S-value, MPa			300	300
Minimum M-value			0.300	0.300

Notes:

a. PG-TR grades require a minimum of 10 percent by weight ground tire rubber content.

b. D 5546 is allowed as an alternate test to D 2042

c. This specification may be waived if the supplier certifies the asphalt binder can be adequately pumped and mixed at temperatures meeting applicable safety standards.

d. In desert climates, the PAV aging temperature may be specified as 110 °C

e. "PAV" means Pressurized Aging Vessel.

Figure 4.33. Performance Graded Tyre Rubber Modified Binder (PCCAS, 2008)

The stability of NO agitation TR-MBs during prolonged storage at high temperatures seems to be similar to other blended PMBs. Some patented procedure states that they are storage-stable binders, as long as the tyre rubber is fully digested into the binder (solubility is above 97 percent) it is possible to store them without phase separation. (Asphalt Institute online magazine, 2008).

Like PMBs. Terminal blends are manufactured at the refinery or terminal like any other polymer modified bitumen (PMB). The bitumen is heated under a controlled environment in a tank to an elevated temperature. The crumb tyre rubber, probably better named as tyre rubber powder, is then introduced into the tank and digested into the bitumen. During this process, an operator takes samples and runs a solubility test to ensure that the rubber is completely digested. Typical solubility of the finished material is above 97.5 percent, which makes it a homogeneous material.

Recently in the United States the specifications used for Terminal Blend (PCCAS, 2008) have utilized the PG grading system, named PG-TR system, similar to the ones used for polymer modified asphalt (Fig. 4.33).

In California, PG-TR grades are specifically targeted for use in the same applications for which PG-PMB binders are used, including dense-graded mixes for thick structural sections.

Performance. In 2010 Hicks et al. made a preliminary study, comprenshive of field and laboratory testing. Results have shown that Terminal Blend hot mix is a promising paving material for preventing reflective and fatigue cracking.

It performs better than conventional hot mix and chip seal and, in many of the tests is equal to or superior to the performance of asphalt rubber. However, more research needs to be done on determining the amount of rubber in TB, moisture susceptibility of TB binder, and evaluating the long-term performance of existing Terminal Blend projects.

Over 100 projects in 8 states are being monitored and the average performance ranges from good to excellent conditions.

Applications. Terminal blends can be used in all paving and maintenance applications requiring crumb rubber content. They can be used in dense-graded, open-graded and gap-graded mixes. They can be used in chip seal applications, emulsions, slurry seal applications and tack coat applications. NO agitation TR-MBs can be used with rubber contents as low as 5 percent and as high as 25 percent, depending on the application and the project’s requirements.

NO-Agitation TR-MB vs High Viscosity TR-MB

NO-Agitation Tyre Rubber Modifed Bitumen (NO agitation TR-MB), also named Terminal Blend binder, and High Viscosity Tyre Rubber Modifed Bitumen (HV TR-MB), are distinctly different binders in terms of material properties, possible applications and performance.

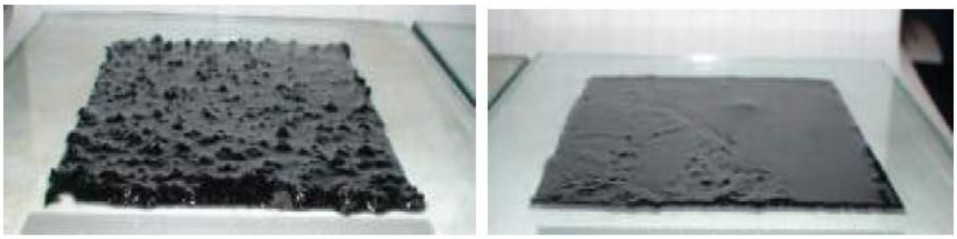


Figure 4.37. TR-MB from Wet process (left) and Wet Process-NO agitation (right) (PCCAS, 2008)

In terms of binder properties, the main differences are the viscosity and their storage stability. Viscosity for NO agitation TR-MB can range between 500-1000 centipoises at 135ºC, lower than the viscosity for HV TR-MB which is in the range of 1500-5000 centipoises at 177.5ºC (Table 4.10). For a better comparison, laboratory tests were conducted on both binders at 177.5ºC, results showed a viscosity of 75 centipoises for the Terminal Blend which is on the average over 36 times less than the viscosity for Asphalt-Rubber.

With regards to the storage stability, No agitation TR-MB born with the idea of obtaining a TR modified binder comparable to the normal PMBs, therefore on contrary to HV TR-MB, it is usally possible to store it as conventional PMBs.

HV TR-MB has more performance history since this process started over 35 years ago and they have been used successfully with many applications. However, they are not recommended for use on dense graded hot mix projects since the dense gradation cannot adequately accommodate the rubber particle size. On the other hand, NO agitation TR-MBs are most suitable for dense graded mixes.

In this regard, they are more likely to compete with polymer modified bitumen rather than HV TR-MB. NO agitation TR-MBs have been used on limited or experimental basis for chips seal applications, and in open graded and gap graded mixes, so there is still not enough literature to assess its validity in this area.

In terms of performance, the lower viscosity of NO agitation TR-MB implies lower application rates than if the HV TR-MB is used. The lower application rates mean less binder per unit area (5-6 % binder content) indicating less performance life than if Asphalt-Rubber is used (8 – 10% binder content) (Shatanawi, 2010). In fact, the ability to inject more binder in the mix translates to better fatigue and reflective cracking performance.

By analysing the current poor literature on this field (Shatanawi, 2010; Asphalt Institute online magazine, 2008; Khattak & Syme, 2010; Hicks et al., 2010), it can be concluded that both technologies have shown improvements over conventional binders. Shatanawi (2010) states that HV TR-MB have better performance than NO agitation TR-MB, while Hicks et al. say that in many of the tests Terminal Blend is equal to or superior to the performance of HV TR-MB. However, more research needs to be done on this field to understand the differences in terms of performance between the two technologies.

In conclusion, the main advantages of the NO agitation-Wet process in lieu of the McDonald method at the contractor's plant include:

- No need for costly specialised equipment.
- No portable plants required for blending of crumb rubber with asphalts.
- No additional holding areas for storing the crumb rubber product.
- Easiest for the contractor to incorporate into their traditional manufacturing process.
- Mixing, laying and compaction temperatures are comparable to standard mix applications with PMBs.
- Works with all mix designs; does not require any special adjustments to gradation or mix design parameters
- Being prepares at the refinery, completely eliminates potential problems with heating and blending of crumb rubber and asphalt products and
- Eliminates smoke and particulates from entering the atmosphere.

General Experience with Wet process-NO agitation

In terminal blending binder production, two main properties are of concern: first, the development of performance-related properties and, second, binder compatibility or storage stability. The literature indicates that performance-related properties develop early in the process while compatibility requires few hours to stabilise (Abdelrahman and Carpenter 1999, Abdelrahman 2006).

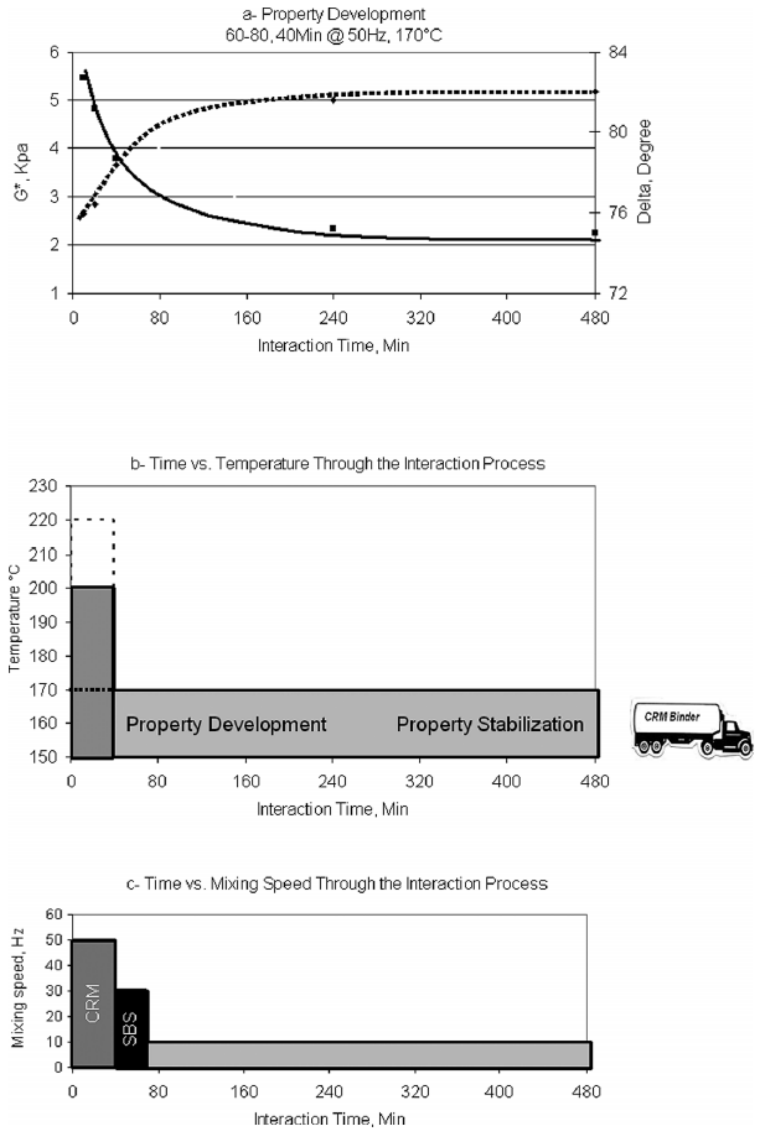


Figure 4.38. Production of NO agitation TR-MB as proposed by Attia & Abdelrahman (2009)

Few investigators have conducted studies on the rheological properties of these binders. For example, Thodesen, et. al. (2009) evaluated several binders using the multiple creep recovery tests. Among the binders studied were an Asphalt-Rubber binder and a NO agitation TR-MB that uses 10% CRM and 1% SBS polymer. The results showed that the Asphalt-Rubber binder exhibited the least creep and the highest percent recoveries under various loading and temperature ranges.

Another example is given by Attia & Abdelrahaman (2009), which investigating the possibility of producing high-performance terminal blending CRM binders, suitable for Superpave applications, found that by accurately regulating the processing conditions it is possible to balance the development of performance-related properties and storage stability. The same researchers proposed a procedure consisting in blending bitumen with 5% of tyre rubber and 2% of SBS at elevated shear stress (30-50 Hz) and with the processing conditions shown in Figure 4. They found that the final products have performance and binder stability (increasing shearing speed to 50 Hz) comparable to those of patent or proprietary products.(Abdelrahman 2006). Hence, interaction temperature on binder stability was not evaluated. Moreover the authors suggest toenhance the stability of binder by reducing the storage temperature at the plant.

5. Effects of tyre rubber bitumen modification

5.1 Introduction

The improvements in terms of mechanical properties due to the use of polymers to modify bitumens in road paving applications have already been widely demonstrated (§ 4.2.5). The aim of this section is to show how the rheology and the performance of a bituminous binder mixed with fine tyre rubber recycled from used tyres (TR-MB), could be comparable with a styrene butadiene styrene (SBS-MB) created with the same base binder and currently used for road applications. Physical, chemical and performance characterization followed by rheological and storage stability analyses have been undertaken as the basis for the comparison. The results of the investigation indicate that the blended TR-MB shows large improvements with respect to the base bitumen, comparable with the SBS-MB under almost all the conditions. However, in order to use this binder for practical purposes, major work regarding the improvement of the storage stability of the TR-MB still needs to be done.

The experimental programme of this and next chapter have been carried out at Nottingham Transportation Engineering Center.

5.2 Experimental programme

5.2.1 Materials

The same base bitumen was used to produce two different binders: a SBS Modified Bitumen (SBS-MB) and Tyre-Rubber Modified Bitumen (TR-MB). In order to obtain the base binder for the subsequent blending with the elastomers, an oil extender (flux) was added to the base bitumen (base binder is therefore a mixture of base bitumen plus flux). The TR-MB was blended using a Silverson high shear laboratory mill to mix the base binder with fine tyre rubber obtained from used tyres. Physical, chemical and performance properties of the base bitumen and base binder are reported in Section 3, while the characteristics of tyre rubber crumbs are reported in Tables 5.1 and 5.2 and the gradation shown in Figure 5.1.

Table 5.1: Properties of the tyre rubber crumbs

Origin :	passenger car tyre rubber processed by ambient grinding
Particle shape :	irregular
Fibre content :	0.5 %
Steel content :	0.1 %

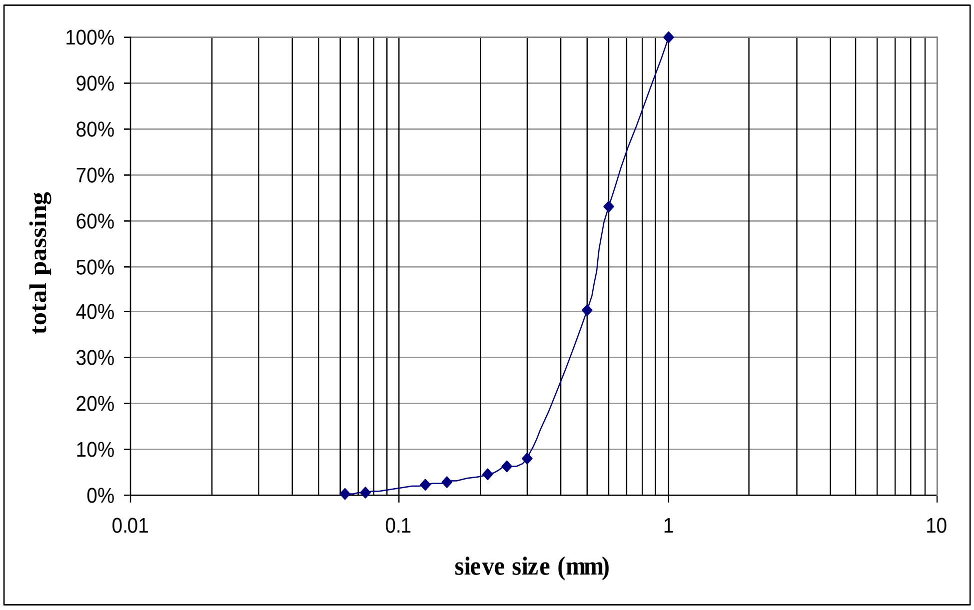


Figure 5.1. Grading curve of the tyre rubber crumbs

Table 5.2. Sieving of the tyre rubber crumbs

sieve size	Mass Retained		retained on sieve	Total passing	
	cumulative	individual			
mm	g	g	%	%	
1.0	0	0	0	100	discarded
0.6	44.1	44.1	37.1	62.9	
0.5	70.9	26.8	22.5	40.4	used
0.3	109.5	38.6	32.4	8.0	
0.25	111.6	2.1	1.8	6.2	
0.212	113.5	1.9	1.6	4.6	
0.15	115.4	1.9	1.6	3.0	
0.125	116.1	0.7	0.6	2.4	
0.075	118.3	2.2	1.8	0.6	
0.063	118.8	0.5	0.4	0.2	
	119	0.2	0.2		
Total mass	119	119			

Summarising, the following binders have been incorporated into this study:

Base bitumen: 40/60 pen (PG 64-16) straight run bitumen

Base binder: blend of 92.5% of 40/60 pen (PG 64-16) straight run bitumen and 7.5% of flux

SBS-MB: commercial SBS modified bitumen produced with base binder

TR-MB: tyre rubber modified bitumen produced as 85% of base binder and 15% of tyre rubber crumbs

All the binders were tested in their unaged (virgin) condition and in order to produce their Superpave performance grading they have also been tested after being subjected to two laboratories ageing procedures:

Short-term laboratory ageing, using the Rolling Thin Film Oven test (RTFOT) according to AASHTO T 240, and long-term laboratory ageing, using a Pressurised Ageing Vessel (PAV) according to AASHTO R 28.

Due to practical concerns (more details in Section 5.3.2) the short term ageing of the TR-MB has been performed by using the Thin Film Oven test (TFOT) according to AASHTO T 240.

5.2.2 TR-MB blending protocol

The blending of rubber and bitumen was carried out using the following protocol:

- Required amount of bitumen was heated at 180°C in the oven and then transferred to a hot plate heated at the same temperature.
- High shear mixing up to 2000 rpm was applied for first 10 minutes while firstly the oil extender and then the rubber later was feed into the bitumen.
- Time was allowed for the temperature to settle at 180°C.
- Once the temperature reached 180°C, blending time was noted and mixing undertaken at 1000 rpm for one hour.

Table 5.3 summarizes the mixing parameters used in the blending procedure.

Table 5.3. Blending protocol

base bitumen mass (78.65%)	oil extender mass (6.35%)	rubber mass (15%)	rubber size	total weight	mixing time	mixing speed	mixing temp.
g	g	g	mm	g	min	rpm	°C
1572.5	127.5	300	0-0.5	2000	60	1000	180

5.2.3 Physical and chemical characterization

The first part of the programme consisted of characterising the base bitumen and base binder in order to analyse the effect of the oil extender. To have a physical classification both bituminous binders were subjected to the following tests: penetration (ASTM D5), softening point (ASTM D36-95), Fraass breaking point (IP 80), ductility (10ºC, ASTM D113) and rotational viscosity at 100 and 160ºC (ASTM T316-04). In order to have an idea of the chemical composition of both binders, asphaltenes content was measured according to ASTM D6560-00. This last evaluation consisted in firstly collecting asphaltenes, wax and inorganic material on a filter paper by heating a mixture of bitumen with heptane under reflux. Secondly, the waxy substances were removed by washing the filter paper with hot heptane in an extractor. Lastly, the inorganic material was removed by using hot toluene. The extraction solvent was evaporated and the asphaltenes weighed. The second part of the programme consisted of comparing the two different modified binders in terms of their rheological characteristics. It also included rotational viscosity measurements at 100ºC and 160ºC which provided an easily determinable physical parameter to determine the consistency of the binders. Finally in the third part of the programme, the storage stability of the binders was evaluated using softening point (ASTM D36-95) and polymer dispersion of the different elastomers in the binders.

5.2.4 Performance grading procedure

In order to classify the binders by their performance properties, all of them were subjected to the Superpave grading procedure according to the AASHTO R 29-02 standard (§ Appendix A). The performance grading is undertaken by testing the binder at three different ageing conditions: unaged, short term aged (RTFO aged) and long term aged (PAV aged). As shown in Table 5.4, the high performance grade (high PG) is determined based on tests performed on the unaged and RTFO aged binder.

Table 5.4. Overview of the grading procedure

High PG Values
Unaged binder: The sample of TR-MB is tested to determine: • the flash point in °C (AASHTO T 48), • viscosity at 135°C (AASHTO T316), • the shear modulus (G*) and phase angle (AASHTO T 315) RTFO aged binder: • The asphalt binder is aged in the Rolling Thin-Film Oven (AASHTO T 240) • and the residue is tested to determine the mass loss (AASHTO T 240), • the shear modulus (G*) and phase angle (AASHTO T 315)

Low PG Values

PAV aged binder:

- The residue from the rolling thin-film oven is aged in the Pressurized Aging Vessel (AASHTO R 28) and this residue is tested to determine:
- the shear modulus (G*) and phase angle (AASHTO T 315),
- the creep stiffness (S) and slope, m of the log creep stiffness versus log time relationship at different instants of load (AASHTO T 313)*,
- eventually the failure stress in Direct Tension (AASHTO T 314),
- and in post-processing the Critical Cracking Temperature (AASHTO PP 42)**

* last step for assigning the low grade using Table 1 of the specification
** last step for assigning the low grade using Table 2 of the specification

Completing the sequence, the low performance grade (low PG) is determined by tests on the PAV aged binder. The low PG of all the binders has been established using Table 1 of AASHTO M 320-05.

5.2.5 Rheological analysis

In order to obtain a rheological characterization of all the binders, a dynamic mechanical analysis (DMA) over a wide range of temperatures and frequency sweeps was performed using a Bohlin GEMINI DSR. The tests were performed under the following conditions:

- Mode of loading:	controlled-strain
- Temperatures:	0ºC to 80 ºC at 5ºC intervals
- Frequencies:	0.10, 0.16, 0.25, 0.40, 0.63, 1, 1.6, 2.5, 4, 6.3 and 10 Hz
- Spindle geometries:	8 mm ϕ and 2 mm gap (0-45ºC), 25 mm ϕ and 1 mm gap (35-80ºC)
- Strain amplitude:	0.5% (within LVE response dependent on *G**)

For each test, samples were prepared by means of a hot pour method, based on Alternative 1 of the AASHTO TP5 Standard. The gap between the upper and lower plates of the DSR was set to a height of 50 μm plus the required testing gap at the mid-point of the testing temperature range. Once the gap has been set, a sufficient amount of hot bitumen (160ºC) was poured on the lower plate of the DSR to ensure a slight excess of material appropriate to the chosen testing geometry. The upper plate of the DSR was then gradually lowered to the required nominal testing gap. The bitumen that was squeezed out between the plates was then trimmed flush to the edge using a hot blade (pouring method). Finally, the gap was closed until there was a slight bulge around the circumference of the testing geometry.

The rheological properties of the binders were measured in terms of their complex (shear) modulus, G^*; and phase angle (viscoelastic balance of rheological behavior), δ. Once measured, the data was used together with the Time Temperature Superposition Principle and shift factors to produce master curves at 25°C. Master curves, isochronal plots and black diagrams have been used as the basis of all the rheological analysis.

5.3 Results and discussions

5.3.1 Base binder

In order to get better compatibility with elastomers, a blend of 92.5% base bitumen and 7.5% of oil extender (flux) was made to get the base binder for the modified binders. It is noticeable from Table 5.5, that the addition of the flux does not affect the asphaltenes content. Analysing the results, it is evident that the oil extender affects the base binder by softening it and thereby enhancing its low temperatures properties.

Table 5.5. Physical properties of the base bitumen and base binder

	base bitumen	base binder
Penetration (ASTM D5)	42 dmm	136 dmm
Softening Point (ASTM D36-95)	51ºC	39.8ºC
Fraass breaking point (IP 80)	0ºC	-14ºC
Ductility (ASTM D113)	1000 mm	1000 mm
Asphaltenes Content	3.4%	3.6%

Table 5.5 and 5.6 show how physical properties are influenced by the flux with an increase in the cracking resistance of the binder at low temperatures as shown by the lower Fraass breaking point temperature and a softening of the binder at high temperatures as shown by a decrease in softening point and reduced viscosity.

Table 5.6. Rotational viscosity of the base bitumen and base binder @ 100 and 160ºC

base bitumen				
	Pa.s	spindle	RPM	% torque
(ASTM T316-04) @ 100ºC	3.86	34	10	77
(ASTM T316-04) @ 160ºC	0.12	21	20	50
base binder				
	Pa.s	spindle	RPM	% torque
(ASTM T316-04) @ 100ºC	1.56	34	20	52
(ASTM T316-04) @ 160ºC	0.08	21	20	33

Table 5.7. Performance properties of base bitumen and base binder

Aging states	ASHTOO specifications	base bitumen	base binder
Unaged binder	Rotational Viscosity @ 135°C (Pa.s)	0.404	0.198
	G*/sin(delta) (kPa) *has to be ≥ 1.00*	@64°C / 1.41	@52°C / 1.28
RTFO Aged residue	G*/sin(delta) (kPa) *has to be ≥ 2.20*	@64°C / 2.90	@52°C / 3.51
RTFO+PAV aged residue	G* x sin(delta) (kPa) *has to be ≤ 5000*	@28°C / 4790	@16°C / 4970
	Stiffness (MPa) *has to be < 300*	@-6°C / 218	@-18°C / 275
	m-value *has to be > 0.3*	@-6°C / 0.36	@-18°C / 0.33
Flash point (°C) has to be > 230		> 300	> 300
Mass loss after RTFO ageing has to be < 1.00%		0.15%	0.09%
Performance grade		PG 64 - 16	PG 52 - 28
Performance temperature range		80°C	80°C

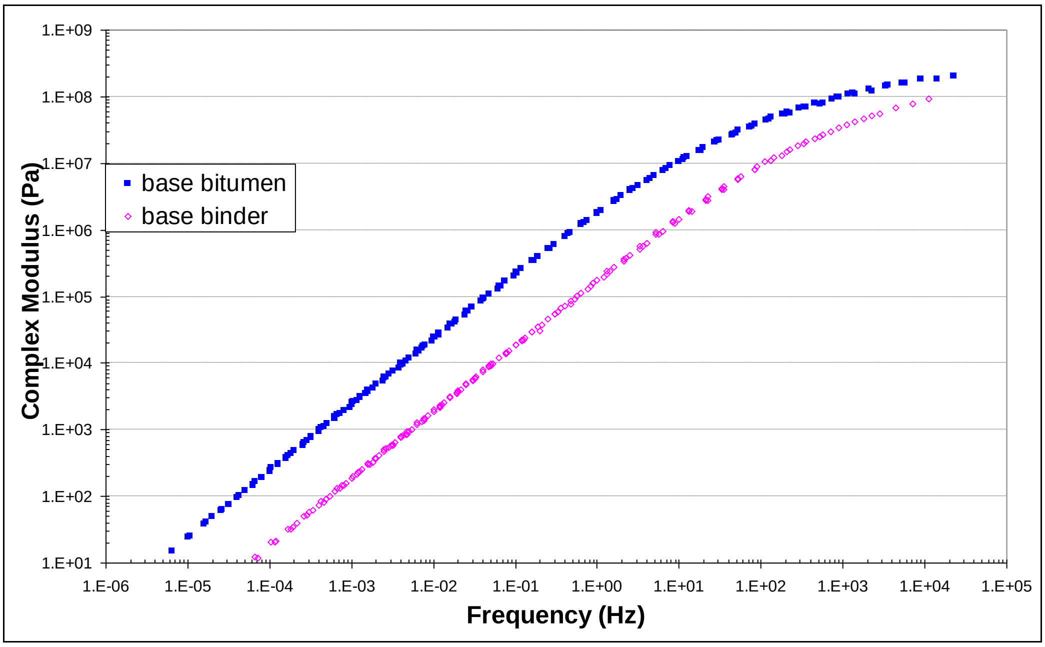


Figure 5.2a. Master curves of complex modulus at 25ºC of base bitumen and base binder

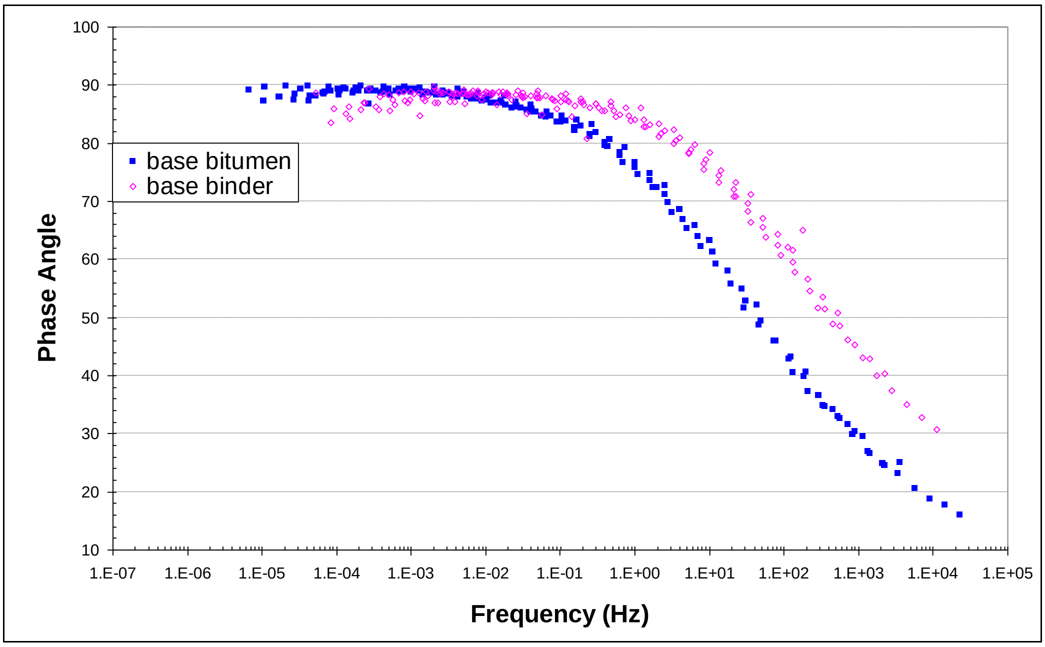


Figure 5.2b. Master curves of phase angle at 25ºC of base bitumen and base binder

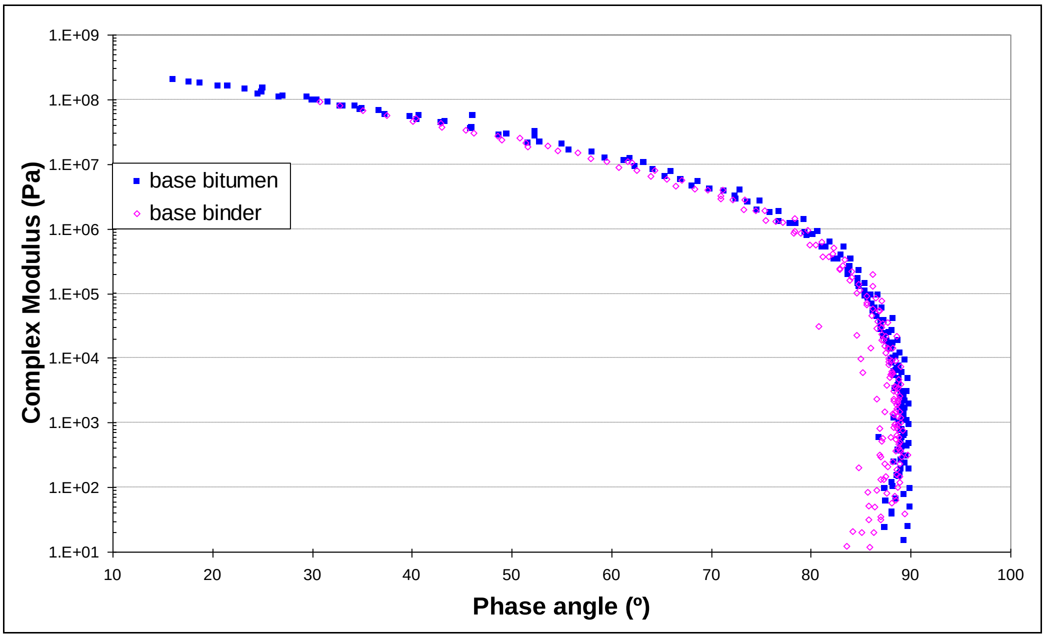


Figure 5.2c. Black diagram of base bitumen and base binder

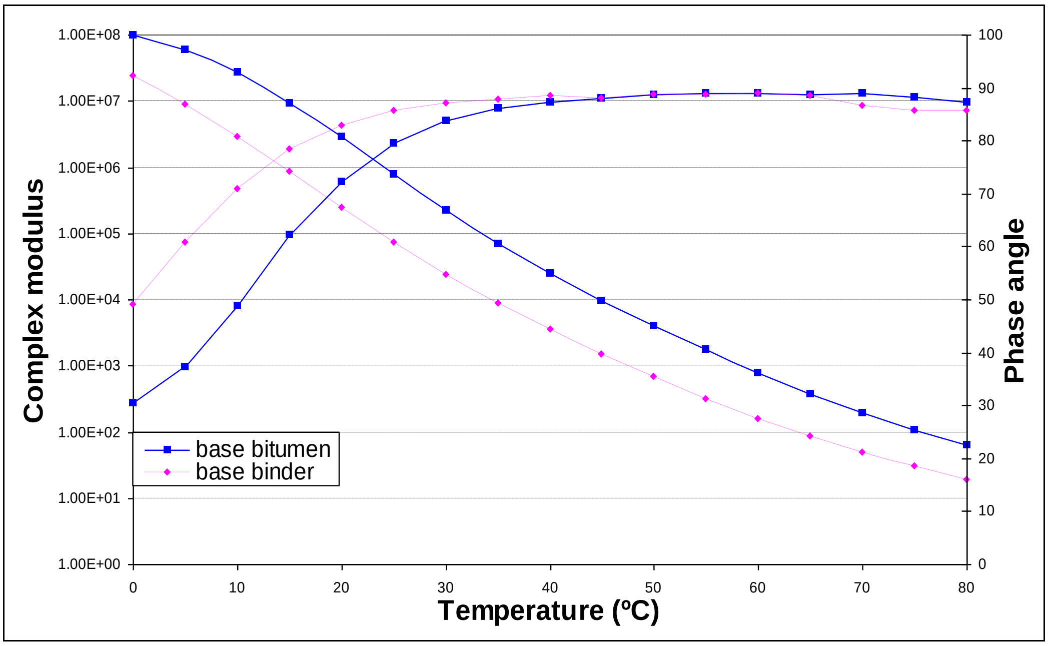


Figure 5.2d. Isochronal plots of complex modulus and phase angle at 0.4 Hz of base bitumen and base binder

The flux even changes the performance grade of the base binder which moves towards lower values but maintains the same performance temperature range (Table 5.7). Also the rheology of the base bitumen (Figs 5.2a to 5.2d) is influenced by the flux with a uniform shifting of complex modulus towards lower values and an increase in the viscous behaviour at high frequencies and low temperatures (higher values of phase angle).

The Black diagrams (Fig. 5.2c) show that even if the base binder contains flux, it has got the same black curve as that of the base bitumen with both binders being considered to be thermo-rheologically simple (Mezger, 2002). Considering that elastomers modify the bitumen mainly by increasing its performance at low frequencies and high temperatures (Airey, 2002), the results demonstrate how the addition of the flux is important to improve the performance of the base binder at high frequencies and low temperatures.

5.3.2 Modified bitumens

A laboratory blended tyre rubber modified bitumen (TR-MB) and a styrene butadiene styrene modified bitumen (SBS-MB) were tested and compared. The comparison was made in terms of rotational viscosity (Table 5.8), performance properties and rheological characteristics. To better understand the test results and properties, both the modified binders were subjected to a storage stability test and then compared in terms of softening point, polymer dispersion and rheological properties of their top and bottom sections after a period of hot storage.

Performance grade

The grading procedure for bitumens (AASHTO R 29-02) has been followed to find the performance grade (PG) of both the modified binders. The grading of the TR-MB encountered some problems due to the nature of the material. The flash point test was not completed because of the presence of too many fumes when high temperatures were reached (~290°C). Short-term ageing, with the use of the RTFO equipment, was impossible to perform due to, firstly, the rubber particles not allowing the binder to form a uniform film (coat) on the internal surface of the glass containers and, secondly, due to roll out problems. The Thin Film Oven test (AASHTO T 240) was therefore used to simulate the short term ageing of the TR-MB.

Table 5.8. Rotational viscosity of modified bitumens @ 100 and 160ºC

SBS-MB				
	Pa.s	spindle	RPM	% torque
(ASTM T316-04) @ 100ºC	10.74	34	5	89
(ASTM T316-04) @ 160ºC	0.61	34	20	20
TR-MB				
	Pa.s	spindle	RPM	% torque
(ASTM T316-04) @ 100ºC	19.95	29	4	64
(ASTM T316-04) @ 160ºC	1.5	34	20	55

The performance grade test results in Table 5.9 show that both modified binders have the same PG and obviously the same performance range of temperature. Comparing the performance of all the binders, the modified binders clearly show better performance and it is interesting to note how their high and low PG values are the same.

Table 5.9. Performance properties of SBS-MB and TR-MB

Aging states	AASHTO specifications	SBS-MB	TR-MB
unaged binder	Rotational Viscosity @ 135°C (Pa.s)	1.48	2.75
	G*/sin(delta) (kPa) *has to be ≥ 1.00*	@76°C / 2.26	@76°C / 0.99
RTFO/TFO[1] aged residue	G*/sin(delta) (kPa) *has to be ≥ 2.20*	@64°C / 2.90	@64°C / 2.60
RTFO/TFO[1] +PAV aged residue	G* x sin(delta) (kPa) *has to be ≤ 5000*	@16°C / 2841	@13°C / 4000
	Stiffness@ (MPa) *has to be < 300*	@-18°C / 183	@-18°C / 143
	m-value *has to be > 0.3*	@-18°C / 0.32	@-18°C / 0.38

[1] Thin Film Oven test (AASHTO T 240) was used to simulate the short term ageing of

the TR-MB		
Flash point (°C) *has to be > 230*	*> 300*	*> 230*
Mass loss after RTFO ageing *has to be < 1.00%*	0.15%	*not possible to perform*
Performance grade	PG 64 - 28	PG 64 - 28
Performance range of temperature	92°C	92°C

<u>*Rheological analysis*</u>

The frequency dependence of complex modulus and phase angle for the modified binders has been assessed in Figuress 5.3a-c by producing rheological master curves at a reference temperature of 25°C and black diagrams. Isochronal plots at low frequency (0.4Hz) were obtained to show the temperature dependency (Fig. 5.3d). A comparison regarding the complex modulus of both the SBS-MB and the TR-MB indicates that the behavior of the two binders is pretty similar over the range of considered frequencies (Fig. 5.3a) and temperatures (Fig. 5.3d). The SBS-MB performs better only at temperatures over 50°C, showing higher values of G*. It is interesting to note the inversions of the trends in the isochronal plots of the phase angle for both the modified binders (Fig. 5.3d). These are typical effects of the elastomers which increase the elastic response of both the modified binders (Airey, 2003). Making a comparison with the original base bitumen, the modified binders have a lower frequency and temperature susceptibility and on average have lower stiffness values. The polymer network effect is clearly noticeable in Figs 5.3b and 5.3d, which show unique phase angle curves due to the typical effect of the elastomers that significantly increase the elastic response of both the modified binders, especially at low frequencies and high temperatures (Airey, 2003). Moreover, the presence of a slight plateau on the complex modulus curves (Figs 5.3a and 5.3d) shows how the dominance of the polymer networks even improves the stiffness of the modified binders. An overall analysis of the graphs of Fig. 5.3 demonstrates how the laboratory blended TR-MB performs better rheologically than the pure bitumen and that it has got a comparable behavior with the commercially used SBS-MB over the considered range of frequencies and temperatures.

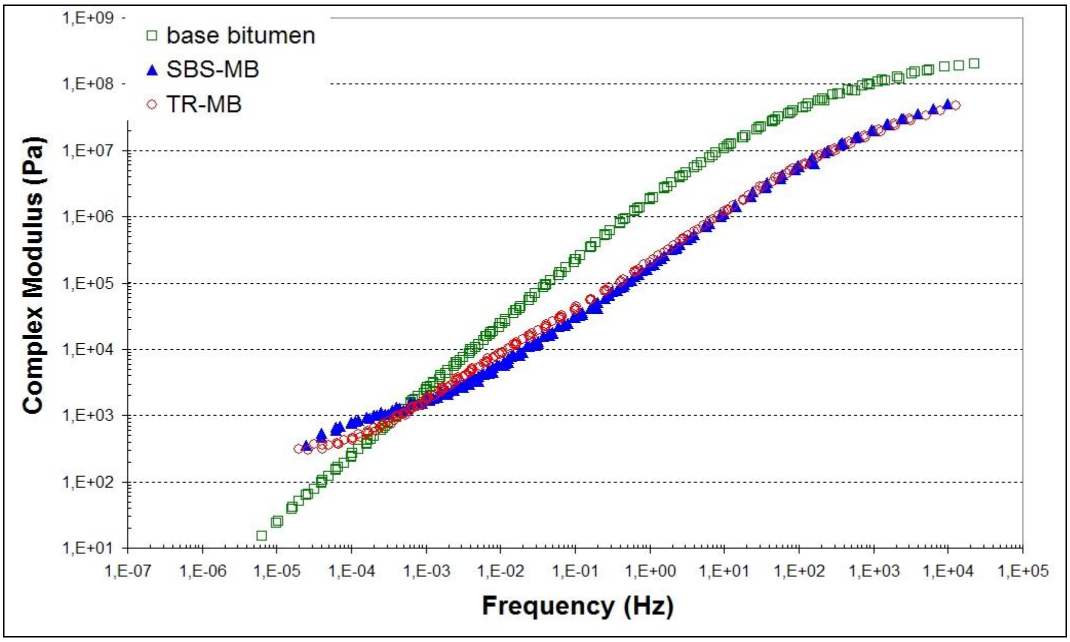


Figure 5.3a Master curves of complex modulus at 25ºC of the modified binders and base binder

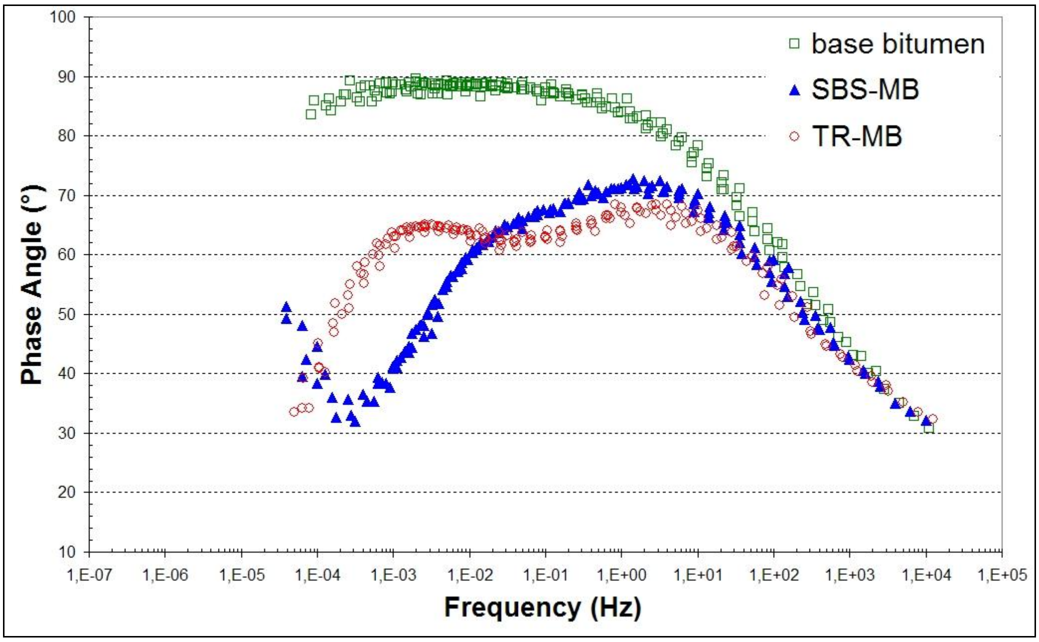


Figure 5.3b Master curves of phase angle at 25ºC of the modified binders and base binder

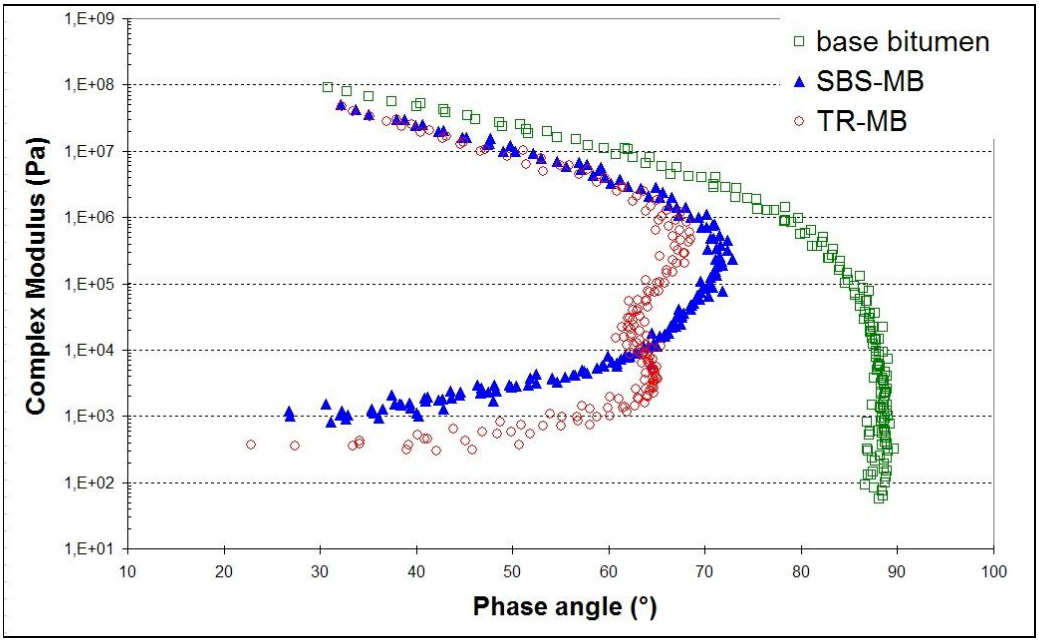


Figure 5.3c Black diagram of the modified binders

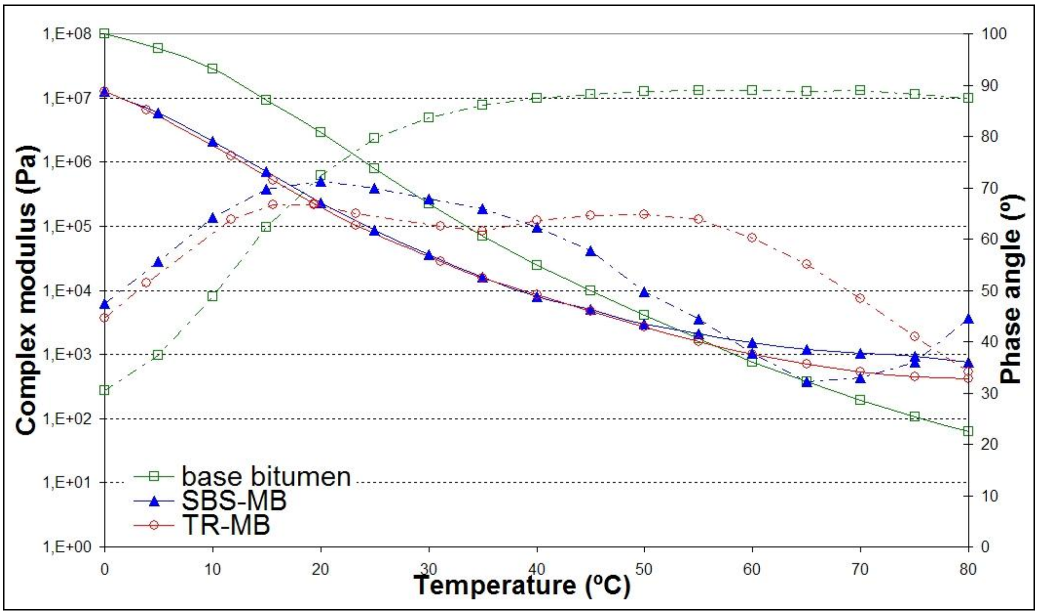


Figure 5.3d. Isochronal plots of complex modulus and phase angle at 0.4 Hz of the modified binders

The finger print of the materials as shown in the black diagrams (Fig. 5.3c) also confirms this fact (Airey, 2002). The only evidence of a difference with the SBS-MB is noticeable in the polymer network dominant area (low frequencies and high temperatures) where the better constitution of the SBS-MB makes it less susceptible to variations of frequency and temperature.

Storage stability analysis

Another fundamental requirement that has been evaluated for the laboratory blended TR-MB was the storage stability. In this analysis both the modified binders have been subjected to a hot storage test based on BS EN 13399, but modified due to the fast phase separation of the rubber.

The procedure consisted in filling six 500 mm beer cans (three for each binder) with pre-heated modified binder (180°C) and then putting them on a grille in the oven at 180°C. After two different periods (3 and 5 hours), one can for each binder was taken out from the oven and was cooled down to ambient (room) temperature before placing it into a freezer at -20°C. After that, the samples were cut into thirds and the top and bottom sections were saved to be further analysis by softening point tests, polymer dispersion analysis, and rheological characterization with DMA.

Table 5.10. Softening points before and after hot storage

Softening point (ASTM D36-95)	SBS-MB		TR-MB	
	top	bottom	top	bottom
	°C			
before hot storage	77.2		49.8	
after 1h of hot storage	78.8	77.2	46.0	51.6
after 3h of hot storage	77.6	77.0	45.2	53.0
after 5h of hot storage	76.8	77.6	46.6	54.6

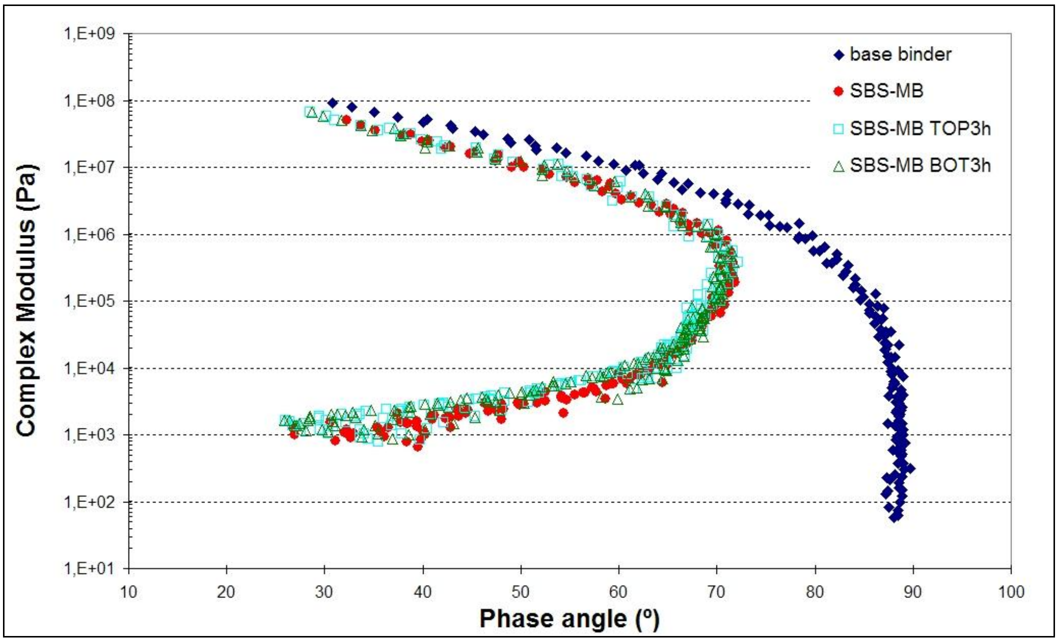


Figure 5.4a Black diagrams of base binder and SBS-MB before and after 3h of hot storage.

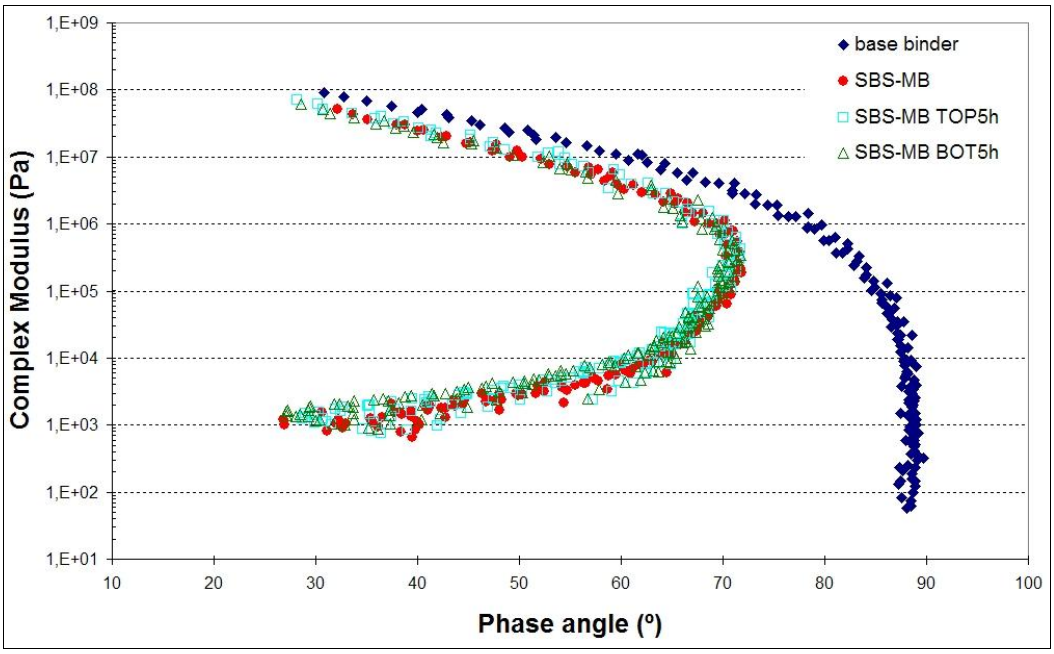
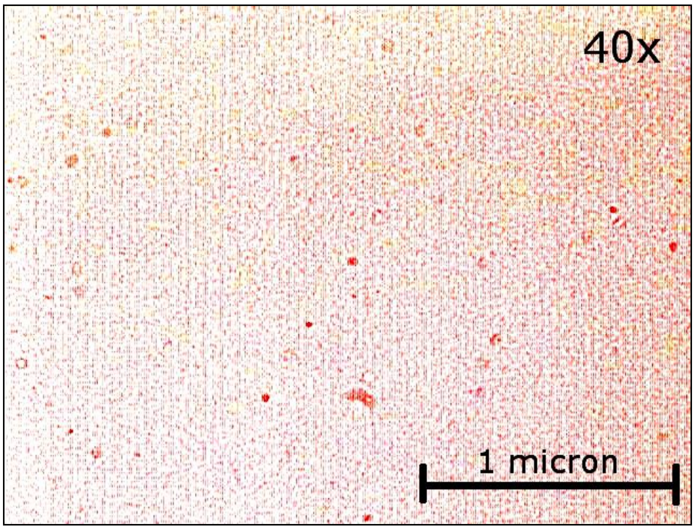


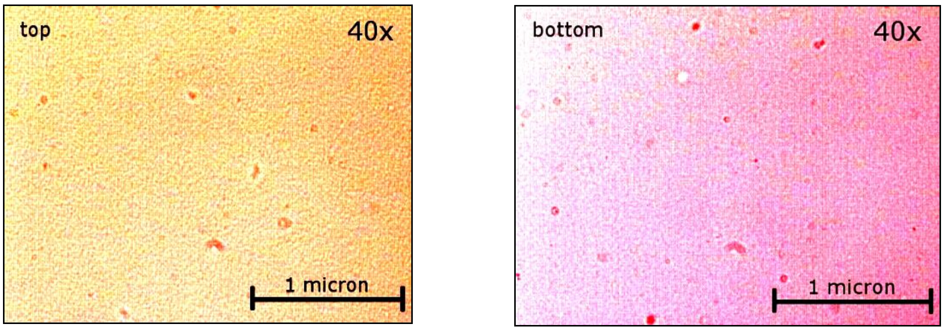
Figure 5.4b Black diagrams of base binder and SBS-MB before and after 5h of hot storage.

before hot storage: fine dispersion



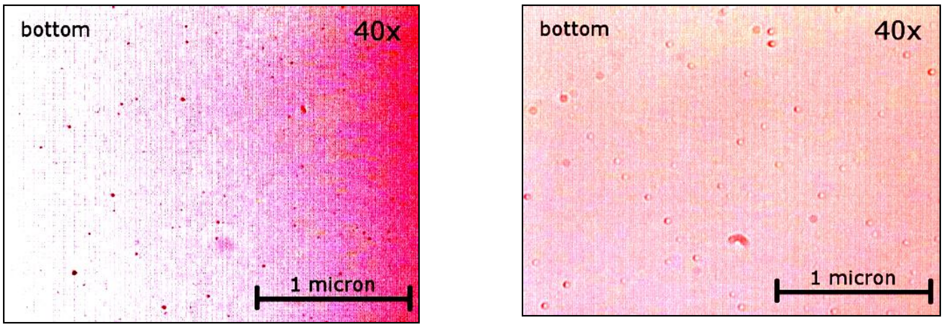
after 3h of hot storage

after 5h of hot storage



top: fine

top: fine



bottom: fine

bottom: fine

Figure 5.5 Fluorescent microscopic images of the top and bottom sections of the SBS-MB and polymer dispersion before and after hot storage

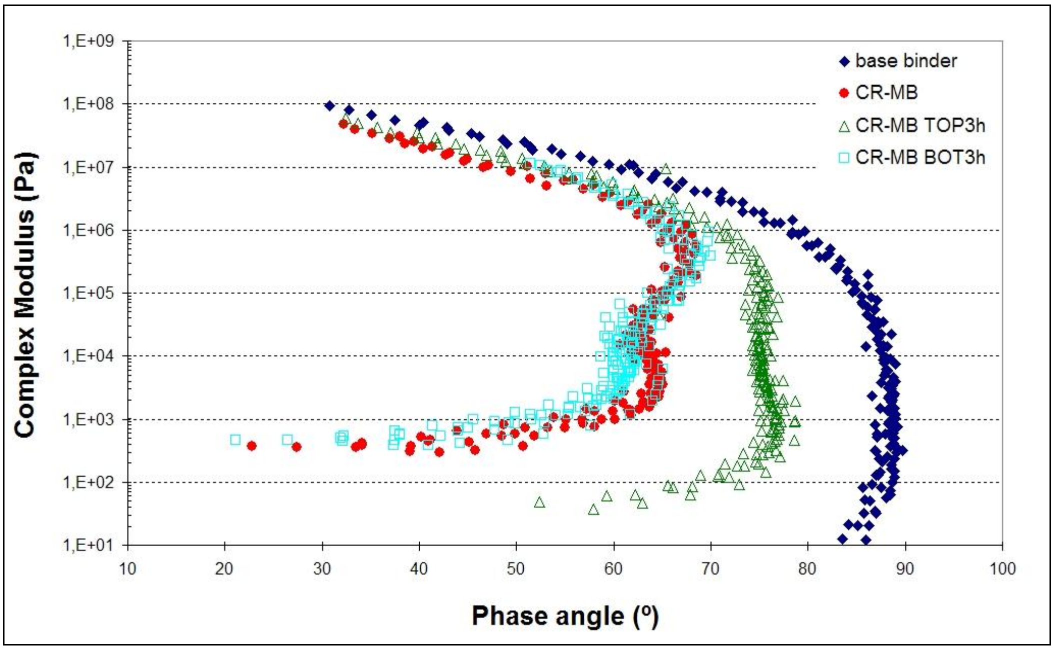


Figure 5.6a Black diagrams of base binder and TR-MB before and after 3h hot storage.

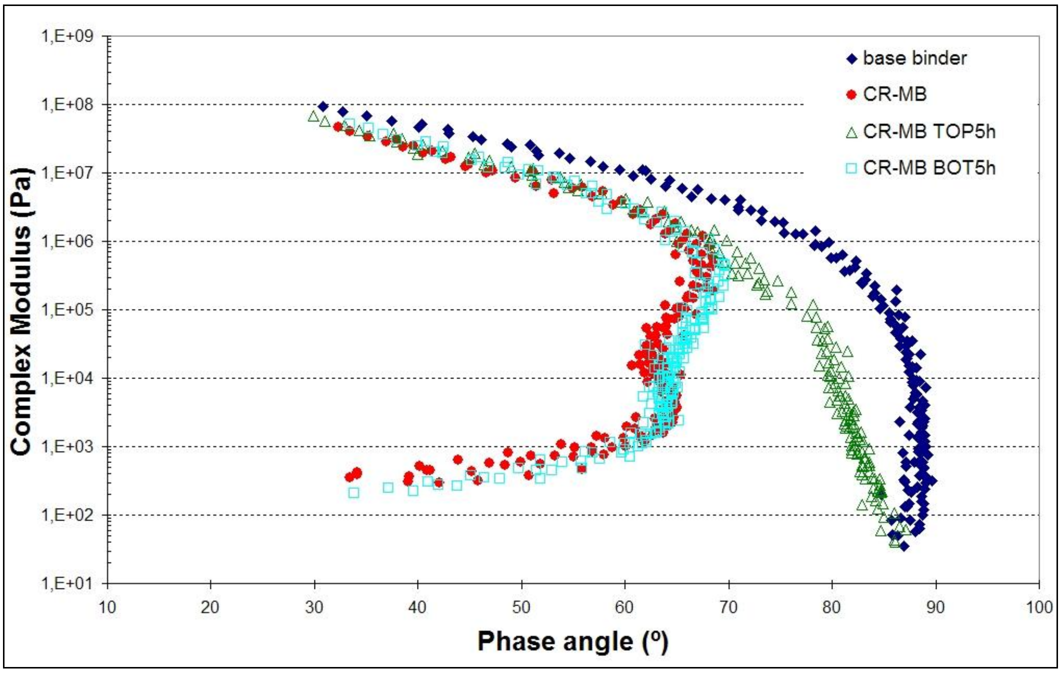


Figure 5.6b Black diagrams of base binder and TR-MB before and after 5h hot storage.

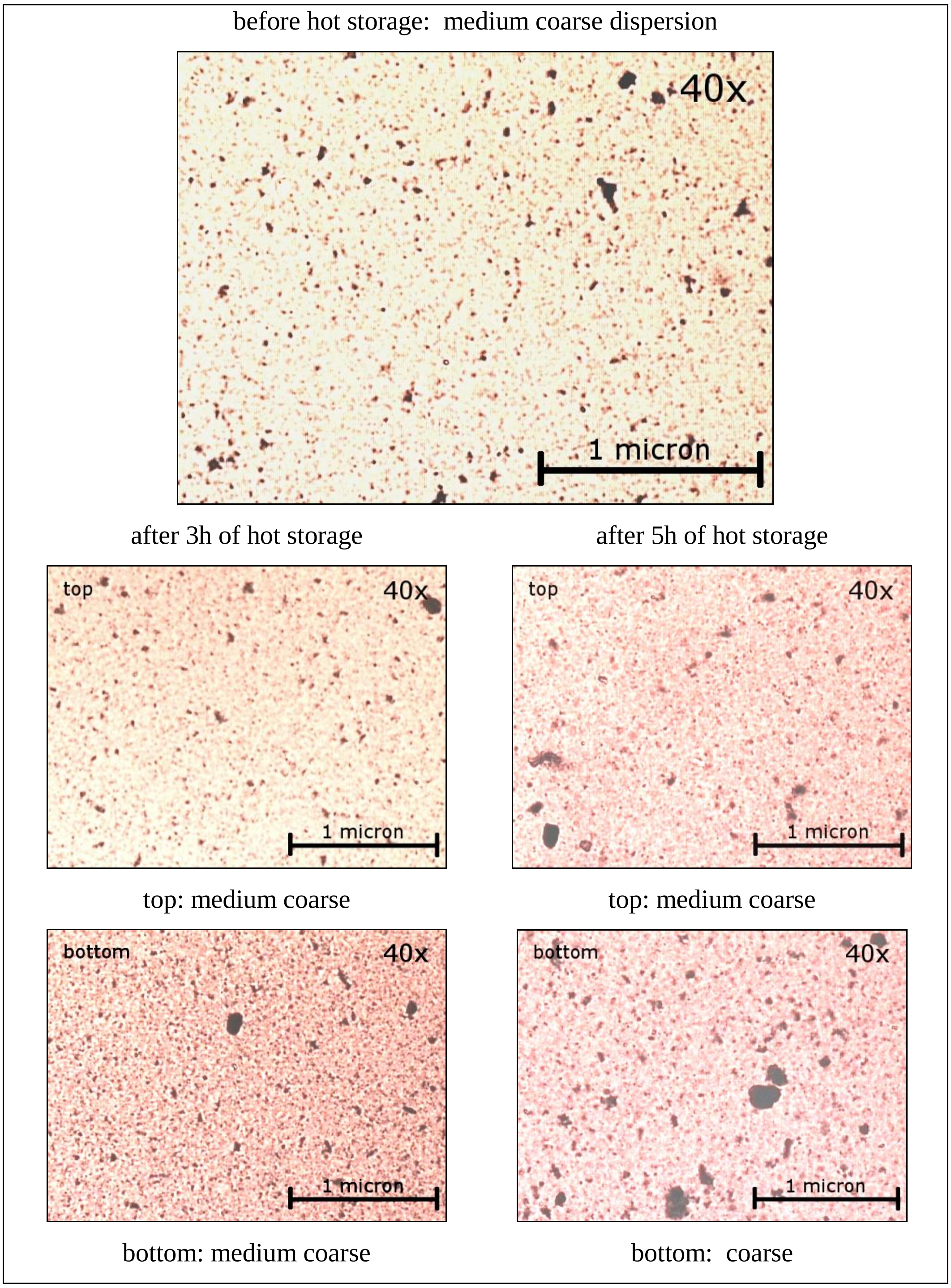


Figure 5.7 Fluorescent microscopic images of the top and bottom sections of the TR-MB showing the polymer dispersion before and after hot storage

In order to have an easy determinable parameter which could give a value of the storage stability, softening points of both the modified binders have been determined for the top and bottom sections at three different periods of storage (Table 5.10). Softening point results show that the phase separation of the rubber starts to be relevant after three hours and at the same time have confirmed the greater stability of the SBS-MB. As found by other researchers (Lu & Isacsson, 1997) the use of the softening point to evaluate the storage stability of modified binders may be inadequate. Therefore, to have more information and more accuracy, a polymer dispersion analysis (PDA) and a rheological characterization of the top and bottom sections of the modified binders, after three and five hours of hot storage, were done. PDA was performed using fluorescence microscopy which provided the images shown in Figures 5.5 and 5.7. These, show, with a magnification of forty times, the dispersion of the SBS and the tyre rubber crumbs within the binder, before and after periods of storage. Lastly, the DMA was performed by frequency sweep tests at the same conditions shown in Section 5.2.5. The results of these analyses confirm, as expected, that the SBS-MB has good stability showing no differences in terms of polymer dispersion between the top and the bottom sections at both periods of storage. It even shows a stable rheology (Fig. 5.4a,b) as well as having a constant softening point (Table 5.10).

Table 5.11. Separation index (Lu et all, 1999) of the modified binders after hot storage periods

	complex modulus (G*) at 25°C and 10 rad/s					I_s @ 3h	I_s @ 5h
	original sample	after 3h hot storage		after 5h hot storage			
		top	bottom	top	bottom		
	Pa						
SBS-MB	2.61E+05	1.51E+06	1.51E+06	1.57E+06	1.36E+06	0,00	0,05
TR-MB	2.00E+05	1.23E+06	9.35E+05	1.45E+06	1.08E+06	-0,09	0,18

Instead, the TR-MB begins to have a relevant phase separation already after three hours of hot storage. As shown in Figure 7 the top section has a fine medium dispersion of rubber which tends to settle toward the bottom.Comparing the images in Figs 5 and 7, TR-MB shows lots of fine rubber but also some big chunks. What it is suggested by the variability of the softening points has been confirmed by the rheological characterization.

The black diagrams of Fig. 5.6 show how the finger print of the top section of TR-MB is a lot different than the bottom one. It is interesting how with increasing storage time the top section tends to have a rheology closer to the base binder than the modified binder, while the bottom section become stiffer and more elastic. To evaluate the storage stability of the modified binders, a separation index, I_s, defined as was calculated (Lu et al, 1999):

$$I_s = \log \frac{G^*_{bottom}}{G^*_{top}}$$

Since G* is temperature dependent, the values of the index are influenced by test conditions (Lu & Isacsson, 1997). I_s values in Table 5.11 were obtained at 25°C and 10 rad/s. Modified bitumens without phase separation during hot storage show I_s values close zero. Table 5.10 clearly shows the difference in stability between the modified bitumens.

5.4 Summary of results

The Superpave performance grade and the detailed rheological properties of a Tyre-Rubber Modified Bitumen (TR-MB) have been compared with those of a commercially available SBS Polymer Modified Bitumen (SBS-MB). Both modified binders have been produced from the same base binder consisting of a standard 40/60 penetration grade bitumen mixed with an extender oil. The results from the study have shown that both modified binders have the same PG and very similar rheological properties expected of an elastomeric polymer modified bitumen. Both modified binders have shown a considerable improvement in terms of their rheological and physical properties compared to the base 40/60 pen bitumen and the softer base binder (base bitumen plus flux oil). However, although TR-MB shows a comparable behavior with that of the commercial used SBS-MB over a wide range of frequencies and temperatures, concerns still exist over the storage stability of the crumb tyre rubber blend with both rheological and morphological evidence of separation occurring after 5 hours of high temperature storage.

6. Desirable base binder properties for modification with tyre rubber

6.1 Introduction

The asphalt rubber blend properties are strongly related to its base components properties. The base bitumen composition is considered as a key factor influencing the final rheological properties of asphalt rubber binder.

This section compares the physical, rheological and performance properties of a series of tyre rubber-modified binders produced using a combination of different base bitumens, and an oil extender to improve the aromatic content. The bitumen testing varies from standard empirical tests, such as the penetration and softening point tests, to more detailed rheological tests using a dynamic shear rheometer. In addition to the rheological properties, the storage stability of the tire rubber-modified asphalt binders has been assessed. Viscoelastic properties measurements demonstrate that base binder composition should be selected carefully to achieve a good compromise between a sufficient rubber swelling and a reasonable properties and stability of the final binder. (Airey 2002, Ould-Henia et al. 2008)

6.2 Experimental programme

6.2.1 Materials

Two different base bitumens, a PG 64-16 (bitumen A) and a PG 64-22 (bitumen B), were used with and without an oil extender (flux) to produce four different tyre rubber-modified asphalt binders (TR-MB). The TR-MBs were blended using a Silverson high shear laboratory mill to mix the base binders with fine tyre rubber crumbs obtained from used tyres. Physical, chemical and performance properties of the base bitumens (with and without flux) are reported in Section 6.4. Table 5.1 reports the characteristics of the tyre rubber crumbs as received by the provider. Table 5.2 and Figure 5.2 show the results of the sieving procedure and the portion of rubber used in this study denominated as “fine”.

The following binders have therefore been incorporated into this study:
bitumen A: PG 64-16 straight run bitumen
bitumen B: PG 64-22 straight run bitumen
binder Af: blend of 92.5% of PG 64-16 straight run bitumen and 7.5% of flux
binder Bf: blend of 92.5% of PG 64-22 straight run bitumen and 7.5% of flux
TR-MB A: tyre rubber-modified asphalt binder produced as 85% of bitumen A and 15% of tyre rubber crumbs
TR-MB B: tyre rubber-modified asphalt binder produced as 85% of bitumen B and 15% of tyre rubber crumbs
TR-MB Af: tyre rubber-modified asphalt binder produced as 85% of base binder Af and 15% of tyre rubber crumbs
TR-MB Bf: tyre rubber-modified asphalt binder produced as 85% of base binder Bf and 15% of tyre rubber crumbs

All the binders were tested in their unaged (virgin) condition and after being subjected to two laboratories ageing procedures:
Short-term laboratory ageing using the Rolling Thin Film Oven test (RTFOT) according to AASHTO T 240. Long-term laboratory ageing using a Pressurised Ageing Vessel (PAV) according to AASHTO R 28. Due to practical concerns, the short term ageing of the modified bitumens was performed by using the Thin Film Oven test (TFOT) according to AASHTO T 240.

6.2.2 Blending protocol

The blending of rubber and bituminous binders was carried out using the following protocol:

1. The required amount of bitumen was heated at 180°C in the oven and then transferred to a hot plate at the same temperature.
2. High shear mixing up to 2000 rpm was applied for the first 10 minutes while the flux (only for binders Af and Bf and TR-MB Af and Bf) and then only the fine portion of the rubber was feed into the bitumen.
3. Time was allowed for the temperature to stabilise at 180°C.
4. Once the temperature reached 180°C, blending time was noted and mixing undertaken at 1000 rpm for one hour.

Tables 6.1 and 6.2 summarise the mixing parameters used in the blending procedure.

Table 6.1. Blending protocol for TR-MB A and TR-MB B

mass of bitumen (85%)	mass of flux (0%)	mass of rubber (15%)	rubber size	total weight	mixing time	mixing speed	mixing temp.
g	g	g	mm	g	min	rpm	°C
1700	0	300	0-0.5	2000	60	1000	180

Table 6.2. Blending protocol for TR-MB Af and TR-MB Bf

mass of bitumen (78.65%)	mass of flux (6.35%)	mass of rubber (15%)	rubber size	total weight	mixing time	mixing speed	mixing temp.
g	g	g	mm	g	min	rpm	°C
1572.5	127.5	300	0-0.5	2000	60	1000	180

6.2.3 Physical, chemical and mechanical characterization

The first part of the programme consisted of characterising the bitumens and base binders in terms of their physical and chemical properties and to quantify the effect of the oil extender. The physical classification consisted of the following tests: penetration (ASTM D5), softening point (ASTM D36-95), Fraass breaking point (IP 80), ductility (10ºC, ASTM D113) and rotational viscosity at 100 and 160ºC (ASTM T316-04). In order to have an idea of the chemical composition of the binders, the asphaltenes content according to ASTM D6560 was measured.

The second part of the programme consisted of comparing the different binders in terms of their performance grade and rheological characteristics. Performance grading procedure and rheological characterization were performed according to the conditions reported in Section 5.2.4 and 5.2.5.

Finally, in the third part of the programme, the storage stability of the binders was evaluated using softening point (ASTM D36-95) and polymer dispersion of the elastomer in the binders.

6.3 Results and discussion

6.3.1 Base bitumens

Two base bitumens were available and both have been characterized in terms of their physical, chemical and performance properties. The two bitumens have similar physical properties, but differ chemically in terms of their asphaltenes content (Table 6.3). This difference in chemical composition potentially has an effect on the modification process when they are mixed with polymers. In general a smaller percentage of asphaltenes means a lower Colloidal Index value that leads to a system with a higher degree of solvency for the polymers (Airey, 2003).

The rheological properties of the two base bitumens in terms of master curves, black diagrams and isochronal plots are shown in Figure 6.1a-c.

Although penetration and softening point for the two base bitumens are similar, their detailed rheological properties shown in Figures 6.1a-c indicate differences in their

Table 6.3. Properties of base bitumen A and base bitumen B

	bitumen A	bitumen B
Penetration (ASTM D5)	42 dmm	54 dmm
Softening Point (ASTM D36-95)	51ºC	52.2 ºC
Fraass breaking point (IP 80)	0ºC	-2 ºC
Ductility (ASTM D113)	1000 mm	1000 mm
Rotational Viscosity @ 100ºC (ASTM T316-04)	3.86 Pa.s	5.13 Pa.s
Rotational Viscosity @ 160ºC (ASTM T316-04)	0.12 Pa.s	0.19 Pa.s
Asphaltenes content	3.4%	16.7%

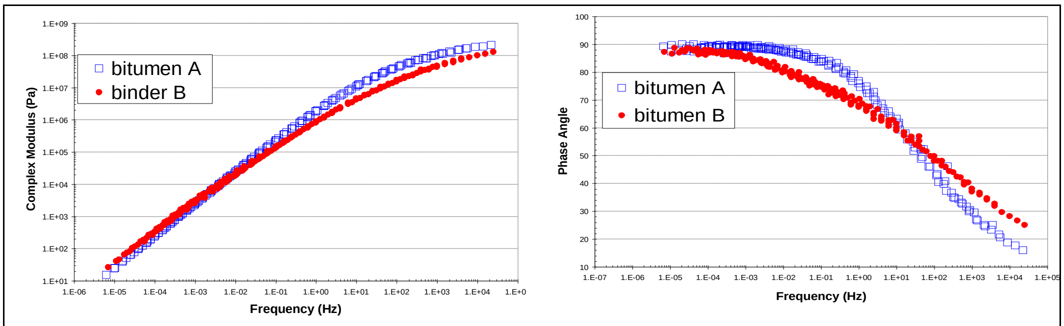


Figure 6.1a. Master curves of $|G^*|$ and δ at 25 ºC for the base bitumens

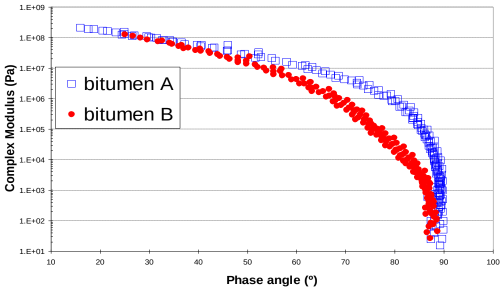


Figure 6.1b. Black diagram for the base bitumens

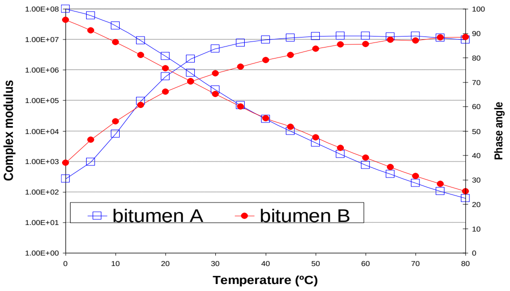


Figure 6.1c. Isochronal plots of $|G^*|$ and δ at 0.4 Hz for the base bitumens

more detailed rheological properties. Bitumen "A" has a higher complex modulus at high frequencies although bitumen "B" tends to be less temperature and frequency susceptible. Both bitumens are thermorheologically simple as shown by their smooth curves in both the master curves and Black diagram (Mezger, 2002). The higher asphaltenes content of bitumen “B” results in a shifting of the viscoelastic balance with a reduction in phase angles (decreasing viscous response/increasing elastic response) compared to the low asphaltenes content bitumen “A”.

6.3.2 Base binders

As seen in the literature review (§ 4.3.4), it is common practice to add an oil extender into the blend to improve the solvating power of the base bitumen and increase the digestion of the tyre rubber crumbs within the bitumen. A blend of 92.5% base bitumen and 7.5% of oil extender (flux) was made for each bitumen obtaining “base binder Af” and “base binder Bf”.

Table 6.4. Physical properties of base binder Af and base binder Bf

	binder Af	binder Bf
Penetration (ASTM D5)	136 dmm	157 dmm
Softening Point (ASTM D36-95)	39.8ºC	40.3ºC
Fraass breaking point (IP 80)	-14ºC	-17ºC
Ductility (ASTM D113)	1000 mm	1000 mm
Rotational Viscosity @ 100ºC (ASTM T316-04)	1.57 Pa.s	2.14 Pa.s
Rotational Viscosity @ 160ºC (ASTM T316-04)	0.07 Pa.s	0.13 Pa.s
Asphaltenes content	3.6%	16.7%

As it is noticeable from Tables 6.3 and 6.4 the addition of the flux does not affect the asphaltenes content. Analysing the results, it is evident that the oil extender affects the base binder by softening it and thereby enhancing its low temperatures properties. Tables 6.4 and 6.5 show how physical properties are influenced by the flux with an increase in the cracking resistance of both binders at low temperatures, as shown by the lower Fraass breaking point temperature, and a softening of the binders at high temperatures, as shown by a decrease in softening point and reduced viscosity. The modification in the performance properties have been investigated and the results in Tables 6.5 and 6.9 show

Table 6.5. Performance grading of bitumen A and binder Af

Aging states	AASHTO specifications	bitumen A	binder Af
Unaged binder	Rotational Viscosity (Pa.s)	@135°C/ 0.40	@135°C/ 0.20
	G*/sin(delta) (kPa) > 1.00	@64°C/ 1.41	@52°C / 1.28
RTFO aged residue	G*/sin(delta) (kPa) > 2.20	@64°C/ 2.90	@52°C / 3.51
RTFO+PAV aged residue	G* x sin(delta) (kPa) < 5000	@28°C/ 4790	@16°C / 4970
	Stiffness@ (MPa) < 300	@-6°C / 218	@-18°C/ 275
	m-value has to be > 0.3	@-6°C/ 0.36	@-18°C/ 0.33
Flash point (°C) has to be > 230		> 300	> 300
Mass loss after RTFO ageing has to be< 1.0%		0.15%	0.09%
Performance grade		PG 64 - 16	PG 52 – 28
Performance temperature range		80°C	80°C

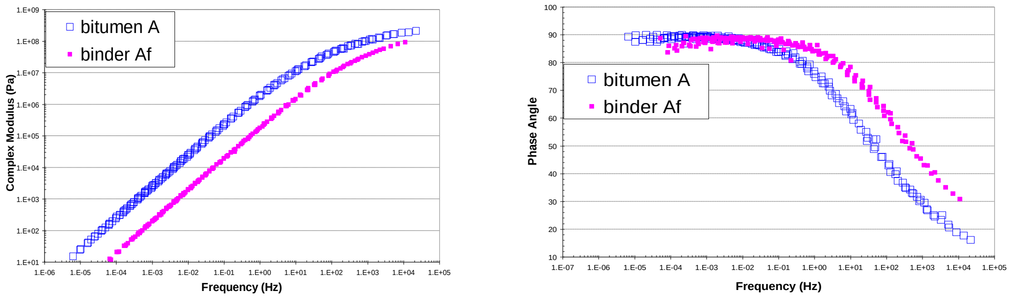


Figure 6.2a. Master curves of |G*| and δ at 25 ºC for bitumen A and binder Af

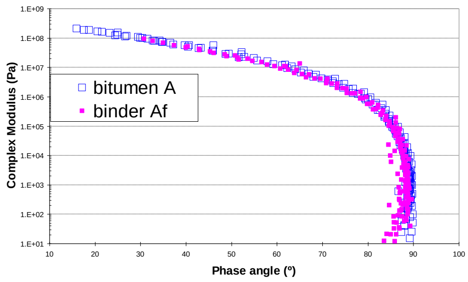


Figure 6.2b. Black diagram for bitumen A and binder Af

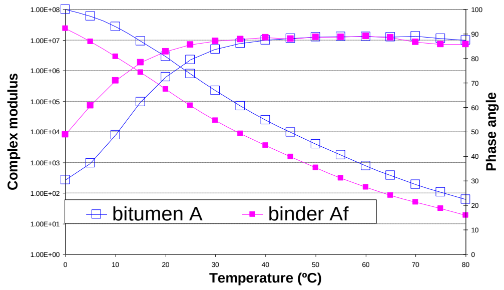


Figure 6.2c. Isochronal plots of G* and δ at 0.4 Hz for bitumen A and binder Af

Table 6.6. Performance grading of "bitumen B" and "binder Bf"

Aging states	AASHTO specifications	bitumen B	binder Bf
Unaged binder	Rotational Viscosity (Pa.s)	@135°C/ 0.45	@135°C/ 0.23
	G*/sin(delta) (kPa) > 1.00	@70°C/ 1.05	@58°C / 1.47
RTFO aged residue	G*/sin(delta) (kPa) > 2.20	@64°C/ 4.56	@58°C / 3.05
RTFO+PAV aged residue	G* x sin(delta) (kPa) < 5000	@22°C/ 5317	@16°C / 4180
	Stiffness@ (MPa) < 300	@-12°C / 225	@-18°C/ 130
	m-value has to be > 0.3	@-12°C/ 0.34	@-18°C/ 0.38
Flash point (°C) has to be > 230		> 300	> 300
Mass loss after RTFO ageing has to be< 1.0%		0.07%	0.01%
Performance grade		PG 64 - 22	PG 58 - 28
Performance temperature range		86°C	86°C

that in both cases the base bitumen changes its performance grade moving towards lower values but maintains the same performance temperature range.

It should be noted that this shifting towards lower performance grade values, due to the oil extender, has a greater effect on the bitumen with the lower asphaltenes content (bitumen A).

The softening of the base bitumens throught the addition of the flux is also seen in the detailed rheological analysis for both base bitumens and binders in Figures 6.1a-c and 6.2a-c. The results show a uniform shifting of the complex modulus towards lower values and an increase in the viscous behaviour at high frequencies and low temperatures (higher values of phase angle). The Black diagrams (Figures 6.1c and 6.2c) show that also if base binder contains flux, it still has the same black curve as that of the base bitumen, (Mezger, 2002).

Considering that elastomers mainly modify the bitumen by increasing its performance at low frequencies and high temperatures (Airey, 2002), the results demonstrate how the addition of the flux is important to improve the performance of the base binder at high frequencies and low temperatures.

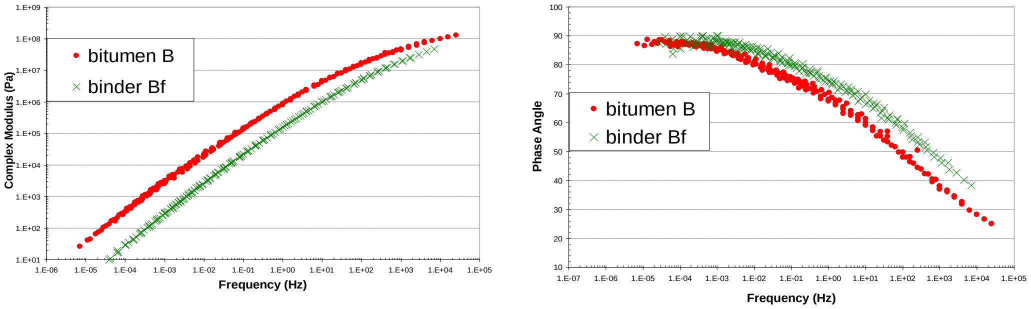


Figure 6.3a. Master curves of |G*| and δ at 25 ºC for bitumen B and binder Bf

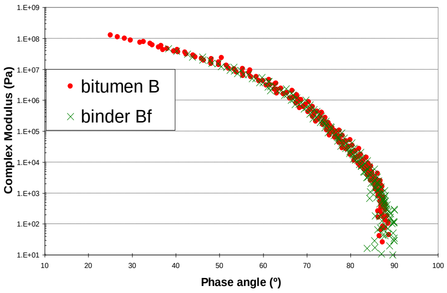


Figure 6.3b. Black diagram for bitumen B and binder Bf

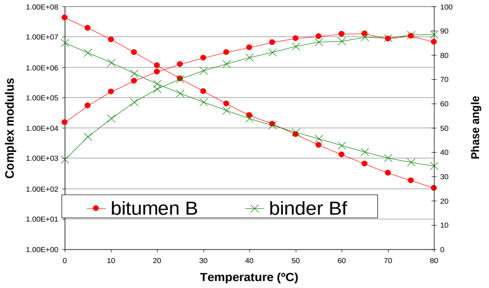


Figure 6.3c. Isochronal plots of |G*| and δ at 0.4 Hz for bitumen B and binder Bf

6.3.3 Modified bitumens

Four laboratory blended tyre rubber-modified asphalt binders (TR-MB), produced using the same kind and amount of rubber but different base binders, were tested and compared. The comparison was made in terms of rotational viscosity (Table 6.7), performance properties and rheological characteristics. Furthermore, to better understand the test results and properties, all the modified binders were subjected to a storage stability test and then compared in terms of softening point, polymer dispersion and rheological properties of their top and bottom sections after a period of hot storage.

Table 6.7. Rotational viscosity @ 100 and 160ºC

Rotational Viscosity (ASTM T316-04)	@ 100 ºC	@ 160 ºC
	Pa.s	
TR-MB A	45.87	2.02
TR-MB Af	19.85	1.46
TR-MB B	49.44	2.40
TR-MB Bf	24.18	2.01

Superpave Performance grade

The grading procedure for bitumens (AASHTO R 29-02) has been followed to find the performance grade (PG) of all the modified bitumens. Short-term ageing using the RTFO equipment was impossible to perform, firstly, due to the rubber particles not allowing the binder to form a uniform film (coat) on the internal surface of the glass containers and, secondly, due to "roll out" problems. The Thin Film Oven test (AASHTO T 240) was therefore used to simulate the short-term ageing of the TR-MB. The performance grade test results in Tables 6.8 and 6.9 show three significant results. Firstly, all the TR-MBs have got a better performance temperature range in comparison with the base bitumen. Secondly, TR-MBs obtained without adding flux perform better at high temperature and show a wider performance temperature range, but have a higher viscosity at operating temperatures (135°C). Finally, comparing the results between the TR-MBs originated from the two different base bitumens, it is possible to notice that after modification with tyre rubber, bitumen B is the one which demonstrates the biggest improvements (Figure 6.3d).

6.3.4 Rheological analysis

The frequency dependence of complex modulus and phase angle for the modified bitumens has been assessed in Figures 6.5, 6.5 and 6.6 by producing rheological master curves at a reference temperature of 25°C and black diagrams. Isochronal plots at low frequency (0.4Hz) were obtained to show the temperature dependency (Fig. 6.7).

Table 6.8. Performance grading of “TR-MAB A” and “TR-MAB Af”

Aging states	AASHTO specifications	bitumen B	binder Bf
Unaged binder	Rotational Viscosity (Pa.s)	@135°C/ 4.41	@135°C/ 2.75
	G*/sin(delta) (kPa) > 1.00	@76°C / 1.12	@76°C / 0.99
TFO[1] aged residue	G*/sin(delta) (kPa) > 2.20	@76°C / 2.38	@64°C / 2.60
TFO[1]+PAV aged residue	G*sin(delta) (kPa) < 5000	@22°C / 4670	@13°C / 4000
	Stiffness@ (MPa) < 300	@-12°C / 181	@-18°C / 143
	m-value has to be > 0.3	@-12°C / 0.35	@-18°C / 0.38

1: Thin Film Oven test (AASHTO T 240) was used to simulate the short-term ageing of the TR-MAB

Flash point (°C) has to be > 230	> 230	> 230
Mass loss after RTFO ageing has to be< 1.0%	*not possible*	*not possible*
Performance grade	PG 76 - 22	PG 64 - 28
Performance temperature range	98°C	92°C

Table 6.9. Performance grading of “TR-MAB B” and “TR-MAB Bf”

Aging states	AASHTO specifications	bitumen B	binder Bf
Unaged binder	Rotational Viscosity (Pa.s)	@135°C/ 6.45	@135°C/ 3.83
	G*/sin(delta) (kPa) > 1.00	@88°C / 1.24	@76°C / 1.83
TFO[1] aged residue	G*/sin(delta) (kPa) > 2.20	@88°C / 2.60	@76°C / 2.96
TFO[1]+PAV aged residue	G*sin(delta) (kPa) < 5000	@19°C / 4610	@10°C / 3720
	Stiffness@ (MPa) < 300	@-18°C / 183	@-24°C/ 150
	m-value has to be > 0.3	@-18°C / 0.33	@-24°C/ 0.34

1: Thin Film Oven test (AASHTO T 240) was used to simulate the short-term ageing of the TR-MAB

Flash point (°C) has to be > 230	> 300	> 230
Mass loss after RTFO ageing has to be< 1.0%	*not possible*	*not possible*
Performance grade	PG 88 - 28	PG 76 - 34
Performance temperature range	116°C	110°C

By comparing the obtained TR-MBs and the respective original base bitumens, the following results:

The modified binders have a lower frequency and temperature susceptibility. Results in Figures 6.4, 6.5, 6.6 and 6.7 indicate that this is true for both kinds of modification, with or without oil extender, but with the softer base binder (with flux) showing, on average, lower stiffness values for the TR-MB binders. The polymer network effect is clearly noticeable in Figures 6.5 and 6.7 which show unique phase angle curves due to the typical effect of the elastomers that significantly increase the elastic response of both modified binders especially at low frequencies and high temperatures (§ 4.2.5).

Moreover, the presence of a slight plateau on the complex modulus curves (Figures 6.4 and 6.7) shows how the dominance of the polymer networks improves the stiffness of the modified binders. An overall analysis of the graphs shown demonstrates that laboratory blended TR-MBs perform better rheologically, than their original base bitumens, showing a lower temperature and frequency susceptibility. The graphs show also the effect of the oil extender on the TR-MBs as it does with the base binder as explained in Section 6.3.2. The addition of the oil extender for the TR-MBs does not significantly change the shape of the black diagrams as shown in Figure 6.6.

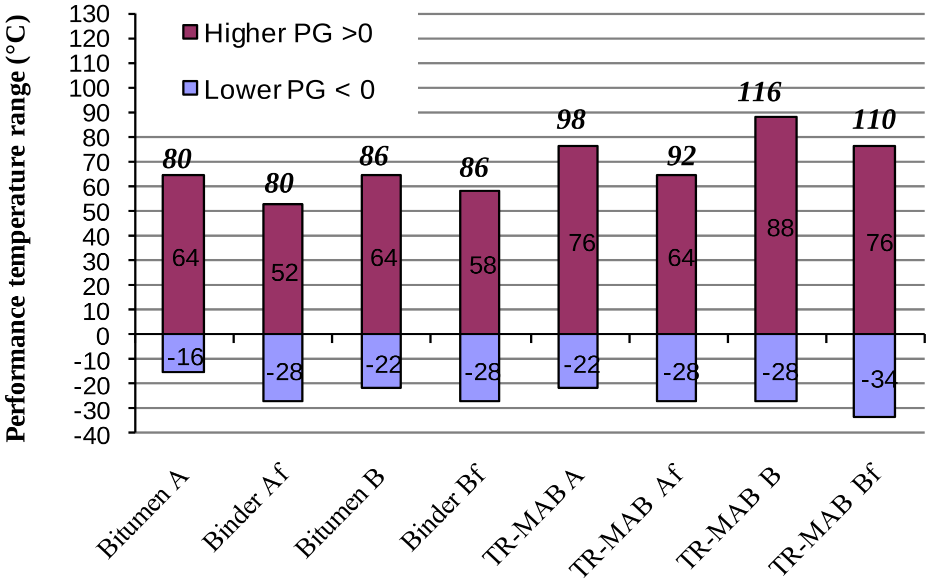


Figure 6.3d. Overview of the performance properties of all the binders

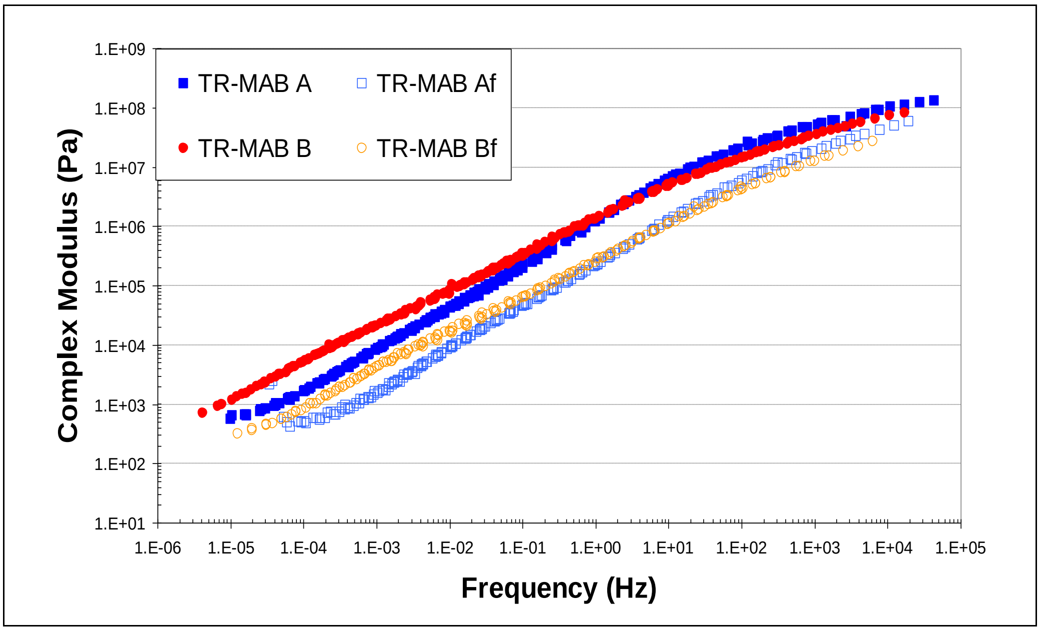


Figure 6.4. Master curves of complex modulus at 25 ºC for all the TR-MBs

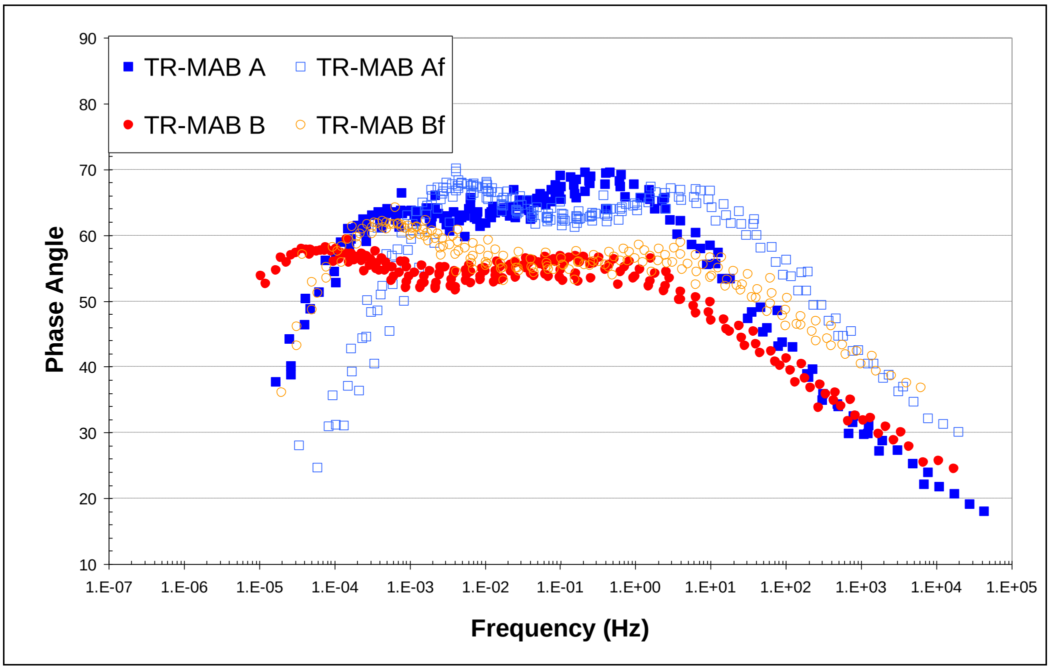


Figure 6.5. Master curves of phase angle at 25 ºC for all the TR-MBs

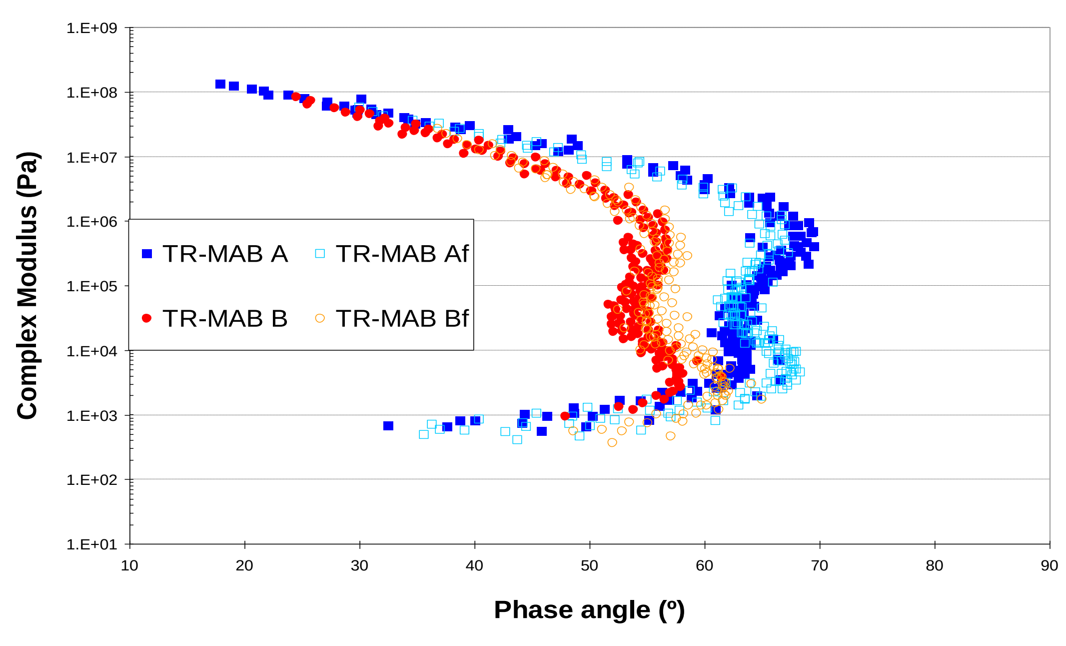


Figure 6.6. Black diagrams for all the TR-MBs

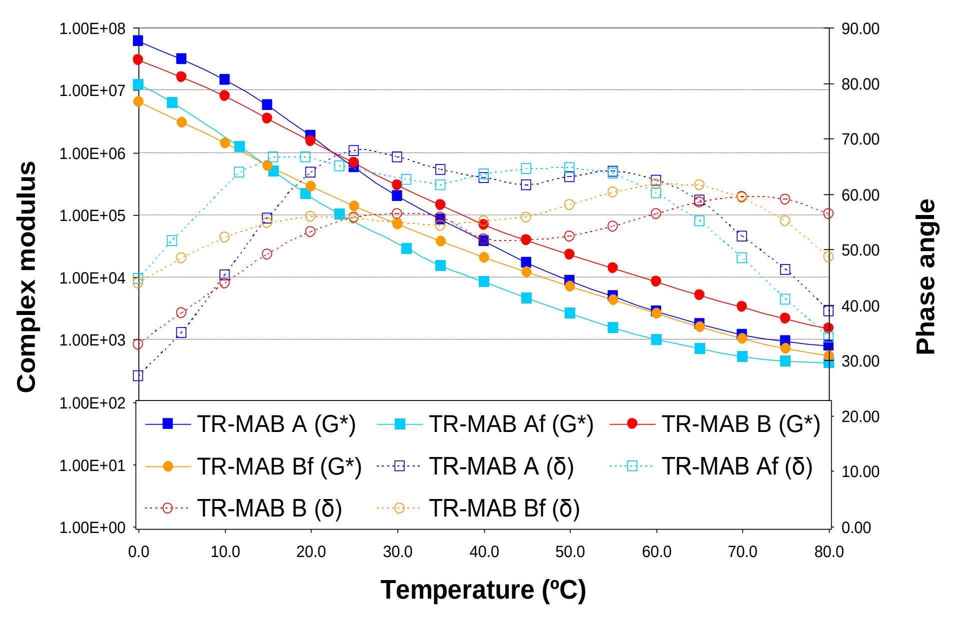


Figure. 6.7. Isochronal plots of complex modulus and phase angle at 0.4 Hz for all the TR-MBs

Further information comes from the comparison between the rheological properties of all the TR-MBs (Figures 6.4 to 6.7).

Comparing the TR-MBs originated from bitumen B with the correspondent TR-MBs created from bitumen A, it is possible to notice that modified binders obtained using the higher asphaltenes content base bitumen (bitumen B) are, on average, stiffer (higher G* values) and more elastic (lower phase angles) over the range of considered frequencies and temperatures (Figures 6.4 and 6.5).

At low frequencies and high temperatures, they show slight plateaus on the complex modulus curves and isochronal plots (Figures 7.9 and 7.12) and have much lower values of phase angle (Figure 7.10). These are typical effects seen for elastomers which tend to increase the elastic response of the modified binders (§ 4.2.5).

6.3.5 Storage stability analysis

Another fundamental requirement that has been evaluated for the laboratory blended TR-MBs was their storage stability. In this analysis all the modified bitumens have been subjected to a hot storage test based on BS EN 13399, but modified due to the fast phase separation of the rubber as explained in the previous chapter (§ 5.3.2)

Table 6.10. Softening points of TR-MB A and TR-MB Af before and after hot storage

Softening point (ASTM D36-95)	TR-MB A		TR-MB Af	
	top	bottom	top	bottom
	°C			
before hot storage	60.5		49.8	
after 1h of hot storage	59.0	61.4	46.0	51.6
after 3h of hot storage	59.0	64.4	45.2	53.0
after 5h of hot storage	57.4	63.4	46.6	54.6

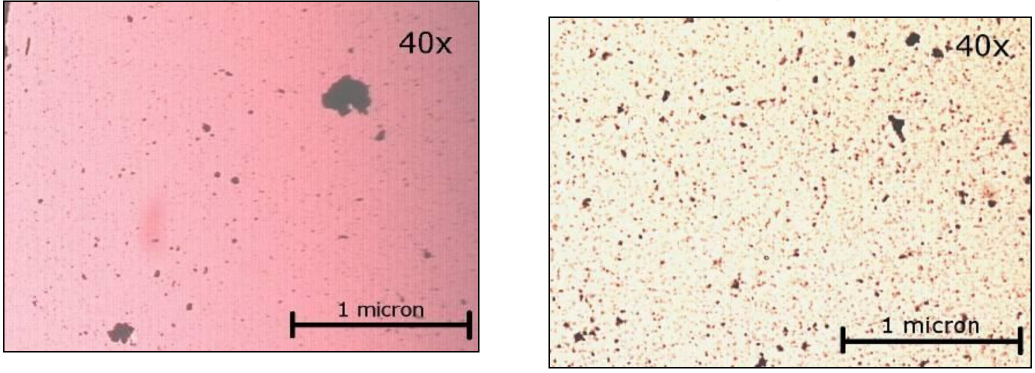
As found in previous research (Lu & Isacsson, 1997) the use of only the softening point to evaluate the storage stability of modified binders may be inadequate.

TR-MB A

TR-MB Af

before hot storage: coarse dispersion

before hot storage: medium coarse

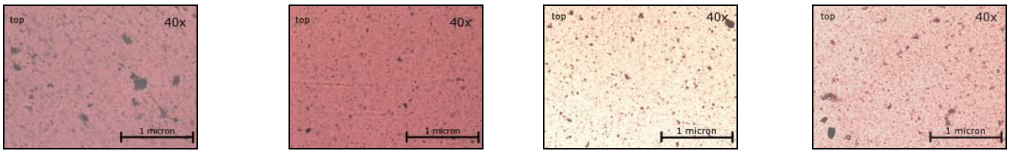


after 3h of hot storage

after 5h of hot storage

after 3h of hot storage

after 5h of hot storage

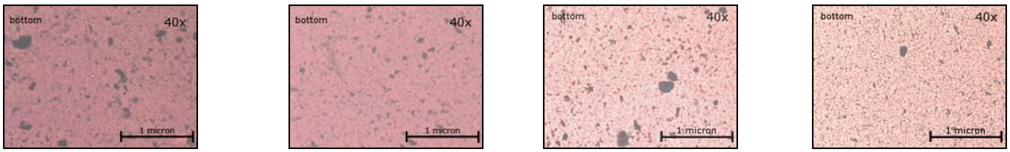


top: medium coarse

top: fine medium

top: medium coarse

top: medium coarse



bottom: medium coarse

bottom: medium

bottom: medium coarse

bottom: coarse

Figure 6.8. Polymeric dispersion analysis of the top and bottom sections of “TR-MB A” and “TR-MB Af”

Therefore, to have more information and more accuracy, a polymer dispersion analysis (PDA) and a rheological characterization of the top and bottom sections of the modified binders, after three and five hours of hot storage, have been performed. PDA was performed using fluorescence microscopy which provided the images shown in Figures 6.8 and 6.13.

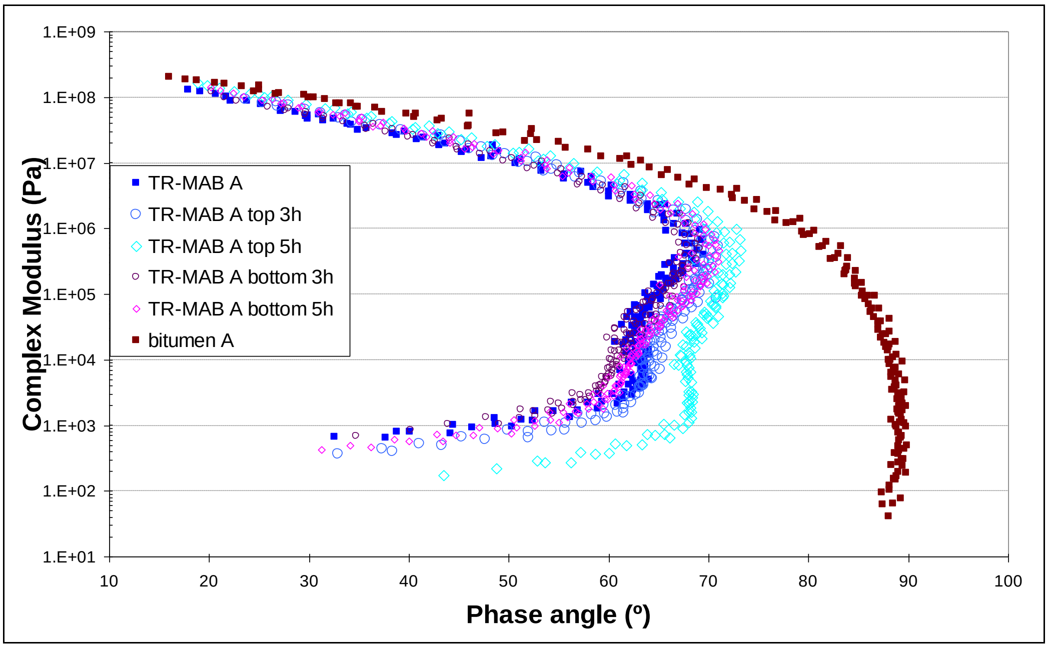


Figure 6.9. Black diagrams of base bitumen A and TR-MB A before and after hot storage; a) 3h hot storage, b) 5h hot storage

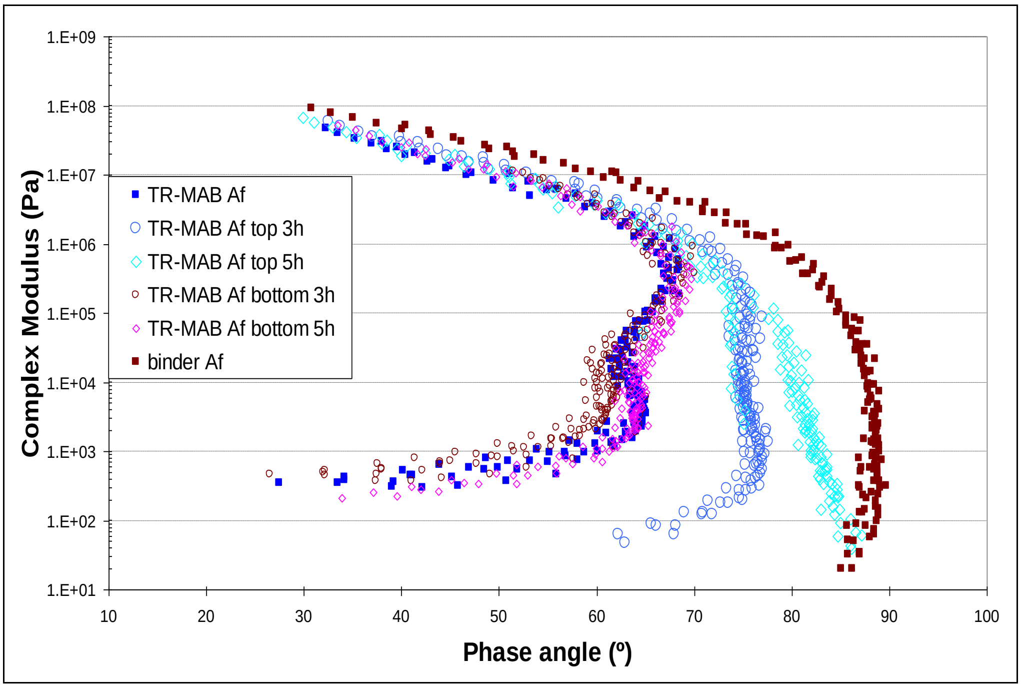


Figure 6.10. Black diagrams of base binder Af and TR-MB Af before and after hot storage; a) 3h hot storage, b) 5h hot storage

Table 6.11. Softening points of TR-MB B and TR-MB Bf before and after hot storage

Softening point (ASTM D36-95)	TR-MB B		TR-MB Bf	
	top	bottom	top	bottom
	°C			
before hot storage	71.0		60.5	
after 1h of hot storage	72.5	69.8	61.6	58.0
after 3h of hot storage	73.4	70.2	61.9	59.8
after 5h of hot storage	71.8	71.0	59.0	62.6

These show, with a magnification of forty times, the binder dispersion of the tyre rubber before and after periods of storage. Lastly, the DMA was performed using the same conditions as used in Section 5.2.5 and presented in Figures 6.9, 6.10, 6.11 and 6.12.

The results of these analyses show that both TR-MBs originating from bitumen A (low asphaltenes content) begin to have a relevant phase separation after three hours of hot storage. As shown in Figure 6.8, the top section of TR-MB A has a coarse dispersion of rubber which tends to settle toward the bottom. Comparing the images from the PDA in the same figure, TR-MB A shows a lower variability between the top and bottom sections than the TR-MB Af obtained after adding the flux to the same base bitumen. What it is suggested by the variability of the softening points has been confirmed by the rheological characterisation.

The black diagrams in Figure 6.10 show how the finger print of the top section of TR-MB Af differs considerable from that of the bottom. Moreover, it is interesting to note how, with increasing storage time, the top section tends to have a rheology closer to the base binder than the modified binder, while the bottom section becomes stiffer and more elastic. The same behaviour, but less emphasised, is shown by TR-MB A in Figure 6.9. PDA and rheological analyses for TR-MBs created from bitumen B (high asphaltenes content) confirm the results of the softening point tests (Table 6.11). These modified binders tend be much more stable than the ones obtained by modifying bitumen A. TR-MB B has good stability showing no significant differences in terms of polymer dispersion between the top and the bottom sections after both periods of storage. It even shows a stable rheology (Fig. 6.12) as well as having a constant softening point (Tab. 6.11).

Rheological characterisation in Figure 6.12 shows how TR-MB Bf is less stable than the base bitumen without flux. Contrary to what was expected, the laboratory blended TR-MBs produced with base bitumens without the addition of an oil extender tended to be more stable than the modified binders produced with the base binder (base bitumen plus flux) especially for the base bitumen with the lower asphaltenes content (bitumen A).

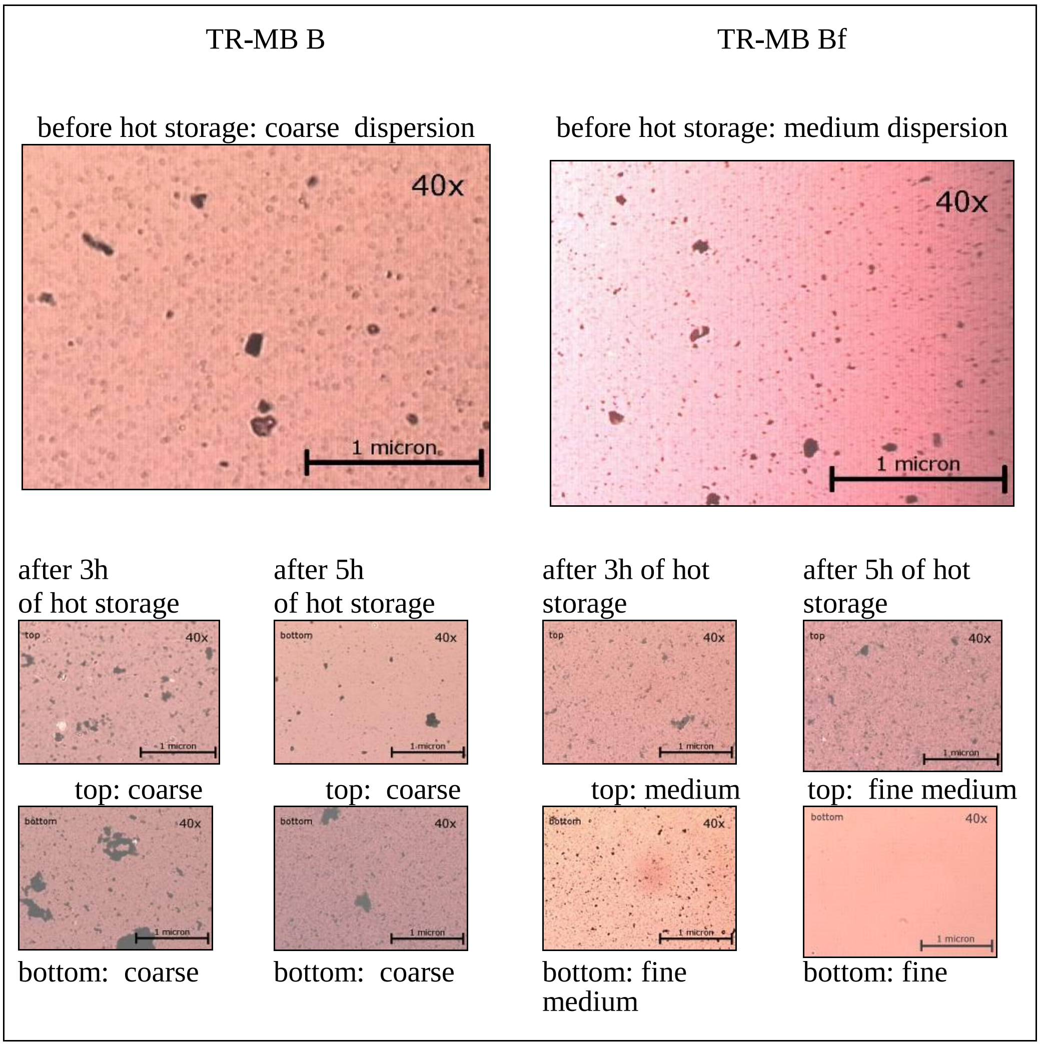


Figure 6.11. Polymeric dispersion analysis of the top and bottom sections of “TR-MB B” and “TR-MB Bf”

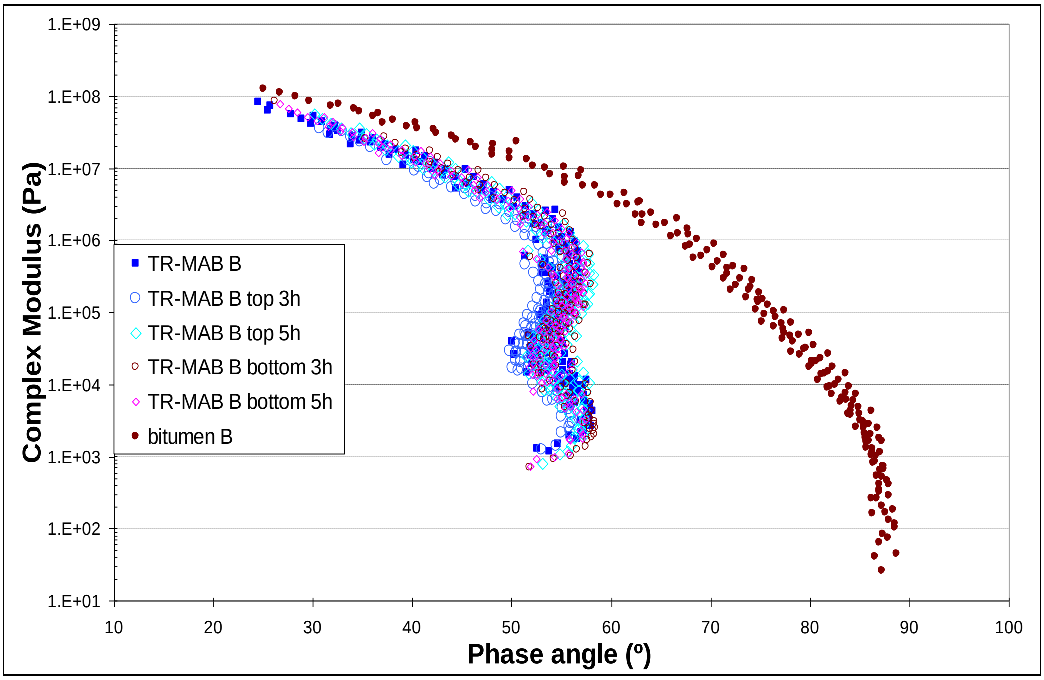


Figure 6.12. Black diagrams of base bitumen B and TR-MB B before and after hot storage; a) 3h hot storage, b) 5h hot storage

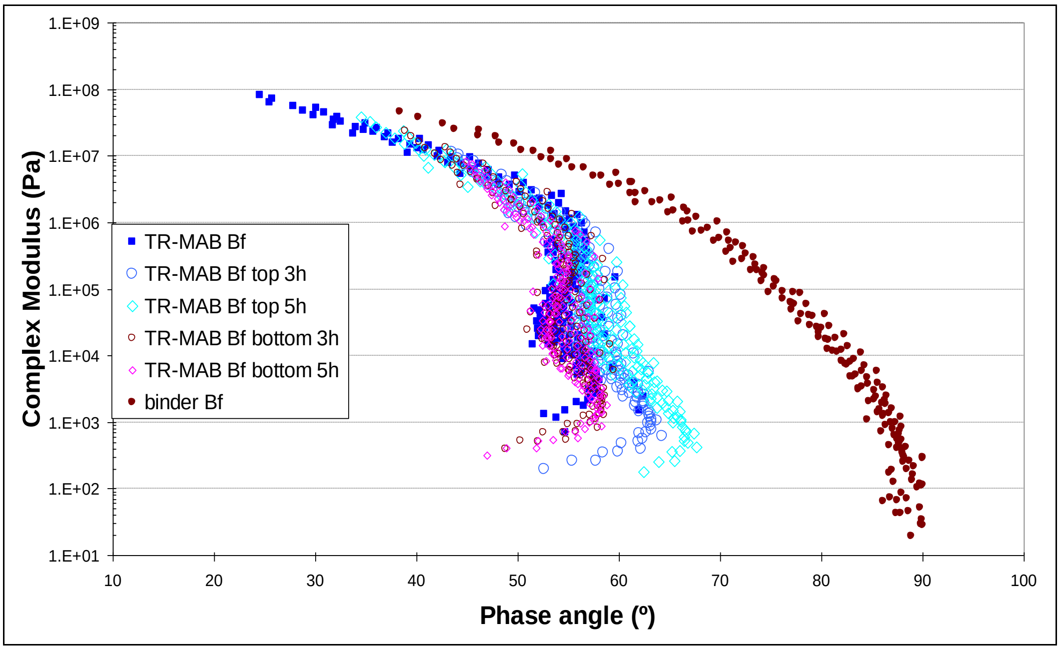


Figure 6.13. Black diagrams of base binder Bf and TR-MB Bf before and after hot storage; a) 3h hot storage, b) 5h hot storage

6.4 Summary of results and critics

6.4.1 Base bitumen chemistry

This study highlights that is possible to produce a high performance TR-MB by mixing fine tyre rubber with high asphaltenes content bitumen (bitumen B) without the need to add an oil extender, or at least not the high content used in this study. In fact, TR-MBs obtained from base bitumen B (higher asphaltenes content), show high viscosity, a better performance grade, lower temperature and frequency susceptibility and better storage stability than the one obtained from the base bitumen with the lower asphaltenes content (bitumen A).

What has been found suggests that bitumen composition has to be selected carefully to obtain optimised viscoelastic properties for the final product. Therefore when a TR-MB has to be produced, the compatibility between rubber and base bitumen cannot be predicted only by estimation of the asphaltenes content, but needs deeper investigations. For example, it is important to asses also the amount of aromatics which should be sufficient for swelling rubber without increasing excessively the viscosity. Moreover, by assessing the aromatic content is possible to know when, and in which amount, it is necessary to provide an external aromatic source (flux), which, as highlighted from this study, it is not always suggested.

6.4.2 Oil extender effect

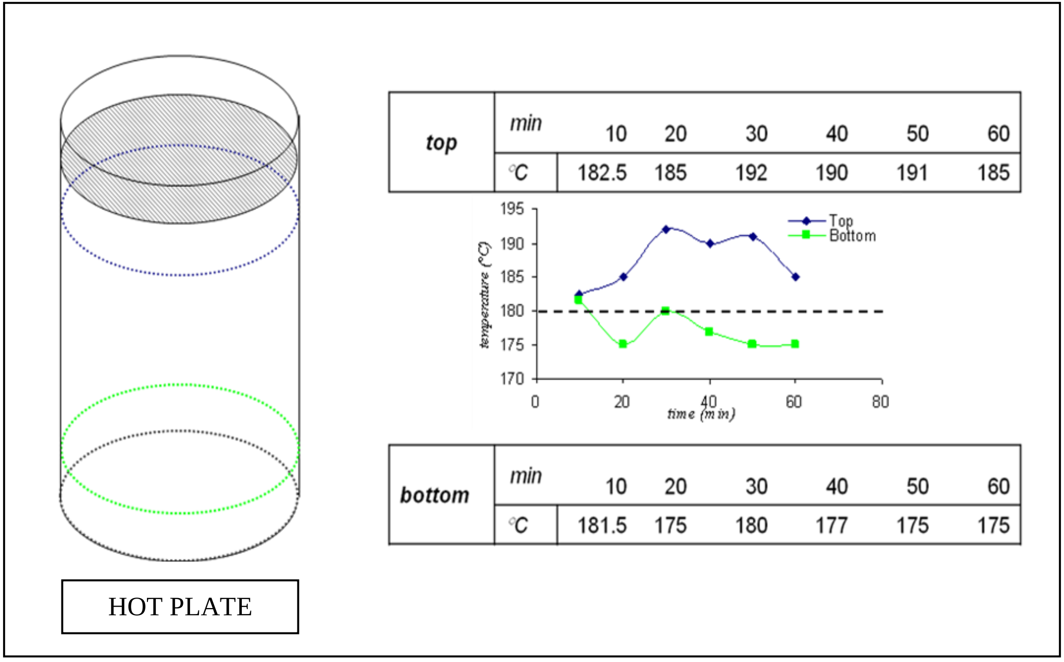
The addition of the oil extender effects the physical properties of the TR-MBs by soften the modified binder that has got, therefore, reduced viscosity and lower softening point. Results show that oil extender effects also enhancing the low temperatures properties of the modified binders by decreasing the Fraass breaking point and shifting their Performance Grade, that moves towards lower values, but maintains the same performance temperature range. The rheological analysis highlights that even if the base binders contain flux, it has got the same black diagrams that of the base bitumens: The finger print does not change.

The overall effect of adding the oil extender is the same whether it is added solely to the base bitumen, to form the base binder, or used as a component in the production of TR-

MBs. Furthermore, the addition of an oil extender to low asphaltenes content bitumen could have a detrimental effect on the modification in terms of the materials stability as happened by modifying bitumen A.

6.4.3 Possible improvements of the processing conditions

A sure improvement on the experimental programme, regards the blending equipment.
In fact, by using a hot plate to maintain the temperature within the sample and a tin with thin walls as container, it was noticed a huge variability between the temperature of the top and bottom sections of the sample. An immersion thermometer was used to take measurements every 10 minutes. Differences of even 15°C between the sections were noticed. The importance of the processing temperature on TR-MB production (§ 4.3.3) suggest that it is necessary to make some improvements of the blending/heating system toward a better control of the curing temperature.



top	*min*	10	20	30	40	50	60
	°C	182.5	185	192	190	191	185

bottom	*min*	10	20	30	40	50	60
	°C	181.5	175	180	177	175	175

Figure 6.14. Diagram of temperature variability of top and bottom sections of the sample, due to the usage of the hot plate method

6.4.4 Conclusions

Four different Crumb-Rubber Modified Bitumens (TR-MBs), originating from two base bitumens with different asphaltenes content, have been blended and tested. Superpave performance grade, detailed rheological properties and storage stability analysis have been undertaken and used as the basis for the comparison. The results have indicated that all the modified binders have a considerable improvement in terms of their rheological, physical and performance properties compared to the original base bitumens (40/60 pen).

However, fundamental differences, related to base bitumen chemistry, have been found between the different blends and the effect of adding an oil extender to the base bitumen was clarified. Moreover, some defects in the processing conditions were highlighted and possible improvements suggested.

Therefore, the main conclusion that comes out from this experimental part is that any bitumen has to be specifically studied to assess compatibility with the particular polymer that has to be used for the modification, and in order to predict if a bitumen is adapt for a specific modification process, and if usage of oil extender is necessary, it is fundamental to investigate more on chemical properties of the bitumen.

7. New protocols to optimise laboratory curing of Tyre Rubber Modified Bitumen

7.1 Introduction

The mechanical properties of the modified binder are strongly affected by the processing conditions selected. It is necessary to establish optimum curing conditions, involving temperature and operation time, in order to get suitable properties (§ 4.3.2 and 4.3.3). As mentioned in the literature review (§ 4.3.3 and 4.3.6), mixing device employed in bitumen modification, cover a particular role in the optmisation of the performance and stability of the modified binder. In any case, it is necessary to evaluate the extent of modification obtained with simple laboratory tests that may be part of a mixing protocol for optimizing Tyre Rubber-Bitumen blends, in order to guarantee the required improvement in the mechanical performances as a result of the introduction of rubber in the blend.

Therefore, in this section, all performed at the Road Infrastructure Engineering Department of the University of Palermo (DIIV), an experimental study was carried out n order to define an optimised laboratory protocol. The aim of this protocol were: it has to be simple to perform, consumes the smallest amount of material possible and is able to provide useful information for controlling and optimizing the modification process of bitumen with rubber, as well as the performance of the final product. All this has been done by using common laboratory equipment and procedures that are capable of ensuring the consistency of the final product to be tested.

7.2 Processing devices and procedures

In order to achieve a tyre rubber-asphalt blend with improved performance the rotational viscosity is the physical parameter that is easiest to control during the modification process, from an operative point of view. In fact, the rubber-bitumen interaction (§ 4.3.3), at a certain temperature, implies an increase in the blend viscosity up to a maximum value and a subsequent noticeable decrease with the reaction time (Kahndal, 2006; Takallou & Sainton 1992). Thus, in this section, the provided equipment and procedures used to define the optimization of a rubber-bitumen blend via continuous monitoring of its rotational viscosity will be shown.

7.2.1 Low shear protocol

As seen in the literature review (§ 4.3.3), there are two type of mixing: (1) distributive mixing and (2) dispersive mixing (Fig. 4.24). Dispersive mixing refers to reduction of component size, and it occurs only when stress in the melt exceeds the coherent strength of the component. Instead, Distributive mixing refers to uniform distribution of different components in space, and it does not require a high stress (Chung, 2000). Asphalt rubber is tipycally produces in low shear (Shatanawi, 2010). However, if the temperature is not high enough to produce rubber depoyimerisation/devulcanization to a great extent, the influence of processing device is not significant (Navarro et al 2006).

Rotational viscometer, usually used to measure viscosity, offers the possibility of mixing bitumen with fine polymers at very low shear rate, with an accurate control of the temperature and, at the same time, it gives the chance to constantly taking viscosity measurements by using a tool made to disturb the sample as little as possible. A similar device, known as a “rheomixer” has been successfully used in many mixing applications. Extra details can be found elsewhere (Garcıa-Morales et.al, 2007).

In the second stage of the protocol, a Dynamic Mechanical Analyses (DMA) of the blended sample is performed in order to characterise its rheology.

Mixing Device: The low shear blending equipment consists of an adaption of the Brookfield rotational viscometer DV-III Ultra as a low shear mixer. The main reason for using this, probably new, application of the viscometer in this research, is for constantly monitoring the viscosity of the binder in order to control the modification process.

This system offers the opportunity of understanding what is physically occurring during a blending process by monitoring the key parameter, rotational viscosity. It is to be noted that the Brookfield Viscometer allows one to take measurements of only 10-15 grams of material, therefore by using this protocol it is possible to obtain a maximum of 15 grams of modified bitumen for further tests. This quantity is not enough to perform conventional tests like penetration, but it is sufficient to perform tests with a DSR.

Procedure:

1. A little tin of bitumen is rapidly heated at 180°C in the oven, transferred into the container of the viscometer, weighed and then inserted into the thermocell which is set at the mixing temperature of 180°C;
2. Spindle n°27 is immersed in the sample and then slowly set to 200 RPM;
3. When the viscosity of neat bitumen at 180°C is reached, at the equilibrium time, the rubber is slowly fed in over 10-15 minutes and the spindle is allowed to create a vortex on the surface of the sample to help dispersion of the rubber;
4. Once all the rubber has been fed in, mixing is undertaken at a constant shear of 200 rpm.
5. Viscosity is constantly monitored and every 5-15 minutes (depending on temperature and mixing time) the spindle is moved up and down in order to homogenize the sample. The speed must be decreased in order to preserve the equipment anytime that the spindle is raised from the measuring position.
6. The blend is stirred for the time necessary to reach the viscosity plateau, which was fixed at the point when viscosity does not increase by more than 10% within a 15 minute period;

7.2.2 High shear protocol

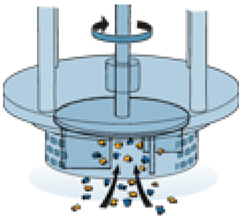
This protocol was set up to try to obtain a dispersive mixing of bitumen and rubber by appling a costant high shear (3000-4000 rpm) for two hours. By adapting a thermostatic bath as a processing vessel, has been possible to accurately control the temperature but higher amount of materials are needed (~ 3 Kg of bitumen). Nevertheless, such big amount of material allows to perform several sampling during the mixing and also to assess storage stability of the final blend. In order to understand the modification process, every 20 minutes about 100g of binder were sampled and stored for further viscosity test and DMA.

Mixing Device: A thermostatic bath IKA HB4 basic of 4 liters, with double walls containing oil to control the temperature, adapted as a vessel to process bitumen and rubber at controlled temperature. The vessel has also been equipped with covering metal rings to allow the partial covering of the container during the blending procedure.

This equipment solved all the problems related to the control of the processing temperatures that were encountered previously (§ 6.4.3). In fact, the temperature of the blend while mixing was shown to be uniform at any measured point with a variability of ± 1ºC. A high shear mixer device Silverson L4R HEAVY DUTY, coupled with a LDD douplex disintegrator head, adapted to reduce the size and disperse polymers in bitumen. The advantages of Silverson's high shear rotor/stator laboratory mixer over simple conventional stirrers or agitators stem from the multistage mixing/shearing action as materials are drawn through the specially designed Silverson workhead.

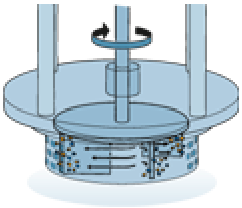
Figure 7.1. Thermostatic vessel and covering metal rings

The mixing process is summarised in the following 4 stages (Silverson website, 2010):



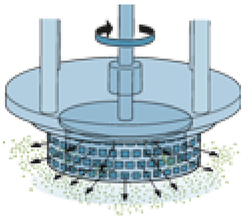
Stage 1

The high-speed rotation of the rotor blades within the precision machined mixing workhead exerts a powerful suction, drawing liquid and solid materials upwards from the bottom of the vessel and into the center of the workhead.



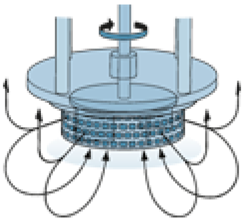
Stage 2

Centrifugal force then drives materials towards the periphery of the workhead where they are subjected to a milling action in the precision-machined clearance between the ends of the rotor blades and the inner wall of the stator.



Stage 3

This is followed by intense hydraulic shear as the materials are forced, at high velocity, out through the perforations in the stator and circulated into the main body of the mix.



Stage 4

The materials expelled from the head are projected radially at high speed towards the sides of the mixing vessel. At the same time, fresh material is continually drawn into the workhead maintaining the mixing cycle. The effect of the horizontal (radial) expulsion and suction into the head is to set up a circulation pattern that minimizes aeration caused by the disturbance of the liquid's surface.

Procedure:

1. The required amount of bitumen is heated at 180°C in the oven and then transferred into a thermostatic vessel of 4 l provided with double walls containing oil to control the temperature. At least 3 liters of bitumen per blend is necessary.

2. The vessel is then transferred into the hood, the duplex head of the high shear mixer is totally immersed into the hot bitumen, but in an off-central position to favor the rubber dispersion, then low shear mixing (500-700 RPM) is undertaken until the target temperature is reached (180°C).
3. Once equilibrium temperature is reached, rubber is rapidly added (as prescribed by the Silverson mixer manual to better disperse polymers), the agitation speed raised to 3000-4000 RPM and the blending time started.
4. The high-shear homogenizer is used for 120 min, at agitation speeds within the range of 3000-4000 RPM, which maintains a constant temperature during the entire process and uniformly within the binder.
5. Every 20 minutes about 100 g of binder were sampled for further tests of rotational viscosity and DMA, in order to control the modification process.

7.3 Materials and methods

7.3.1 Base bitumen selection

Six bitumens were available as base for the production of a TR-MB. All of them were provided from various Italian plants and classified as bases for modification. In order to choose the best base, a brand new SARA analysis equipment based on the method B of the ASTM D4124 standard, has been set up in the laboratory of the University of Palermo. All the base bitumens were chemically characterized through separations of the asphaltenes first, and then by fractionation of the maltenes by low pressure chromatography (Fig. 7.2). Extra details on the performed SARA analyses are reported in Appendix A.

Figures 7.2, 7.3 and 7.4, and Tables 7.1 and 7.2 show different interpretations of the same results obtained from the performed SARA analyses on the available bitumens.

A triangular representation of the four constituents of each bitumen (resins, aromatics, asphaltenes + saturates) allows the selection of the main bitumen family that can be represented by individual regions (cluster)(Loeber L. *et al*, 1998). The SARA analysis allows the main bitumen fractions to be distinguished and also lead to the determination of some important ratios: the resin/asphaltene ratio, the aromatic/asphaltene ratio and the calculation of the colloidal index, as listed in Table 7.2.

Table 7.1 SARA analyses results

Bitumen	Asphaltenes	Maltenes		
	Asphaltenes [%]	Saturates [%]	Aromatics [%]	Resins [%]
UB01	9.6	11.9	61.4	17.1
UB02	8.3	11.7	63.6	16.4
UB03	5.1	15.8	60.4	18.7
UB04	14.4	9.9	58.8	16.9
UB05	18.5	16.1	51.7	13.7
UB06	11.4	22.5	50.3	15.8

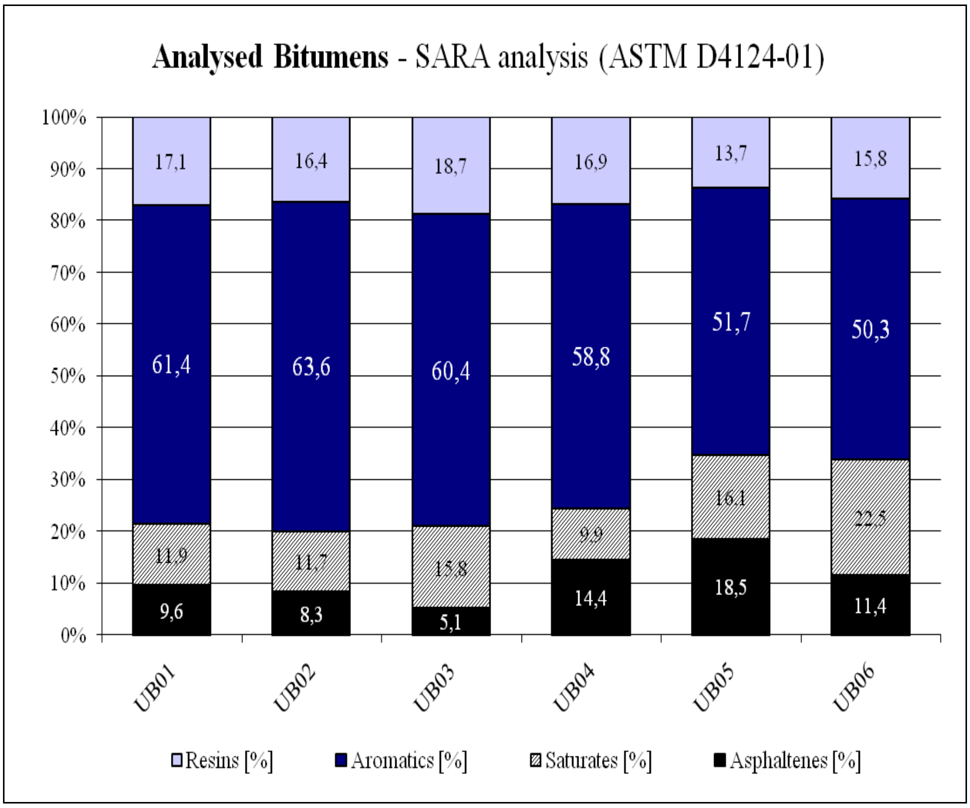


Figure 7.2. SARA analyses results

Table 7.2 Colloidal parameters

Bitumen	I_c (Asph + Sat/ Ar + Res)	X (1 / I_c)	Ar./Asf.	Res/Asf.
UB01	0.27	3.65	6.4	1.8
UB02	0.25	4.00	7.7	2.0
UB03	0.26	3.78	11.8	3.7
UB04	0.32	3.12	4.1	1.2
UB05	0.53	1.89	2.8	0.7
UB06	0.51	1.95	4.4	1.4

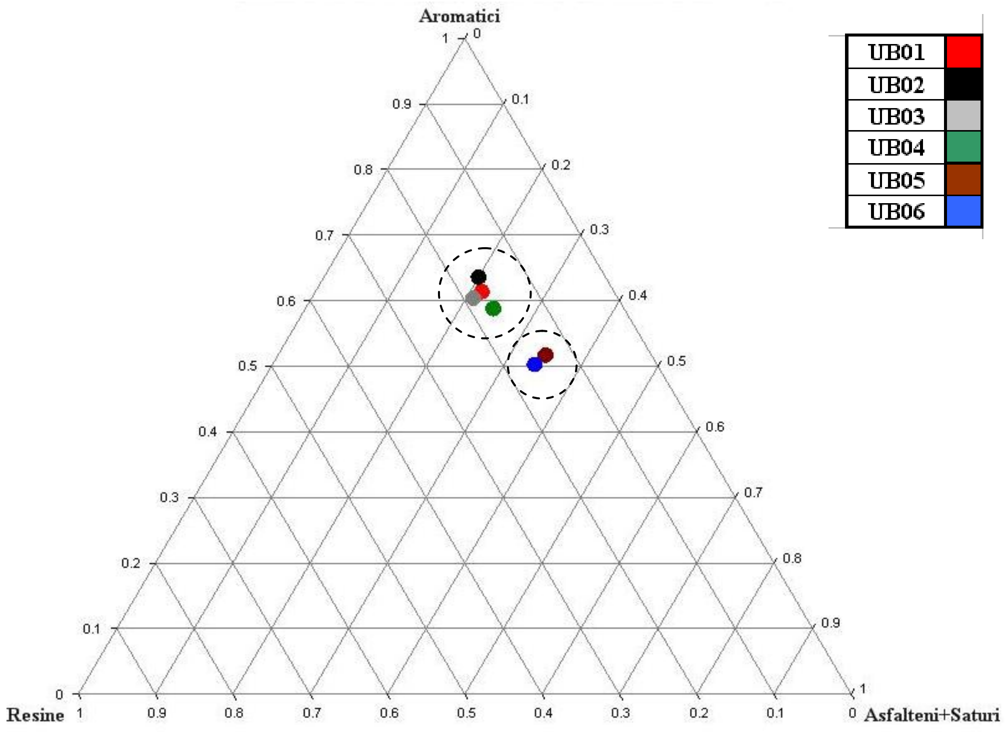


Figure 7.3 Triangular representation of the different bitumen families.

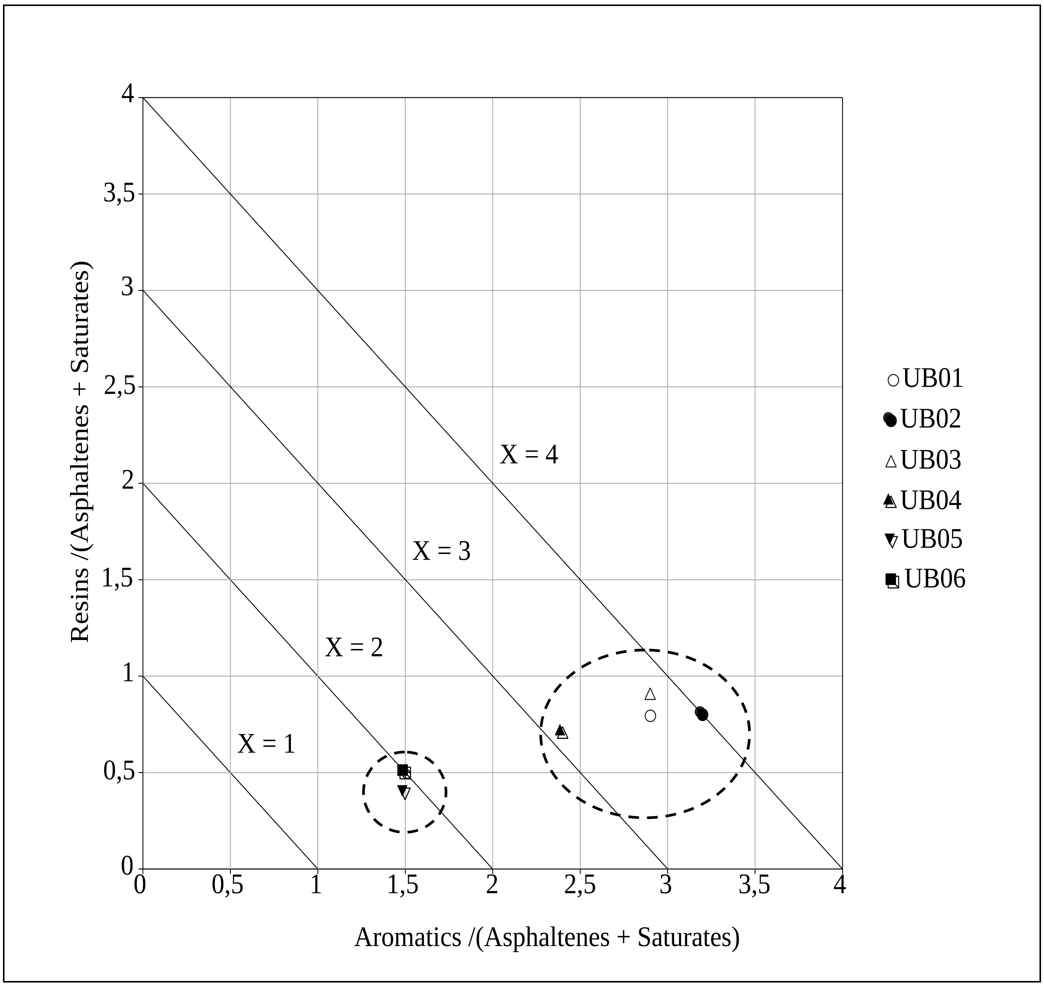


Figure 7.4 Isolines of the dispersion factor

Morevoer, figure 7.4 represents the different bitumen families by their dispersion factor (inverse of the colloidal index). The resin/(asphaltene + saturate ratio) is plotted versus the aromatic/(asphaltenes + saturates) ratio; the intermediate straight lines (isolines) give the values of the dispersion factor Xi.

As can be seen in Figure 7.3 and 7.4, in this study two families have been identified: the group formed by UB01, UB02, UB03 and UB04 and the second family composed by UB05 and UB06. The first group is characterised as having the lower colloidal indecies (CI) and a much better ratio of aromatic/asphaltenes and resins/asphaltenes. As a matter of fact, the second group has a higher content of both saturates and asphaltenes and thus a lower dispersion factor. All this means that the asphaltenes of bitumens UB05 and UB06 are more peptised in the oil based medium, whilst the bitumens of the first family have got higher amount of light fractions. Specifications related to the production of TR-MBs (§ 4.3.3 and 4.3.4) indicate to use soft bitumens (from 80 to 200 pen) and eventually oil extenders; so it is suggested use base binders with high content of aromatics. Morevoer, according to what has been found in literature review on the production of PMBs (§ 4.2.2), higher aromatics content and lower colloidal index/higher dispersion factor enhances the compatibility between the bitumen and its modifier. Based on these results, bitumens of the second family were discarded and a bitumen belonging to the first family, UB01,UB02,UB03 and UB04, were chosen as possible bases to modify with tyre rubber.

Table 7.3 Physical properties of the bitumens selected as potential bases for modification

	UB01	UB02	UB03	UB04
Penetration @25°C (mm/10)	49,75	62,90	39,60	68,80
Softening Point (°C)	51,00	46,75	50,00	47,00
Penetration Index	-1.03	-1,53	-1,70	-1,24
Viscosity @ 100ºC (Pa.s)	3.458	2,7283	3,9800	1,9700
Viscosity @ 135ºC (Pa.s)	0.429	0,3210	0,4179	0,2533
Viscosity @ 160ºC (Pa.s)	0.139	0,1105	0,1369	0,0950

Table 7.4 Physical and chemical properties of the selected base bitumen (UB01)

Base bitumen	
Penetration 25°C (mm/10) – EN 1426	50 dmm
Softening Point (°C) – EN 1427	51ºC
Penetration Index	-1.04
Rotational Viscosity @ 100ºC (ASTM T316-04)	3.458 Pa.s
Rotational Viscosity @ 135ºC (ASTM T316-04)	0.429Pa.s
Rotational Viscosity @ 160ºC (ASTM T316-04)	0.139 Pa.s
Asphaltenes [%]	9.6
Saturates [%]	11.9
Aromatics [%]	61.4
Resins [%]	17.1
Colloidal Index (CI = Asph + Sat/Ar + Res)	0.27
Dispersion factor (X = 1/CI)	3.65
Aromatics / Asphaltenes	6.4
Resins / Asphaltenes	1.8

Bitumens of the first family were further characterised by performing conventional physical tests as: penetration (EN, 2000a), softening point (EN 2000b), and rotational viscosity at 100°C, 135°C and 160ºC (EN, 2003). Results are provided in the Table 7.3. Considering the total available amount of bitumen belonging to the first family and based on what has been assessed in this section and in the previous experimental part (§ 6.4.4), the penetration grade 50/70, identified as UB01 has been chosen as the base bitumen for all the modification processes in the remaining experimental programme.

As summarised in Table 7.4, this shows the selected base bitumen is characterized as having a medium-low content of Asphaltenes, almost the highest Aromatic/Asphaltenes ratio and almost the lowest Colloidal Index (therefore almost the highest dispersion factor).

7.3.2 Tyre rubber properties

The rubber used was provided by a Sicilian plant. It was obtained via mechanical grinding (at ambient temperature) of scrap tyres; with regard to the size of the grains, in order to improve the reaction of the rubber with bitumen (§ 4.3.3), only rubber passing 30 mesh was used (Fig.7.5)

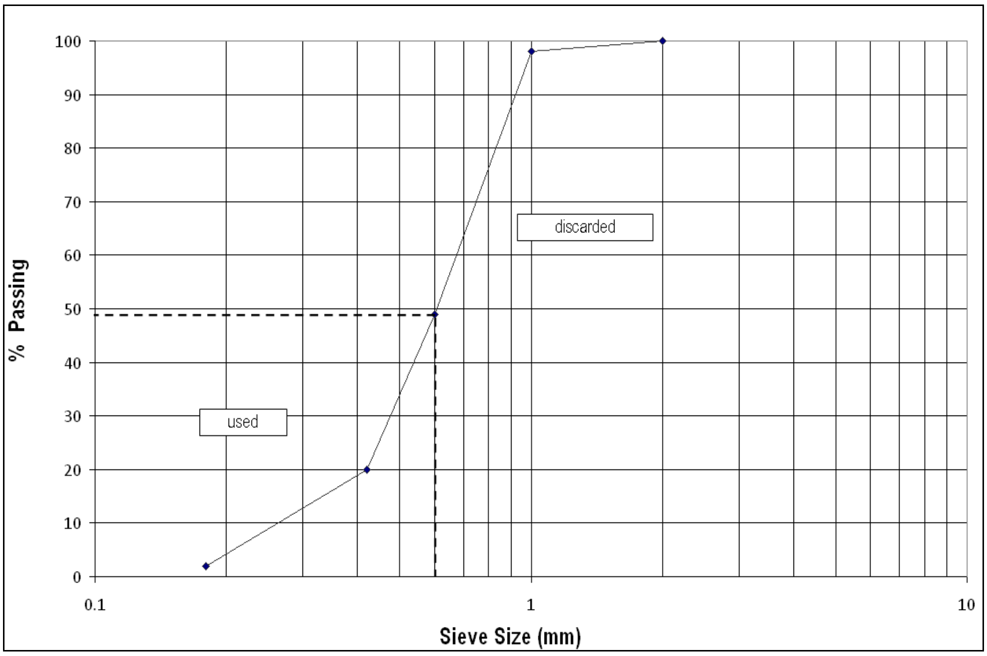


Figure 7.5. Gradation curve of the tyre rubber used, as obtained via mechanical grinding

7.3.3 Bituminous binders

As discussed earlier, 50/70 pen bitumen was selected as the base for the production of a Tyre-Rubber Modified Bitumen (TR-MB) through a protocol involving preliminary estimation of rubber content optimum at low shear (TR-MB LS). Once the optimum rubber content was established, a high shear blending protocol was also performed, maintaining the same mixing temperature of 180°C, in order to optimize time and settling properties of the final product (TR-MB HS). At the end, a comparison with two Styrene-Butadiene-Styrene modified bitumens (SBS-MBs with a medium and a high level of polymer), supplied by an Italian oil company, was also performed. All the binders were characterized performing rheological tests with a DSR and conventional tests as: penetration (EN, 2000a), softening point (EN 2000b), and rotational viscosity at 135° and 160ºC (EN, 2003). Results and comparisons are provided in the following sections. Summarizing, the following binders were considered for this study:

neat bitumen:	pen 50/70 bitumen
TR-MB LS:	Tyre Rubber-Modified Bitumen (TR-MB) produced mixing at Low Shear (LS) a base bitumen with the optimum content of 18% in weight of 30 mesh rubber
TR-MB HS:	Tyre Rubber-Modified Bitumen (TR-MB) produced mixing at High Shear (HS) a base bitumen with 18% in weight of 30 mesh rubber
SBS-MB H:	modified bitumen (SBS-MB) with a high content of SBS (Hard - H)
SBS-MB M:	modified bitumen (SBS-MB) with a medium content of SBS (Medium - M).

7.4 Rheological analysis

Optimizations of the tyre rubber production and performance comparisons were mainly based on the evaluation of the rheological properties. Therefore, in order to obtain a complete rheological characterisation, dynamic mechanical analyses (DMA) have been performed by making frequency sweep tests over a wide range of temperatures with an Antoon Paar Physica MCR 101 dynamic shear rheometer (DSR) since it has been proved that SUPERPAVE DSR protocol can also be applied to rubber modified binders

(Tayebali et al, 1997). The tests were performed under the following conditions and making at least three repetitions:

- Loading Mode: controlled-strain
- Temperatures: 0ºC to 80 ºC with 5ºC intervals (neat bitumen)
  30ºC to 80 ºC with 5 or 10 ºC intervals (TR-MB)
- Frequencies: 0.10, 0.16, 0.25, 0.40, 0.63, 1, 1.6, 2.5, 4, 6.3 and 10 Hz
- Plate geometries: 8 mm ϕ and 2 mm gap (0-50ºC) (only neat bitumen)
  25 mm ϕ and 1 and 1.5 mm gap (30-80ºC)
- Strain amplitude: 0.5% with 8 mm plates (within LVE response dependent on G^*)
  0.5% and 2%-12%@80°C with 25 mm plates (within LVE response dependent on G^*)

For each test, samples were prepared by means of a hot pour method, based on Alternative 1 of the AASHTO TP5 Standard (AASHTO, 1998). The gap between the upper and lower plates of the DSR was chosen such that the rheological properties taken at wider gap widths (1-1.5mm for 25mm) were independent of the gap (Appendix C).

The rheological properties of the binders were measured in terms of their complex (shear) modulus, G^*; and phase angle, δ. Once the raw data was obtained, Time Temperature Superposition Principle was applied in order to produce master curves at 30°C, isochronal plots and shift factor curves. Black diagrams, Isochronal plots, master curves and binder rutting parameters were used as the basis of all the rheological analyses in this paper. With regards to the rutting parameters, for the seak of simplicity only some of those obtainable from the DMA, previously defined dynamic rutting paremeters (§3.3.4), were considered in this study: SHRP and Shenoy's parameters

7.5 Results and discussions

7.5.1 Optimum rubber content estimation by using the low shear protocol

Polymer Modified Bitumens usually contain an amount of polymer that varies within a range of 3% to 9%. When tyre rubber is used as the only modifier, at least 15% by mass of bitumen has to be used to achieve relevant improvements in terms of performance: primarly complex modulus and phase angle at high service temperatures. By changing the raw materials, bitumen source, rubber and eventually oil extender, the optimum rubber content that gives performance comparable with standard PMB bitumen, varies as well. Therefore, in this case, a preliminary study was thought to be necessary to obtain two pieces of information: first, assessing which is the minimum rubber content to be added to the selected base bitumen, to get relevant improvements in terms of stiffness and elasticity; secondly to establish the maximu rubber content that the selected bitumen can accept, in terms of performance improvements ratio . After determining these limits, the optimum rubber content to significantly improve the selected bitumen was established. This preliminary optimization study was carried out by using the low shear protocol (§7.2.1).

Table 7.5. Low shear mixer blending protocol (Brookfield viscometer with spindle 27)

bitumen mass	**rubber mass (3-24% of bitumen with step of 3%)**	**rubber size (30 mesh)**	**total weight**	**mixing time**	**mixing speed**	**mixing temp.**
g	**g**	**mm**	**g**	**m**	**rpm**	**°C**
10 – 12 (per each blend)	0.3 - 3	0-0.6	10 – 15 (per each blend)	optimized	200	180

Each blend was replicated twice and considering that the investigated range of rubber percentage was from 3% to 24% in weight of bitumen, with a step of 3%, a total of 16 blends were produced by using the low shear blending procedure (Table 7.5). As a matter of fact, adding elastomers to bitumen allows the high temperature performance of paving grade bitumen to be greatly increased, leaving the low temperature one slightly better. More specifically, a rule of thumb is that for every 1% of added polymer, a 2°C rise in high temperature PG is typically gained. Since the PG classes are based on 6°C steps, the typical 3% polymer-content modification generally allows a gain of one high-temperature class leaving the low temperature sometimes unchanged. (Lesuer, 2009).

The first important result coming from this preliminary study is represented by the maximum blending time to use, for each percentage of rubber, in order to get the best performance at low shear (Figure 7.6). This information is important for optimizing repetitions with the same protocol and it could also give information to predict the

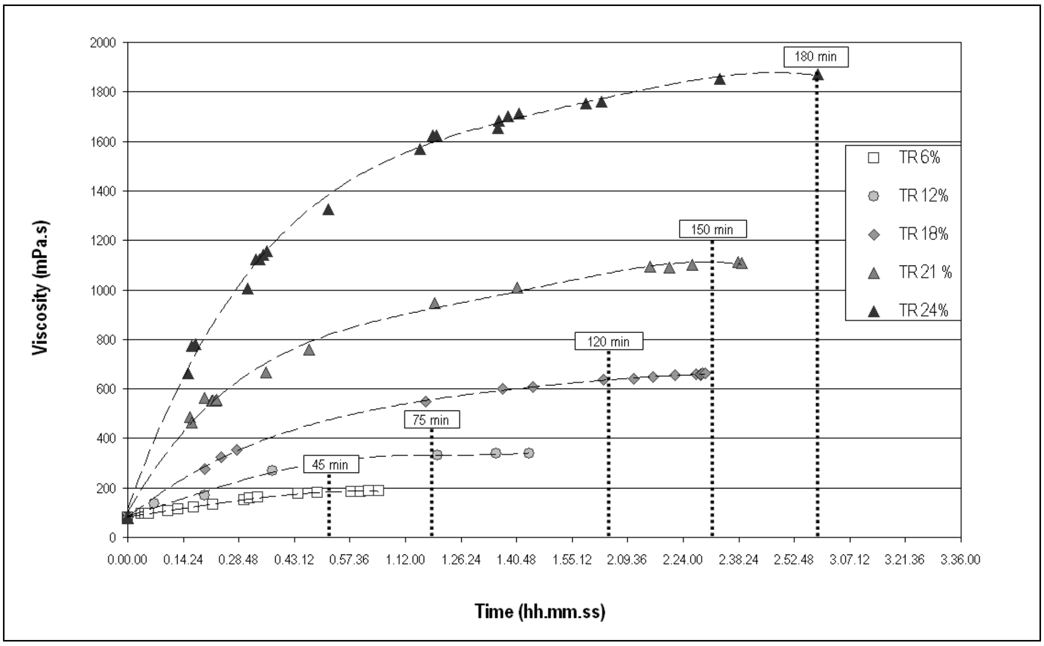


Figure 7.6. Results of constant monitoring using the Brookfield Viscometer as a low shear mixer

optimum blending time in high shear mode, which is expected to be less than the one needed in low shear. Once the best performing material was obtained, it was taken out of the thermocell of the viscometer, immediately stirred with a thin spatula and poured directly into the preheated lower plate of the DSR, or stored in 10 ml vials for further tests. It is easy to realize how this protocol allows optimimum laboratory work, giving the chance to make a large number of blends with a really low consumption of materials, which in some cases are a precious resource.

DMA allows one to have various kind of information on the rheology of the tested material over the selected range of temperatures. The rheological analysis carried out for this part of the study was performed only at the high service temperatures range (30 ÷ 80 °C) with a step of 5°C from 50 to 80°C and a gap width of 1-1.5 mm. The frequency dependence of complex modulus and phase angle for the modified binders were assessed by means of the following Black diagrams (Fig. 7.7), rheological master curves at a reference temperature of 30°C (Fig. 7.8a,b), isochronal plots (Fig. 7.9a,b) and rutting parameters evaluation (Fig. 7.10a,b). Shift factors obtained to build the master curve of the TR-MB, were found to be different from the ones of its base bitumen (Appendix E).

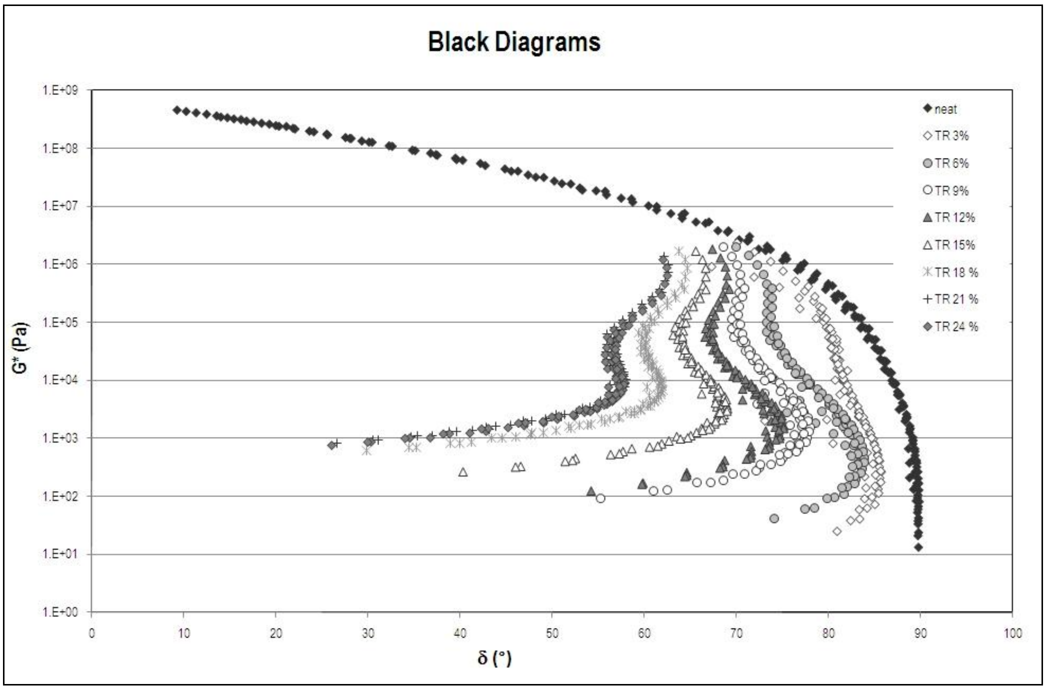


Figure 7.7. Black diagrams of low shear TR-MBs with various rubber contents and neat bitumen

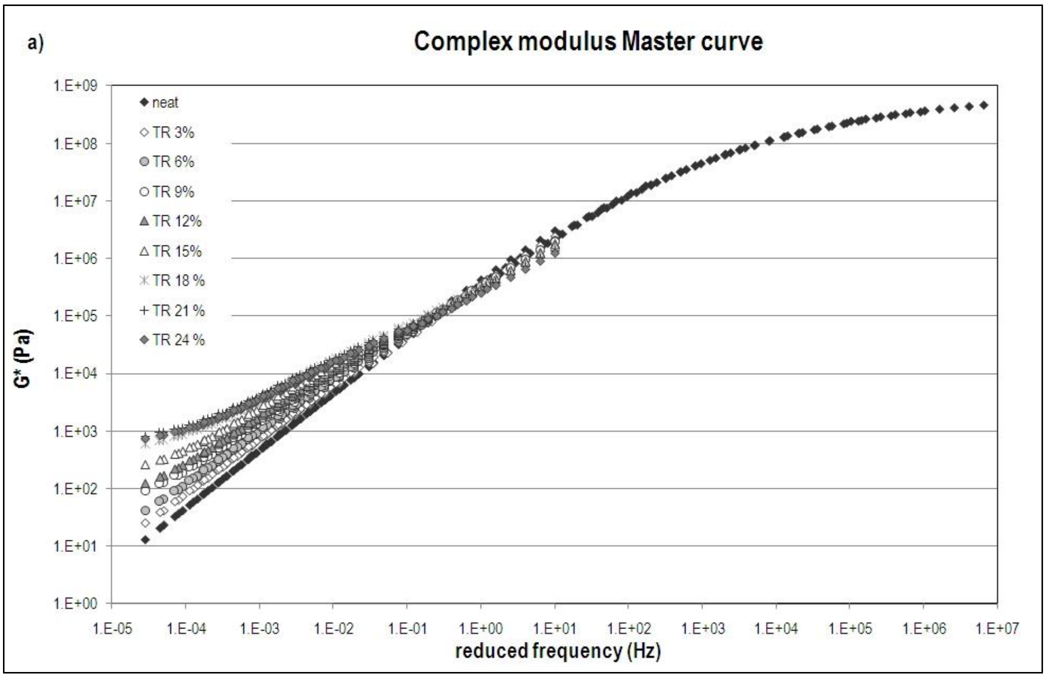


Figure 7.8a. Master curves of G*at 30°C of low shear TR-MBs with various rubber contents and neat bitumen

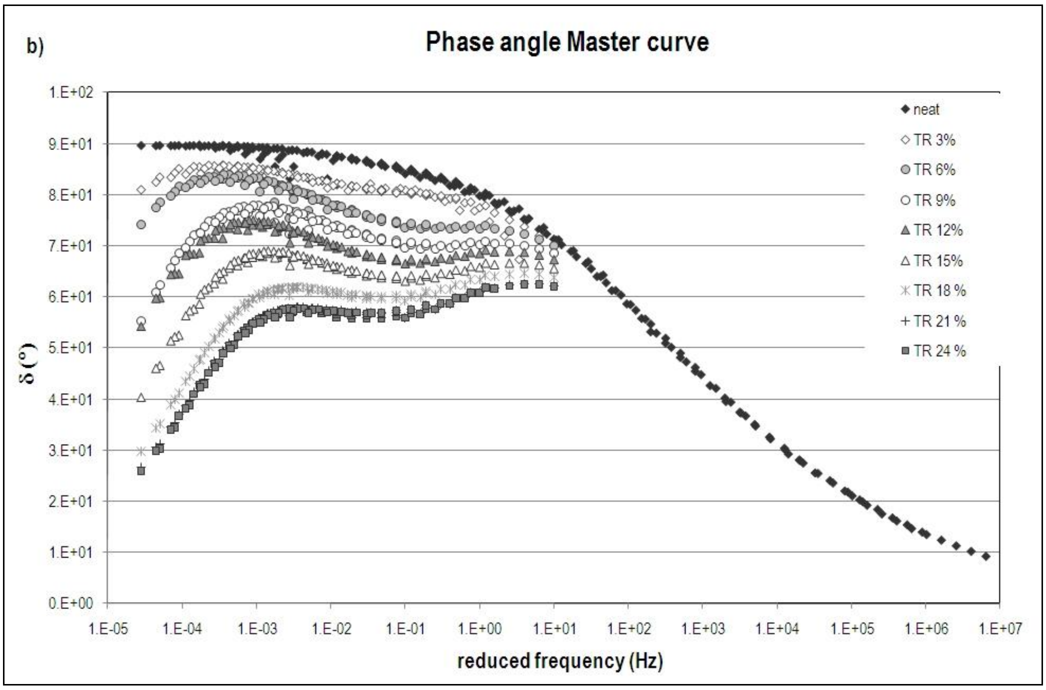


Figure 7.8b. Master curves of δ at 30°C of low shear TR-MBs with various rubber contents and neat bitumen

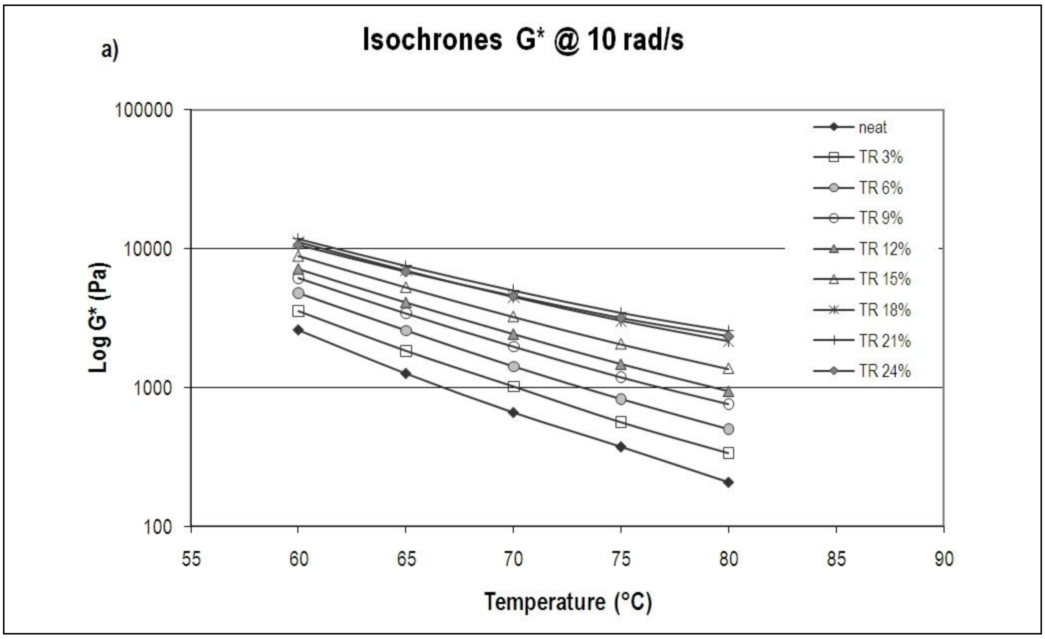


Figure 7.9a. Isochronal plots of G*of low shear TR-MBs with various rubber contents and neat bitumen

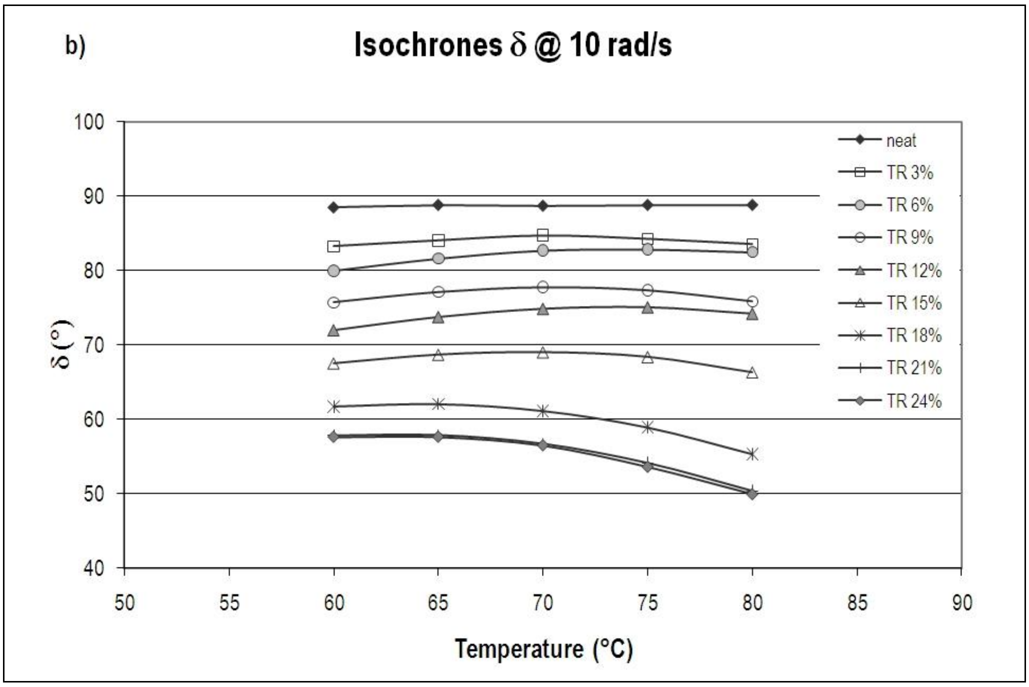


Figure 7.9b. Isochronal plots of δ of low shear TR-MBs with various rubber contents and neat

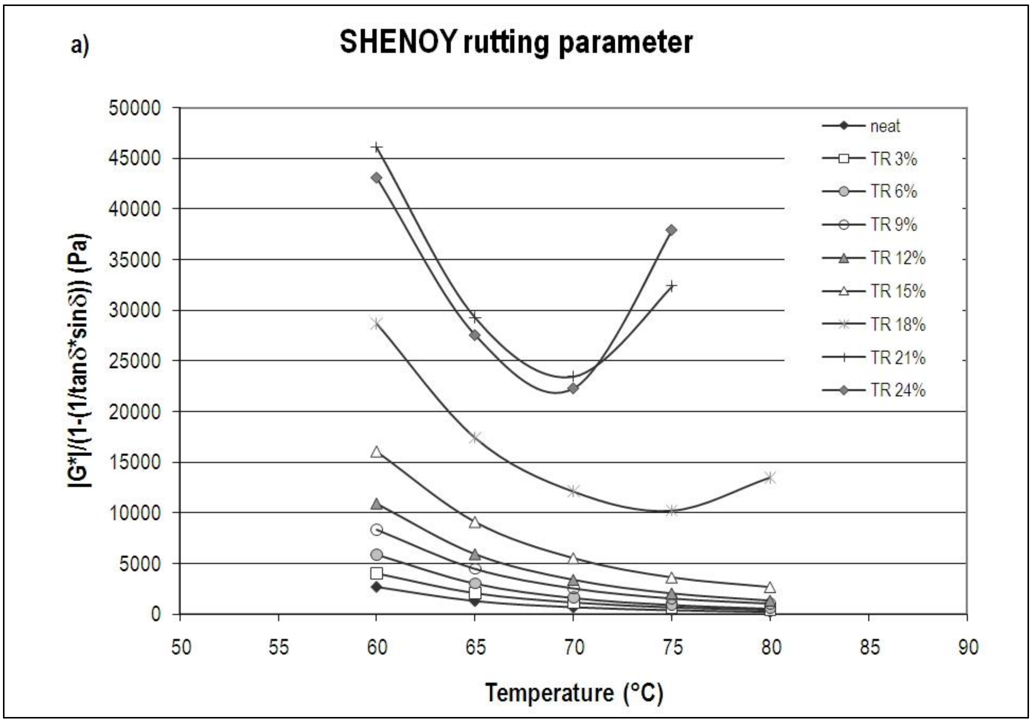


Figure 7.10a. Shenoy rutting parameters of low shear TR-MBs with various rubber contents and neat

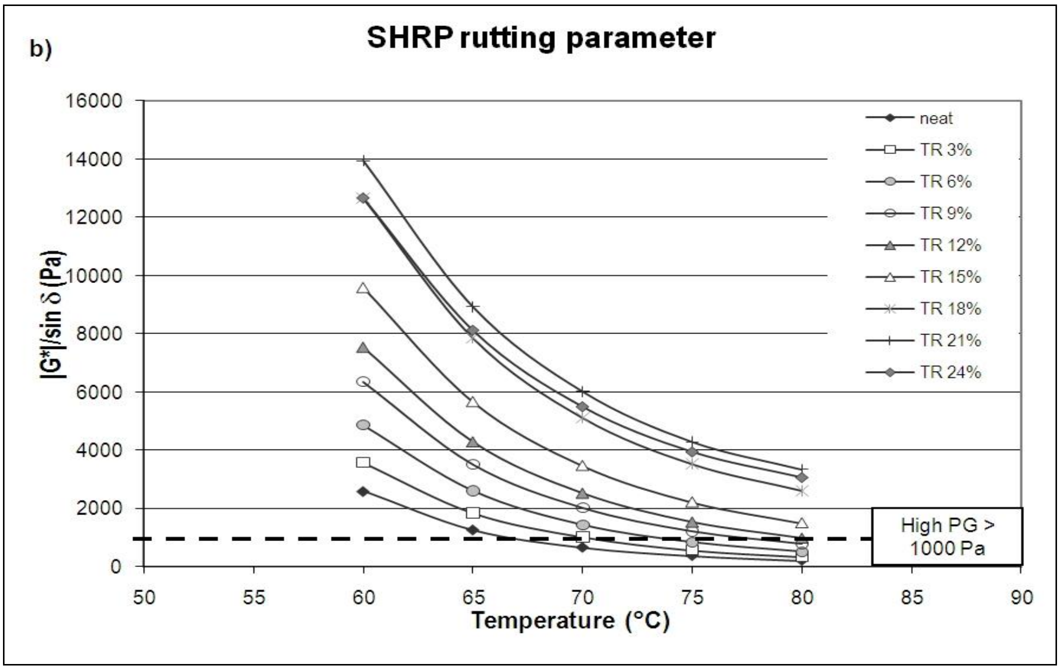


Figure 7.10b. SHRP rutting parameters of low shear TR-MBs with various rubber contents and neat bitumen

Results, show that at low frequencies, which corresponds to high temperatures, modification with rubber makes the binder stiffer (increase of the complex modulus) and confers a better elastic behavior (decrease in the phase angle).

This phenomenon is a clear effect of the formation of a polymer network, in which the elastic characteristics of the modifier agent (rubber) prevail over the typical viscous behaviour of the bitumen at high temperatures.

As can be seen in the diagrams, this trend has a direct correlation with the rubber percentage: by increasing the concentration of rubber the binder became stiffer and more elastic (Fig. 7.8a,b). The isochronal plots show the clear improvements in thermal susceptibility and elastic properties of the asphalt rubber binders at high temperatures (Fig. 7.9a,b). Other important information is given by the evaluation of the rutting parameters as determined via the SHRP parameter |G*|/sinδ and that suggested by Shenoy for modified binders (Bahia et al. 2000; Bahia et al., 1999; Shenoy, 2001) (Fig.6°b). From the former it is possible to notice that the high critical temperature (higher value of the SHRP Performance Grade) of the un-aged neat bitumen increases from 66°C to more than 80°C when at least 15% of rubber is added. Shenoy's parameter

$|G^*|/(1-(1/\sin\delta\tan\delta)$ gives similar information, but at temperatures above 70°C and over 18% of rubber content, it shows a non coherent trend; this is probably due to the prevalent effect of the rubber matrix at high temperatures. All the diagrams highlight one fundamental datum, which is also confirmed with the selected bitumen, 15% of rubber content seems to be the minimum tyre rubber content that has to be added in order to obtain a TR-MB with good performance, expecially by looking at the elastic properties in phase angle master curve (Fig.8.5b). In this work, it is believed that a good level of modification with tyre rubber is achieved only when three conditions are all verified: phase angle is constantly lower then 70°C, secondly when phase angle master curves and isochronal plot reach a plateau at low frequencies; at last when TR-MB show a high critical temperature over 80°C (measured with SHRP or Shenoy's parameter).

Moreover, from the rheological analyses it appears that it is not possible to gain any further significant improvement in terms of stiffness, elastic behavior, thermal susceptibility and rutting resistance when passing from 21% to 24% of tyre rubber in the blend.

For all these reasons 18% of rubber was fixed as optimum rubber content to be used in the second part of the study.

7.5.2 Optimum time estimation by using the high shear protocol

The Low shear protocol provided information on the rheological properties of the TR-MBs, obtained by having a very low consumption of the selected raw materials. It also allowed the optimum rubber content to be established, but it still cannot give correct information regarding the minimum blending time necessary to modify bitumen with tyre rubber when high shear blending protocol is used. In fact, high shear mixing reduces particles size of tyre rubber and provides enough energy to breaks the particle-particle bonds, thus allowing the interaction process to progress with greater speed (Attia & Abdelrahman, 2008).

The blending of rubber and bitumen at high shear was carried out using the high shear protocol (§ 7.2.2). Table 7.6 summarises the mixing parameters used in the blending procedure. All the samples, differing in terms of mixing time, were tested by estimating the so-called apparent viscosity at 177.5°C (ASTM, 2009) that is used in the asphalt rubber production as the key parameter to assess the optimum performance. Rubber particles react with the bitumen improving its stiffness and elastic properties until a peak performance is reached. In practical applications of asphalt rubber, this peak is considered to be achieved when apparent viscosity, after a constant increasing trend reaches a pleateau level (Kandhal, 2006). When bitumen is blended with tyre rubber without any additional additive, the best blending time is usually around 45-60 minutes (§4.3.3 and 4.3.4; Tabatabaee et al. 2004). Similar results were obtained in this study.

Table 7.6: High shear mixer blending protocol

bitumen mass	rubber mass (18% of bitumen mass)	rubber size (30 mesh)	total weight	mixing time	mixing speed	mixing temp.
g	g	mm	g	m	rpm	°C
2890	520	0-0.6	3410	120	5000	180

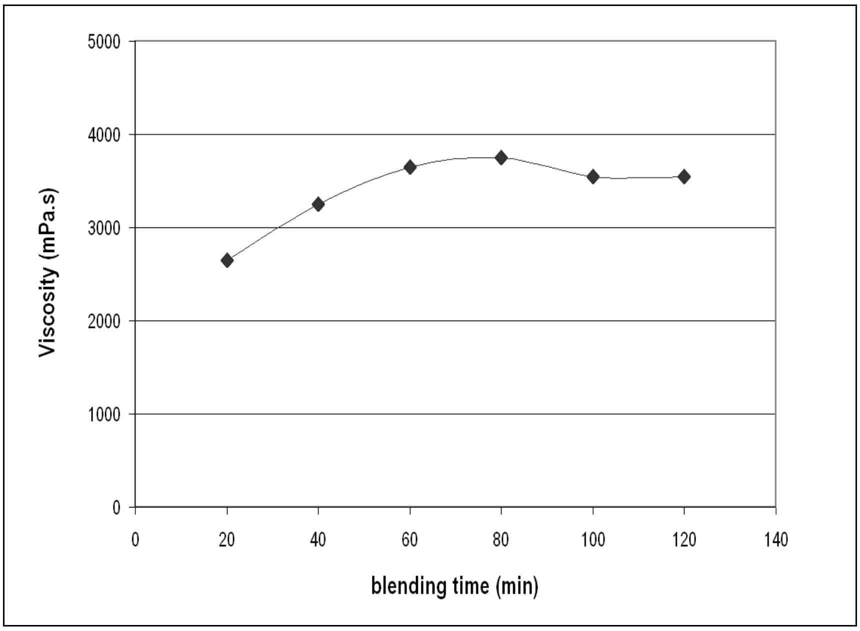


Figure 7.11. Apparent viscosity of TR-MB HS at different blending time

By analyzing the results shown in Figure 7.11, all the samples collected after 40 minutes proved to have the highest apparent viscosities, between 3000 and 4000 mPa·s, with a plateau at about 60 minutes, but a really high variability in the measurements between repetitions was noticed. Therefore, from the apparent viscosity results it is possible to confirm that best performing blends are obtained only after a mixing time of at least 40 minutes and, once reached, those properties are pretty much maintained also up to 120 min of interaction with high shear mixing.

In order to go into more depth, all the samples were also tested with DSR, which is able to indicate the specific variability of stiffness and elastic properties of the binder. DMA at high service temperatures (30÷80°C) was, therefore, performed for all the TR-MB HS samples, and then it was followed by a comparison between the rheological properties of the neat bitumen and those offered by the best performing blend obtained using the low shear protocol: TR-MB LS. Particular care was taken with regards to the gap settings: 1.5mm, for the 25mm plates, was assessed to give the most reliable results for the modified binders, while 1mm gap was maintained for the neat bitumen (Appendix C). From these comparisons, it is possible to notice that all the samples, if compared with the neat bitumen, show improvements in terms of stiffness and elastic properties at high temperatures. As far as the optimization of the blending time is concerned, a blending time of 20 minutes provides a blend whose properties may be improved (phase angle values higher than 70°C), while a blending time equal to 120 minutes leads, in this case, to a blend with poorer properties, while this was exactly the optimum time for the low shear mode (Figs 7.12 – 7.15).

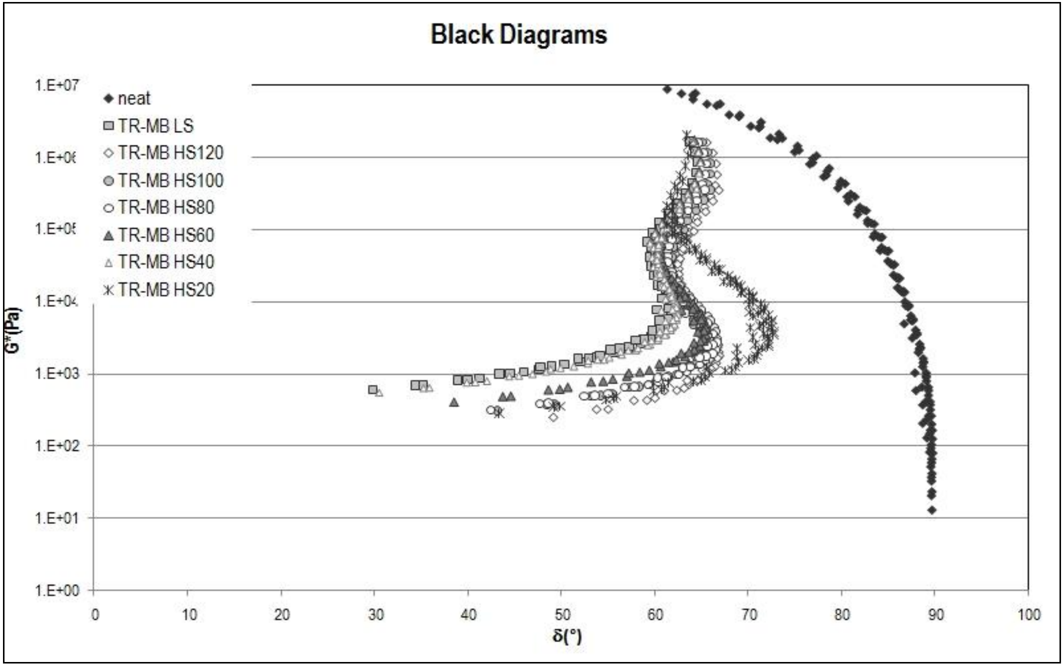


Figure 7.12. Black diagrams of: TR-MB HS at different blending time, TR-MB LS and neat

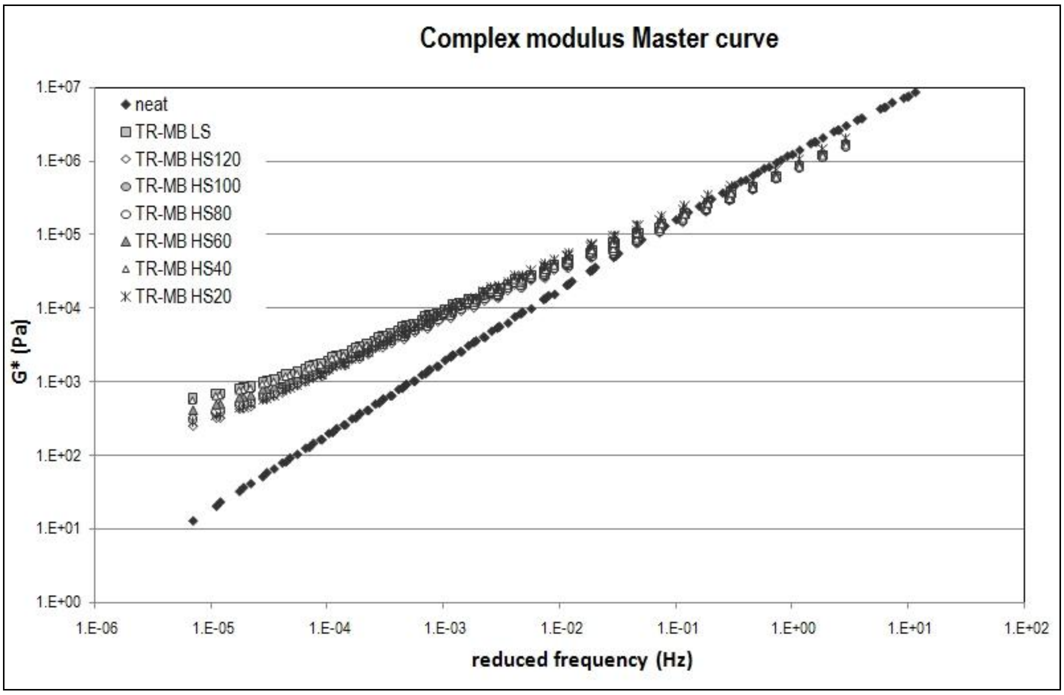


Figure 7.13a. Master curves of G at 30°C of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

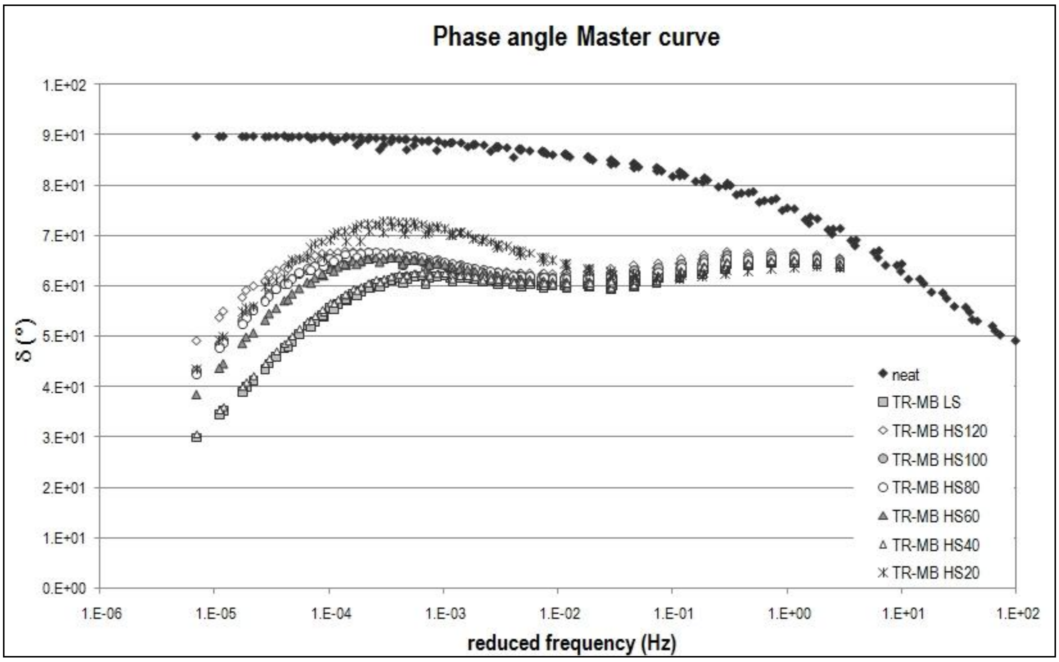


Figure 7.13b. Master curves of δ at 30°C of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

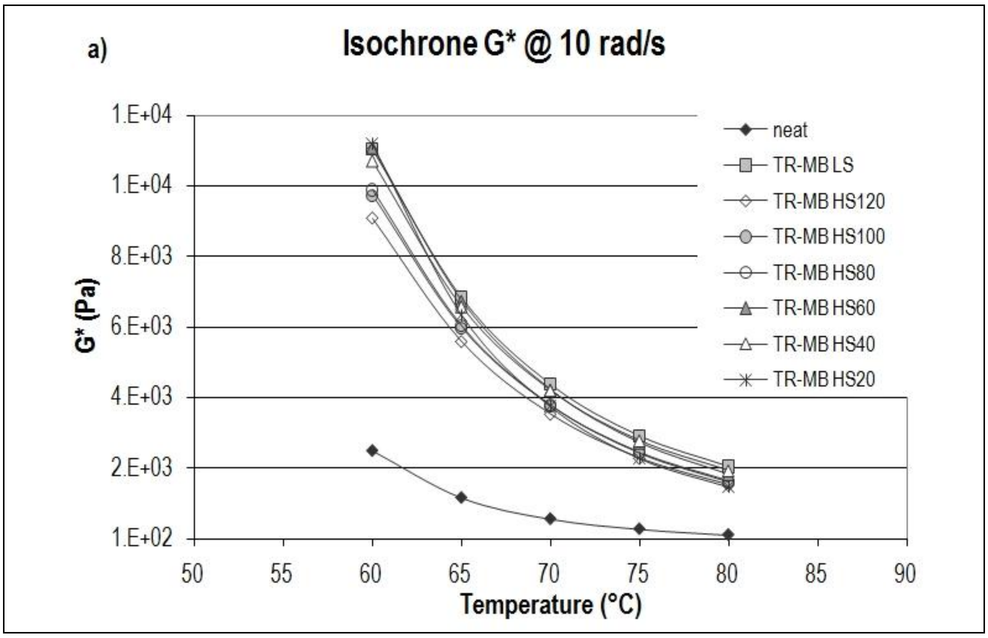


Figure 7.14a. Isochronal plots of G* of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

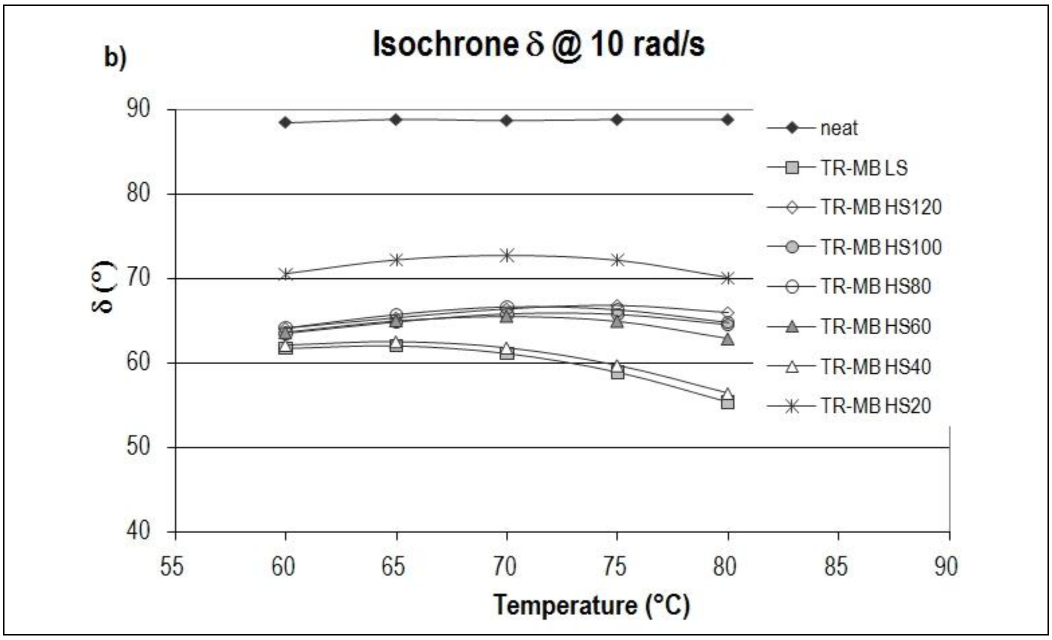


Figure 7.14b. Isochronal plots of δ of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

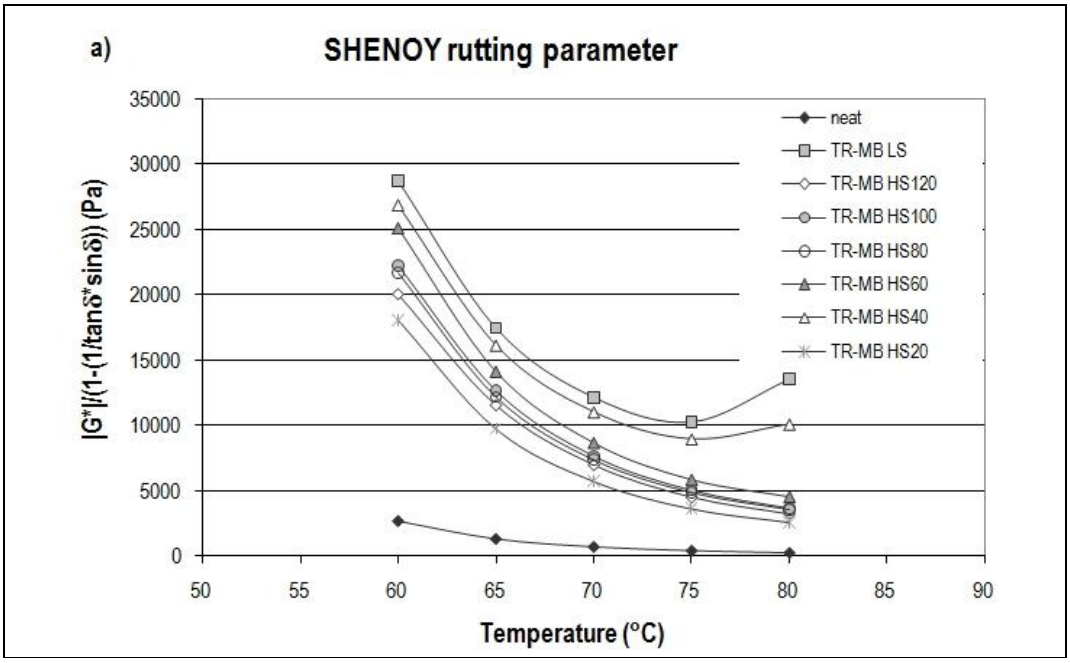


Figure 7.15a. Shenoy rutting parameters of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

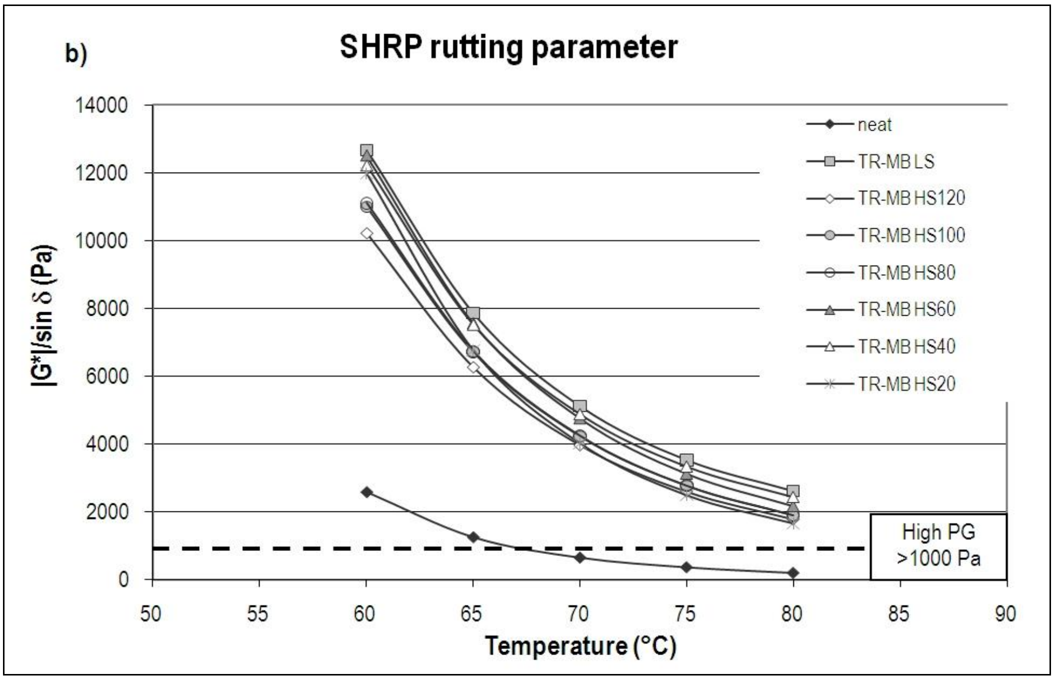


Figure 7.15b. SHRP rutting parameters of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

The TR-MB LS blend is the best performing amongst the ones produced, in terms of both stiffness and elastic properties. This result is probably explainable by considering that high shear mixing reduces tyre rubber crumbs size and its mechanical properties (§ 4.3.3). However, a high performing blend can also be obtained by using the HS protocol. In fact, the results obtained show that with a minimum blending time of about 40-60 minutes it is possible to obtain a blend, TR-MB HS40, produced with high shear but with similar rheological properties of the TR-MB LS that was obtained with mixing time of 120 minutes (3 times higher) and with a distributive mixing (no high shear). Morevoer these blends show phase angles value lower than 70°C, high critical temperature much higher than 80°C (Figures 7.15a,b) and, at low frequencies, phase angle master curves and isochronal plot show a plateau (Figures 7.13b, 7.14b.)

After 60 minutes, the high shear effect consisting in reducing the size of the rubber and quickening the reaction between the two phases, influences the rheological properties of the blend by decreasing its performance. This result is in agreement to what was found by other Authors (Takallou & Sainton, 1992). Therefore it is possible to confirm that the LS protocol can effectively provide a correct indication about the level of modification that it is possible to achieve when mixing bitumen with tyre rubber.

Other fundamental information coming from the DMA regards the maximum blending time. In fact, as it is possible to notice from the master curves and isochronal plots (Figures 7.10a,b and 7.12a,b), the best performing blend produced with high shear, TR-MB HS40, proves to be as stiff as the blend produced with 60, 80, 100 minutes of blending time. Moreover, a clear trend consisting in the decrease of the elastic properties and rutting resistance of the binders at high temperatures (low frequencies) with increasing the mixing time was observed.

As can be noticed from Figure 7.15b, all the TR-MBs have high critical temperature above 80°C (only the un-aged state was investigated). Moreover, it should be mentioned that by also evaluating the rutting parameters, at the temperature of 60°C (usally considered as the upper service temperature), it is possible to see again differences between the tested binders; this confirms the existence of the clear trend of mechanical properties decrease with the mixing time increase.

Finally it is possible to say that by using the high shear protocol to blend the selected raw materials at 180°C, a mixing time within a range of 40-60 minutes is considered to be the optimum time to have the highest level of performance. Moreover, a trend consisting in the decrease of the elastic properties and rutting resistance of the binders at high temperatures (low frequencies), with increasing high shear mixing time was noticed. By the way, at the selected processing temperature of 180°C, there is a low rate of decrease of properties with increasing the blending time up to 120 minutes. In fact, the final product TR-MB HS180 shows that it is still a well performing binder with clear rheological improvements.

7.5.3 Performance comparison with PMBs

Conventional properties

In this part of the study the optimized TR-MB was compared with two SBS polymer modified bitumens with two different levels of modification: SBS-MB Hard and SBS-MB Medium. Conventional physical properties i.e. Penetration (Pen), Softening Point (SP), Rotational Viscosity (RV) at 135°C and 160°C and rheology were used as the basis of the comparison. Table 7.7 shows the results of binder characterization. From the classical identification tests, it can be concluded that the TR-MB HS40 shows improvements in terms of SP, closer to the ones found for the SBS-MB Medium than to the one obtained for the SBS-MB Hard. Nevertheless, the rubber modified binder proves to be much stiffer and more viscous than the the SBS-MB Hard. Therefore, it is difficult

Table 7.7 : Physical and mechanical characteristics of the binders studied

Characteristic	**neat bitumen**	**TR-MB HS40**	**SBS-MB H**	**SBS-MB M**
Penetration 25°C (mm/10) - EN 1426	50	30	47	51
Softening Point (°C) - EN 1427	51	63	85	64
Apparent Viscosity at 177°C (Pa s) – ASTM D6114	-	3.150	-	-
Viscosity at 135°C, (Pa s) - EN 13302	0.429	5.950	2.450	1.290
Viscosity at 160°C (Pa s) - EN 13302	0.139	2.300	0.742	0.472

to make comparisons only based on conventional classification. Furthermore, it has to be noticed that the optimized TR-MB proves to have the characteristics (in terms of standard requirements for Pen, SP and Apparent Viscosity) to be classified as Asphalt Rubber type I or II (ASTM, 2009).

Optimum rubber content in low shear

Results obtained previously (§7.5.1) are confirmed when the performance of the different TR-MBs are compared with the rheological properties of two polymer modified bitumen modified with medium (SBS-MB M) and high content of Styrene Butadiene Styrene (SBS-MB H), selected, respectively, as lower and upper level of modification. Since the aim of this study is to obtain a binder containing tyre rubber but performing as well as a standard PMB, it is important to keep rheological properties of polymer modified bitumen as reference. Diagrams show that 15% is the minimum rubber content to be used in order to get a tyre rubber modified binder with significant improvements. In terms of stiffness (Fig. 7.17a), TR-MB with 12% of rubber is comparable with the SBS-MB M, but when looking at elastic properties (Fig. 7.17b) at least 15% of rubber is required to have similar performance.

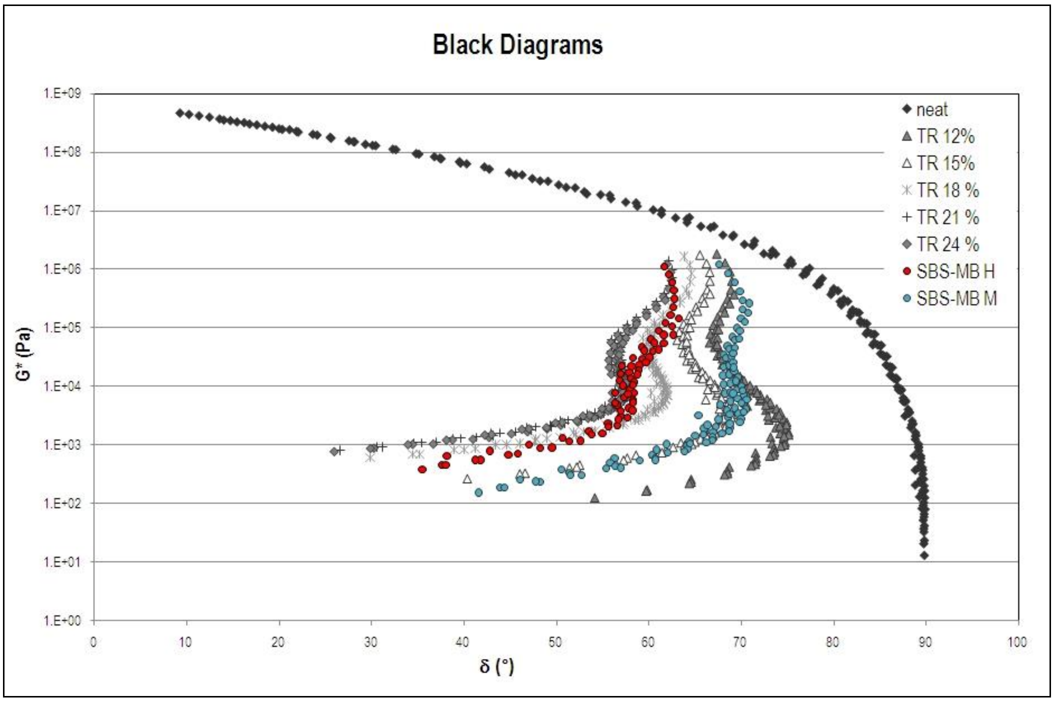


Figure 7.16. Assesing optimum rubber content thorugh analysis of Black diagrams

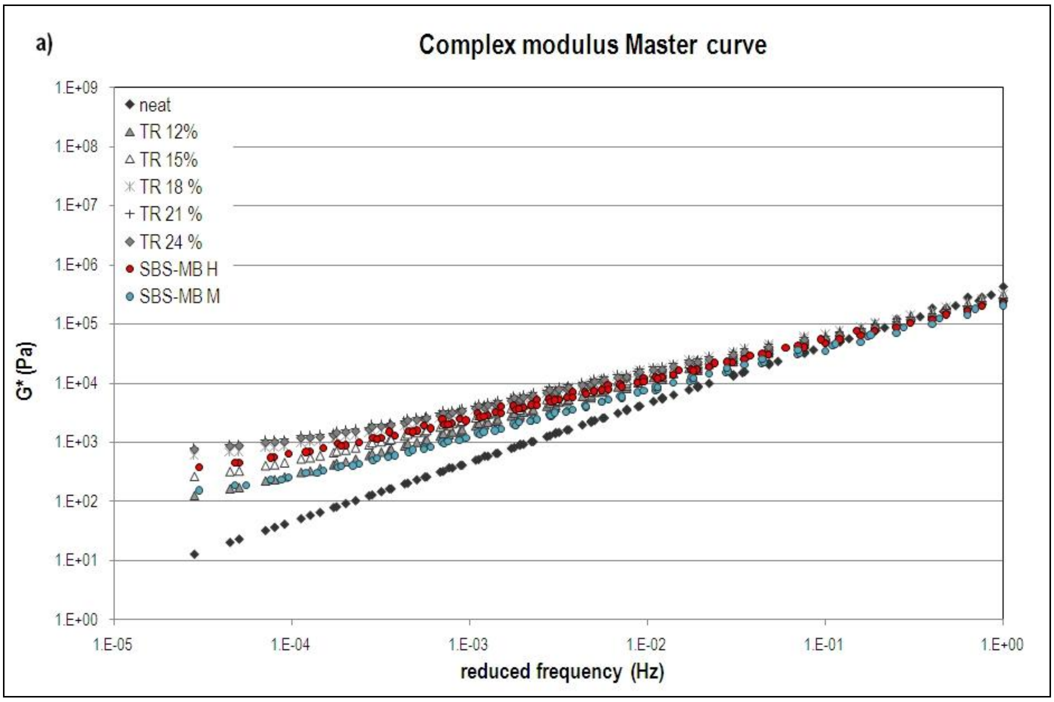


Figure 7.17a. Assesing optimum rubber content thorugh analysis of Master curves of G*at 30°C

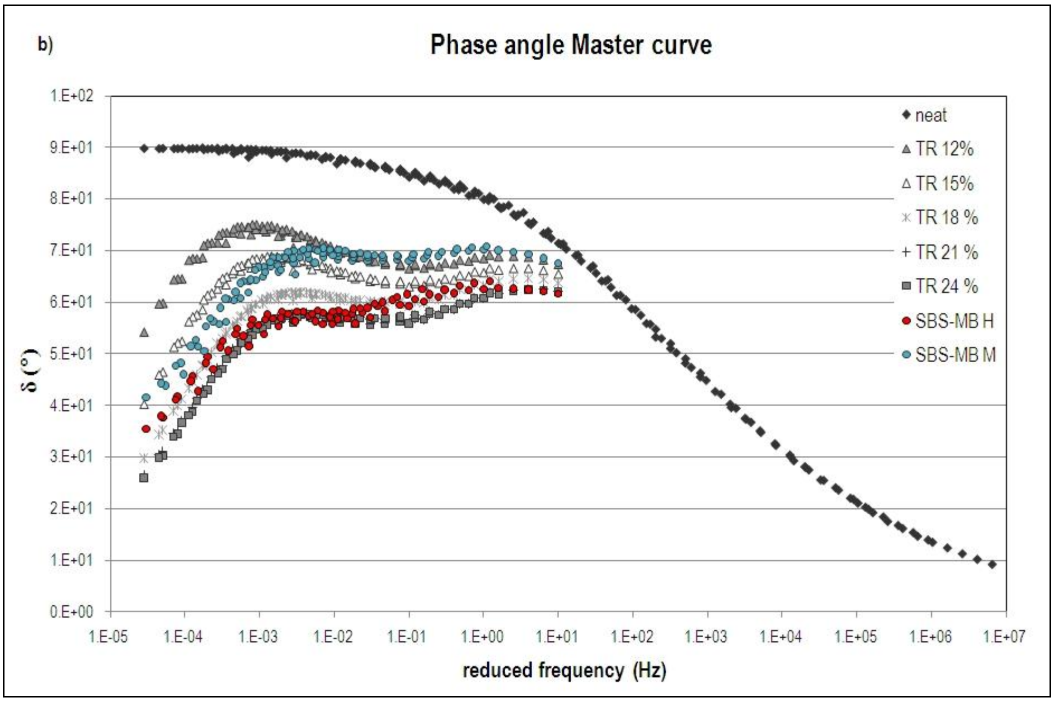


Figure 7.17b. Assesing optimum rubber content thorugh analysis of Master curves of δ at 30°C

As always, a good synthesis of the rheology of the binders is provided by Black diagrams (Fig. 7.16) that confirm what was previously assessed. Moreover if it is considered that passing from 18% to 24% of rubber content does not imply significant improvements, and taking SBS-MB H as rheological upper limit in terms of performance, the level of 18% as optimum rubber content is confirmed to be reasonable.

<u>Optimum mixing time in high shear</u>

The rheological analysis at high service temperatures confirms the results of the conventional tests and better demonstrates improvements in the elastic properties as well as in the reduction of the binder's temperature susceptibility. TR-MB HS120 (far above the optimum blending time) was included to emphasize the importance of the mixing time. In terms of Stiffness (G*) and elastic properties (δ) master curves and Black diagrams (Figs 7.18a,b and 7.19) show that both the TR-MBs are comparable to the SBS-MBs, but it is also clear to what extent the optimization of the blending time is fundamental in order to get a well-performing TR-MB. In fact, analyzing the phase angle master curve and the isochronal plot (given in Figure 7.18b and 7.20b), the TR-MB HS120 ends up being less elastic and, at high service temperatures, it is comparable only with the PMB with a medium level of modification (SBS-MB M).

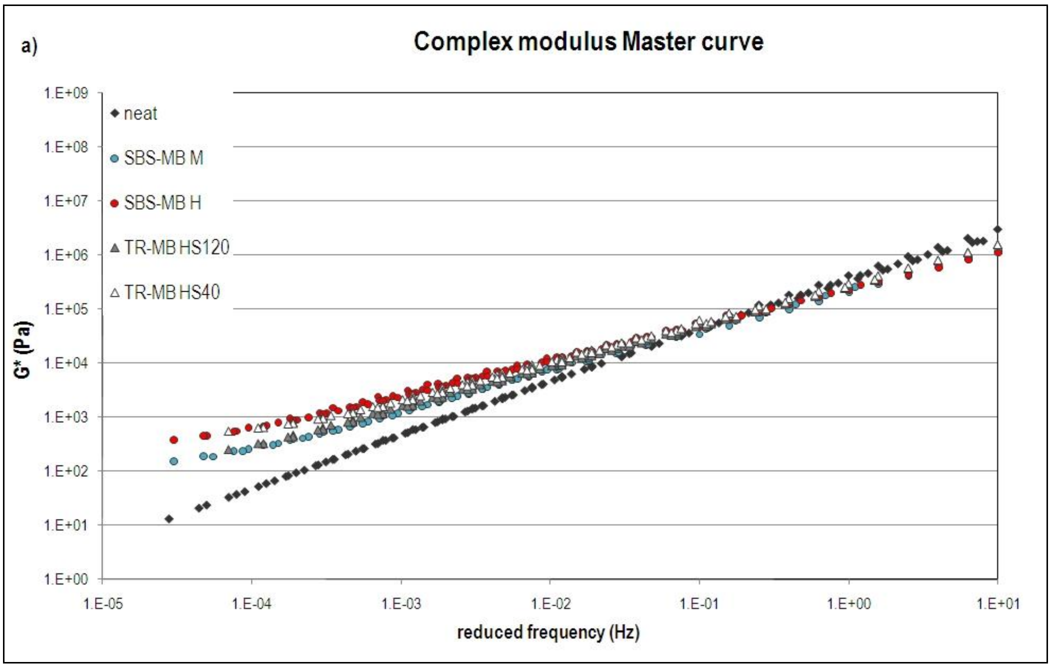


Figure 7.18a. Master curves of G* at 30°C of : TR-MB HS40, TR-MB HS120, PMBs and neat

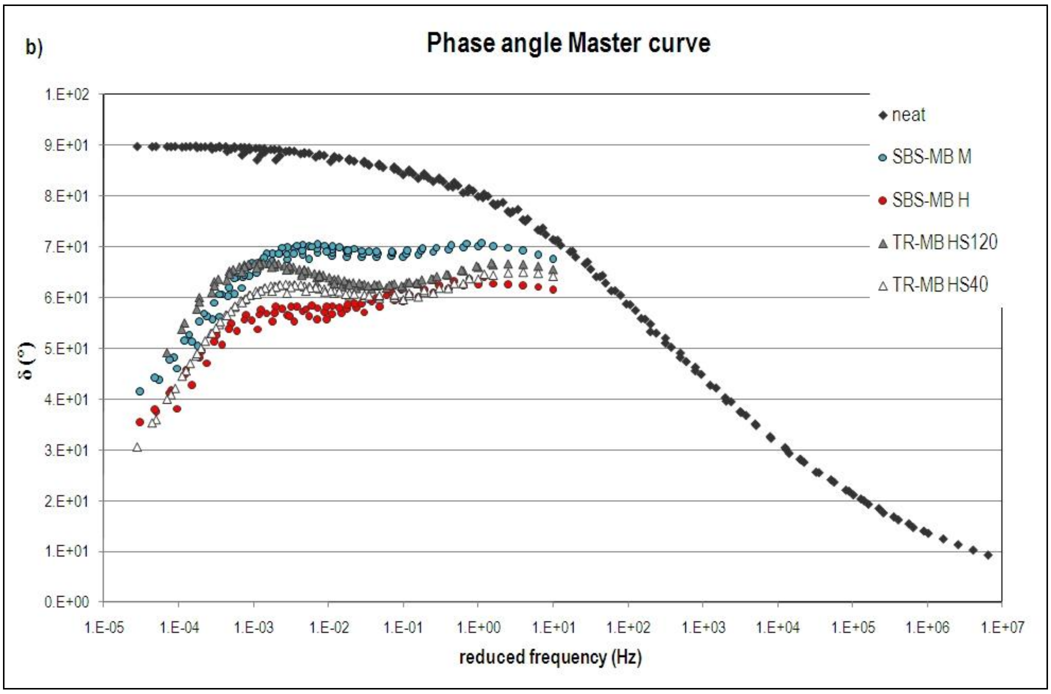


Figure 7.18b. Master curves of δ at 30°C of : TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

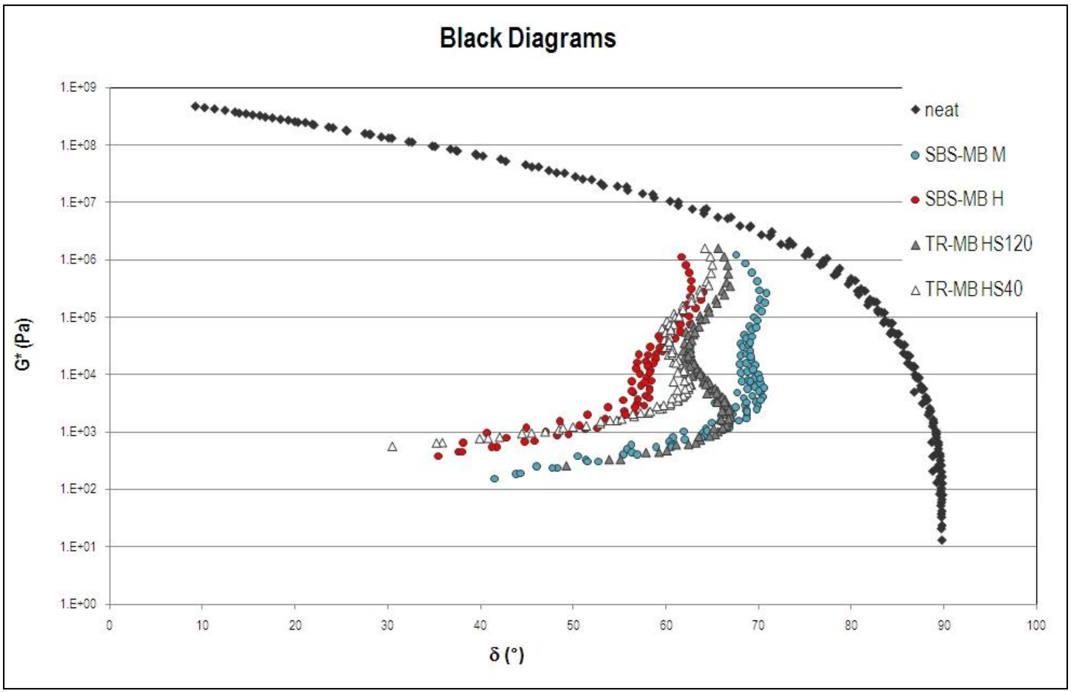


Figure 7.19. Black diagrams of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

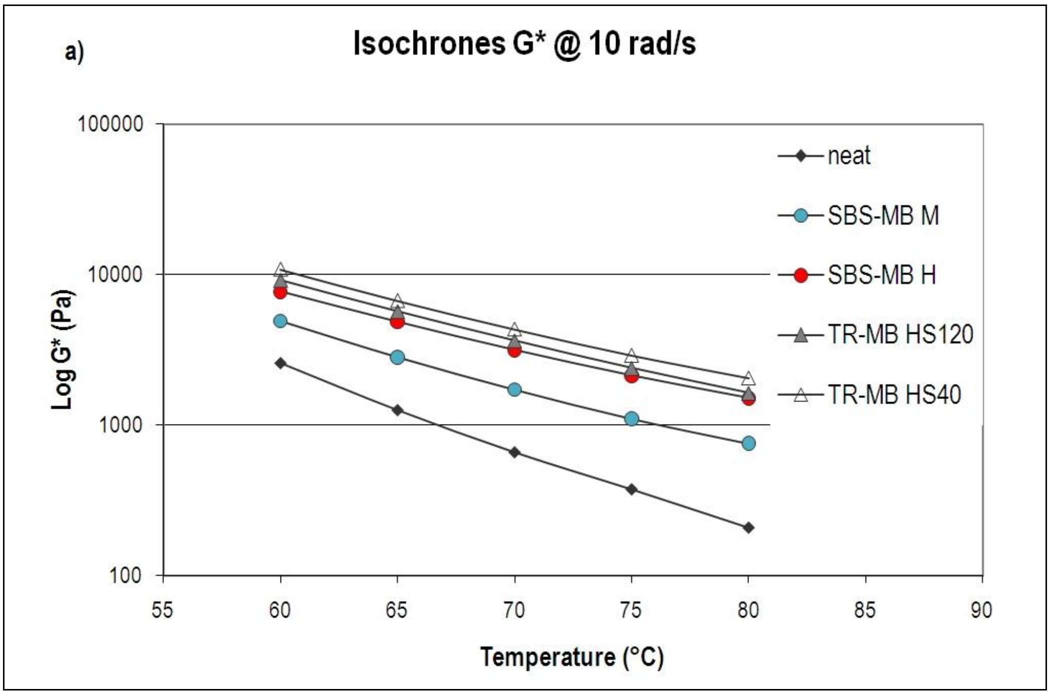


Figure 7.20a. Isochronal plots of G* of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

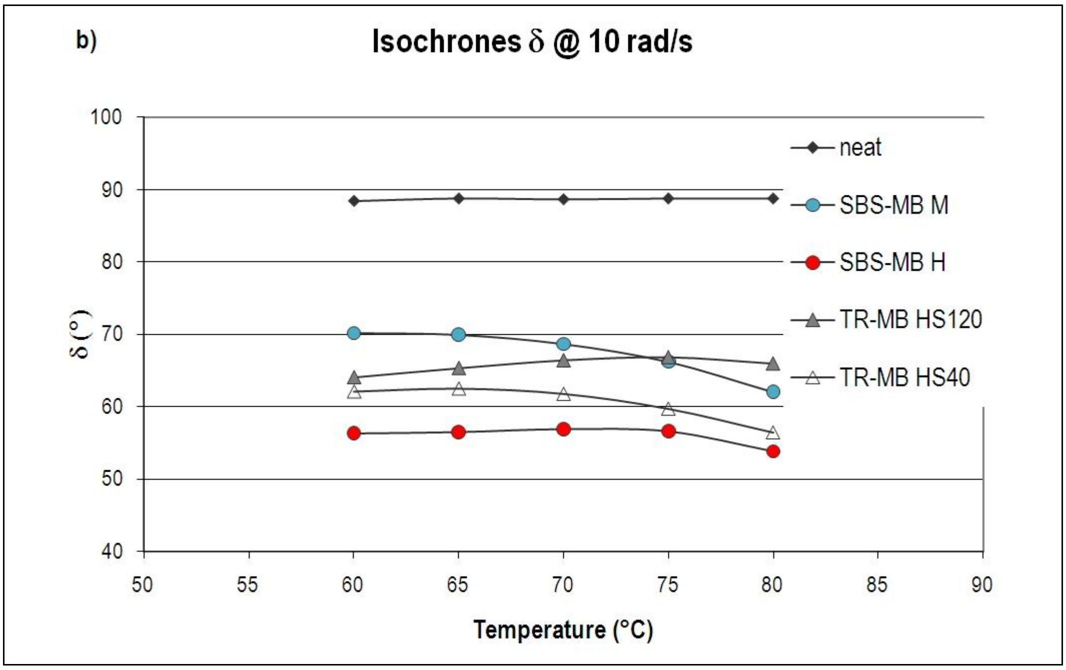


Figure 7.20b. Isochronal plots of δ of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

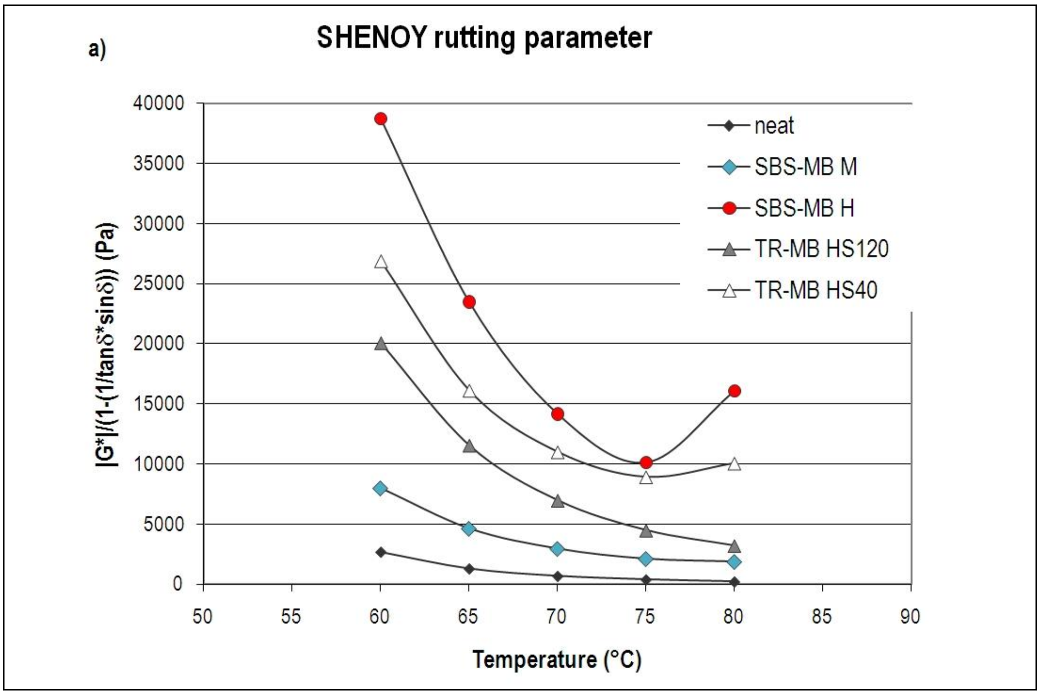


Figure 7.21a. Shenoy rutting parameters of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

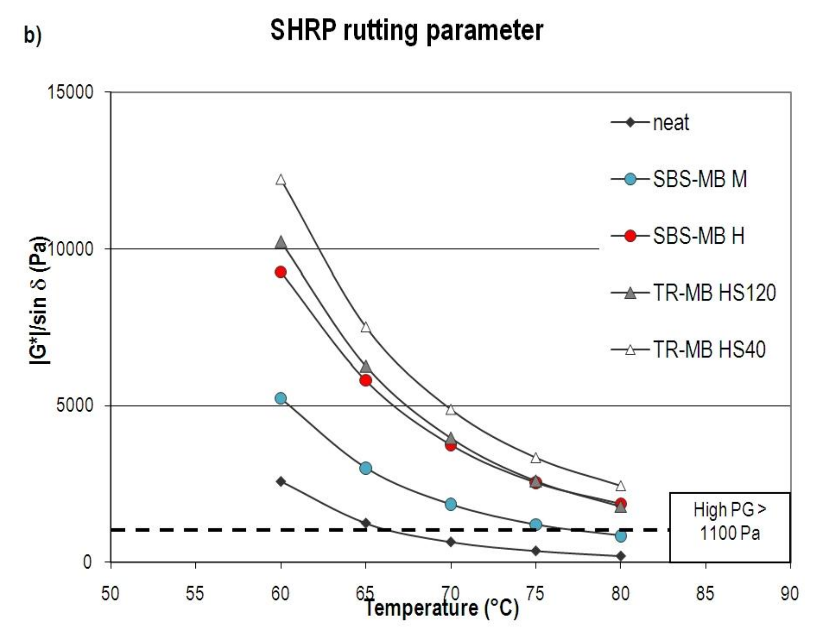


Figure 7.21b. SHRP rutting parameters of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

In conclusion, evaluation of the rutting parameters (Figure 7.21a,b) confirms the results explained before, but in this case SHRP and Shenoy's parameter, give different results. In fact, the best binder for SHRP seems to be the TR-MB HS40, while Shenoy's parameters indicate that SBS-MB H is the best binder against rutting, emphasising the differences clearly present also in the phase angle master curve. (Figs. 7.18b and 7.20b).

7.6 Summary of results

The aim of this section was to optimize the modification process and governing performance improvements that is possible to achieve when modifying road bitumen with tyre rubber using a wet process. The optimization study was performed by choosing the most suitable base bitumen according to its chemical properties (SARA analysis). Once the base bitumen was selected, a low shear protocol (LSP) was used for rubber content optimization, and high shear protocol to optimize the mixing time.

The LSP, consisted of adapting a Brookfield viscometer as a low shear mixer and checking rheological properties with a DSR. It proved to be a very useful tool in order to properly optimize a blend of tyre rubber with bitumen. Moreover, it involves a very low material consumption and also reduces testing time.

The defined protocol allowed comparison of the different bitumen-rubber blends, in relation to the different content of rubber, as well as to the blending times, with the possibility of carefully controlling the production temperature throughout the production process in low shear mode.

In order to prove the effectiveness of the studied protocol as well as the consistency of the final product, the obtained rubber-bitumen blends were characterized via rheological tests and afterwards compared with:

- rubber-bitumen blends obtained via high shear mixing performed with equipment able to keep a constant temperature throughout all the binder during the entire mixing process; all the other process variables were kept constant;
- two commercially available modified bitumens, with different content of elastomeric polymer type SBS, termed, “Medium” and “Hard.”

From the results obtained, it is possible to confirm that the LSP can effectively provide a correct indication about the reaction that occurs when mixing bitumen with tyre rubber.

Moreover, due to the fact that the Brookfield viscometer aims to disturb the sample as little as possible (distributive mixing), when it is adapted as a mixer it has a very low influence on the mechanical properties of the rubber particles, on the contrary of what happens when using a high shear mixer (dispersive mixing). This gives the possibility to obtain a high performance tyre rubber-bitumen blend, though it will not have a good dispersion of the particles within the mix. A consequence of this is that hot storage stability will probably be worst. Therefore, it is concluded that for the “production” of the TR-MBs, it is probably better to use the high shear mixing in order to enhance compatibility between the materials and reduce the time of mixing, but the low shear protocol was shown to be a really useful tool for the “predicition” of the rheological properties of the blends. In fact, due to its easy handling, LSP allowed finding the optimum tyre rubber content, and the minimum rubber content to be added to the selected bitumen to produce a well performing TR-MB. On this regards, In this work, it is believed that a good level of modification for a TR-MB is achieved only when three conditions are all verified: phase angle is constantly lower then 70°C, secondly when phase angle master curves and isochronal plot reach a plateau at low frequencies; at last when TR-MB show a high critical temperature over 80°C (measured with SHRP or Shenoy’s parameter).Thanks to the possibility of constantly monitoring the viscosity during the mixing, the estimation of the optimum blending time was a result of achieving the highest viscosity.

Establishing the correct mixing time was the other key parameter investigated to optimize the production of tyre rubber modified bitumen. As seen before, it has been proved that high shear mixing, is necessary to enhance compatibility of the rubber with the bitumen, and helps fast reaction of the rubber with the bitumen. So, high shear mixing protocol has been used to produce a TR-MB, with optimum rubber content previously determined, and a detailed DMA of binders produced at different mixing times were performed and the optimum mixing time established.

Finally, the comparison of the results from testing the TR-MB and those offered by two SBS Modified Bitumens (hard and medium), shows that only by choosing the correct rubber content and the mixing time is it possible to produce a tyre rubber modified bitumen with an high level of modification.

8. Curing variability effect on performance and stability of tyre rubber modified bitumens

8.1 Introduction

In this section of the work a deep investigation, consisting of a preliminary literature review (§4.3.3), an accurate selection of the materials (§7.3) and finally by the manufacturing of tyre rubber bitumen blends obtained by using both low shear and high shear, were performed with the aim of understanding the effect of processing temperature and shear rate on performance and hot storage stability of the final products.

Many studies (§4.3.3), have demonstrated that the applied mixing shear rate is fundamental to ensure proper dispersion of the rubber within the bitumen matrix and it was demonstrated that this helps the storage stability of the final blend (Attia & Abdelrahman, 2008). However, the processing device is secondary to the processing temperature; if the temperature is not high enough to produce rubber depoyimerisation/devulcanization to a great extent, the influence of the processing device is not significant (Navarro et al., 2006).

For this reason, a comparison between storage stability of blends with varying shear rate has not been included within this research. Instead, considering also the lack of results in literature, this section of the research includes a study on the effect of varying the processing temperature on the storage stability of Tyre Rubber Modified Bitumen.

8.2 Experimental programme

Low shear protocol (LSP) (§7.2.1) was firstly used to assess the change in rheological properties caused by the increase of temperature, but also to estimate the optimum rubber content when the processing temperature is raised to 210°C. Secondly, the high shear protocol (HSP) was used, by maintaining the other processing conditions constant, in order to optimise time and settling properties of the final product.

A final comparison with two Styrene-Butadiene-Styrene modified bitumens (SBS-MBs with a medium and a high level of modification), supplied by an Italian oil company, was also performed in order to have a reference in terms of performance and storage stability of the modified binders. All the binders were characterised performing rheological tests with a DSR, with the conditions indicated in the previous chapter (§7.4), and conventional tests such as: penetration (EN 1426, 2007), softening point (EN 1427, 2007) and rotational viscosity at 135°C and 160ºC (EN 13302, 2004).

8.2.1 Materials

A 50/70 pen bitumen (Table 7.4) and a 30 mesh Tyre Rubber (Table 7.5 and Fig. 7.5) were selected as base materials for the production of a Tyre-Rubber Modified Bitumen (TR-MB) in low shear and high shear at two interaction temperatures: 180°C and 210°C. Summarising, the following binders were considered for this study:

neat bitumen: pen 50/70 bitumen
TR-MB LS180: Tyre Rubber-Modified Bitumen (TR-MB) produced mixing at Low Shear (LS) base bitumen with the optimum content of 18% in weight of 30 mesh rubber
TR-MB HS180: Tyre Rubber-Modified Bitumen (TR-MB) produced mixing at High Shear (HS) base bitumen with 18% in weight of 30 mesh rubber

TR-MB LS210:	Tyre Rubber-Modified Bitumen (TR-MB) produced mixing at Low Shear (LS) base bitumen with the optimum content of 18% in weight of 30 mesh rubber
TR-MB HS210:	Tyre Rubber-Modified Bitumen (TR-MB) produced mixing at High Shear (HS) base bitumen with 18% in weight of 30 mesh rubber
SBS-MB H:	modified bitumen (SBS-MB) with a high content of SBS (Hard - H)
SBS-MB M:	modified bitumen (SBS-MB) with a medium content of SBS (Medium - M).

8.3 Effect of temperature on Low Shear blends

A total of 16 blends were made using the low shear mixing procedure (§ 8.4.1) and investigating a range of rubber percentages from 15% to 24%, with 3% steps by weight of bitumen, for both mixing temperatures: 180°C and 210°C. As a matter of fact, adding tyre rubber to bitumen allows to greatly increase the high temperature end of the paving grade, leaving the low temperature slightly better. More specifically, a rule of thumb says that for every 1% of added polymer, 2°C in high temperature PG are typically gained. On the low temperature end, the rule becomes for every 1% of added polymer, there is a 1°C reduction in low temperature PG. Since the PG classes are based on 6°C steps, the typical 3% polymer-content modification generally allows to gain one high-temperature class leaving the low temperature sometimes unchanged. (Lesuer, 2009).

8.3.1 Optimum blending time

The first important result coming from this preliminary study is represented by the maximum blending time, for each percentage of rubber, in order to get the best performance at low shear (peak viscosity). As shown by results in Figures 8.1 and 8.2 and Table 8.1, by increasing the temperature of the process to 210°C gives a significant reduction of both peak viscosity and optimum blending time. Both the effects are probably a consequence of the partial depolymerisation of the vulcanised tyre rubber that implies a loss of performance (Fig. 8.3).

Table 8.1. Results of the monitoring of the Low Shear mixing procedure at 180°C and 210°C

	180°C		***210°C***	
	Viscosity	*Optimum Time*	*Viscosity*	*Optimum Time*
% TR	*mPa = cP*	*min*	*mPa = cP*	*min*
0	80		30	
15	500	90	330	45
18	725	120	500	60
21	1110	150	820	75
24	1800	180	1100	75

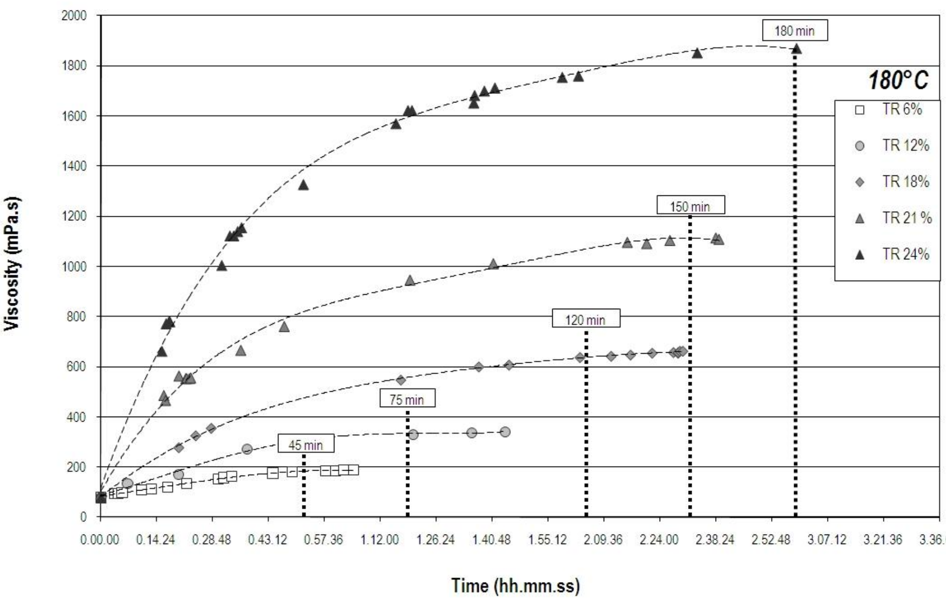


Figure 8.1. Results of the Low Shear mixing at 180°C using the Brookfield Viscometer

It has to be noted how the blending procedure of the low shear protocol helped to verify that the TR-MB LS210 resulted in a less heterogeneous mix than TR-MB LS180. Indeed, during the blending, the viscosity of the binder was similar in both the top and bottom sections of the sample.

A confirmation of these results was obtained by performing a simple test (§8.5.1) consisting in an amplitude sweep, at 10rad/s and at 80°C (higher testing temperature), performed on the binders produced in low shear and on neat bitumen. As it is possible to see in figure 8.3, when subjected to an amplitude sweep neat bitumen keeps its mechanical strength, in terms of performance (G*/sinδ), constant even up to 1000% strain.

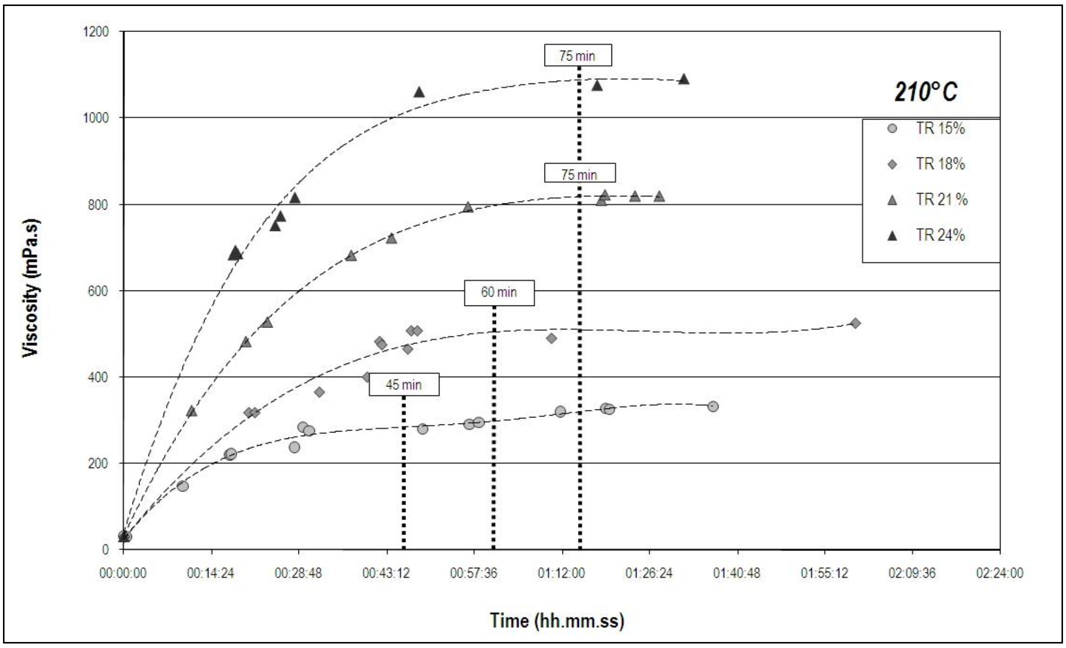


Figure 8.2. Results of the Low Shear mixing at 210°C using the Brookfield Viscometer

For this reason, neat bitumen can be considered as reference of a rheologically homogeneus material. Instead, both modified binders begin dropping their performance (leaving linearity region) much before the neat bitumen. The TR-MB LS180 starts leaving its linearity region already at 1-5% strain and with a much higher rate than the binder produced at 210°C which extends its homogeneous rheology range up to 15-20%. This show that less heterogeneous TR-MB LS210 can be thought as less shear susceptible (Fig. 8.3).

8.3.2 Optimum rubber content

After low shear production, the material was tested through a Dynamic Mechanical Analysis (DMA) which helped to asses, as seen previously (§7.5.1), the optimum rubber content at both temperature 180°C and 210°C. Black diagrams (Figs. 8.4 and 8.5), rheological master curves at a reference temperature of 30°C (Figs. 8.6 and 8.7), isochronal plots (Figs. 8.8 and 8.9) and rutting parameters evaluation (Figs. 8.10 and 8.11) were used as base of the estimation.

Master curves of the tyre rubber modified binders, at both temperatures, were obtained by using the same shift factors.

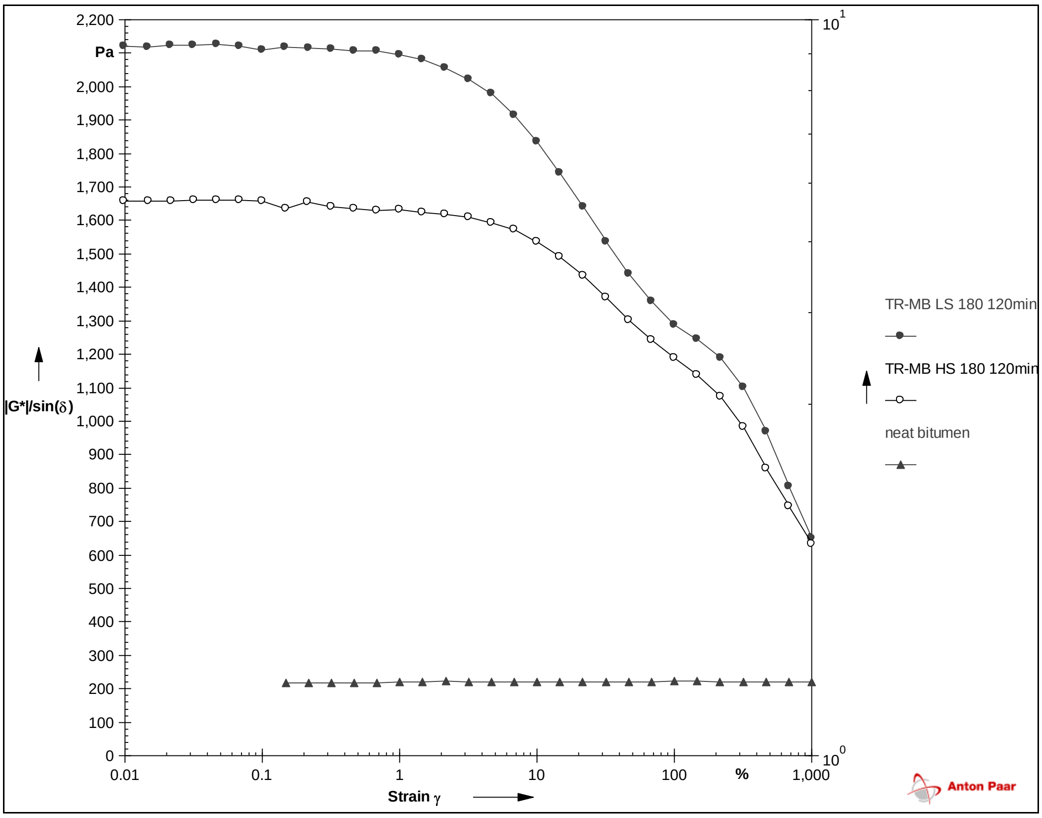


Figure 8.3. Amplitude sweep @ 80°C and 10rad/s performed on neat and TR-MB LS

This shift factors curve were different from the one obtained for their base bitumen (Appendix E). Results show that at low frequencies, which corresponds to high temperatures, modification with rubber makes the binder stiffer (increase of the complex modulus) and infers a better elastic behavior (decrease in the phase angle). It has to be notes how the TR-MB LS210 shows less properties variability with increasing the rubber content: it always shows slightly reduced stiffness than TR- MB LS180 (Fig. 8.5, 8.6, 8.11a and 8.12a), but it has better and more stable elastic behavior at 15-18% rubber content and a smoother phase angle curves (Fig. 8.7, 8.8, 8.11b and 8.12b), resulting in smoother black diagrams (Fig. 8.9, 8.10). This phenomenon confirms the achievement of a more homogeneus blend, due to the higher processing temperature, but highlights also that higher depolymeresation rate of rubber does not prevent to have a tyre rubber-bitumen blend that perform still well. Moreover, isochronal plots show the clear improvements in the thermal susceptibility and elastic properties of both tyre rubber bitumen binders compared to the base bitumen (Figs. 8.11 and 8.12).

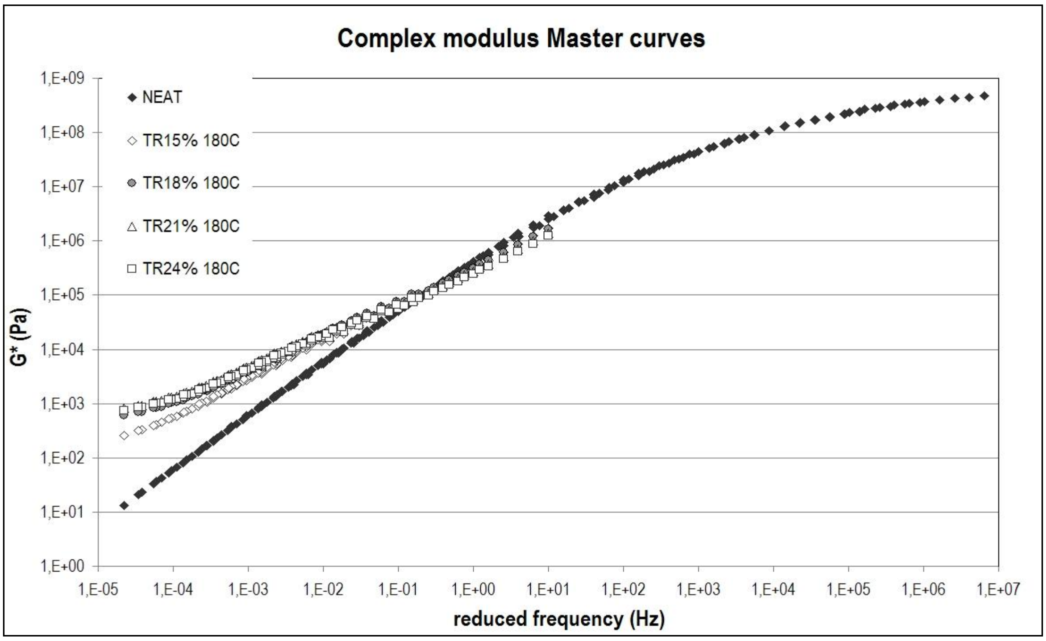


Figure 8.5. . Master curves of G∗ at 30°C of low shear TR-MBs LS 180 and neat bitumen

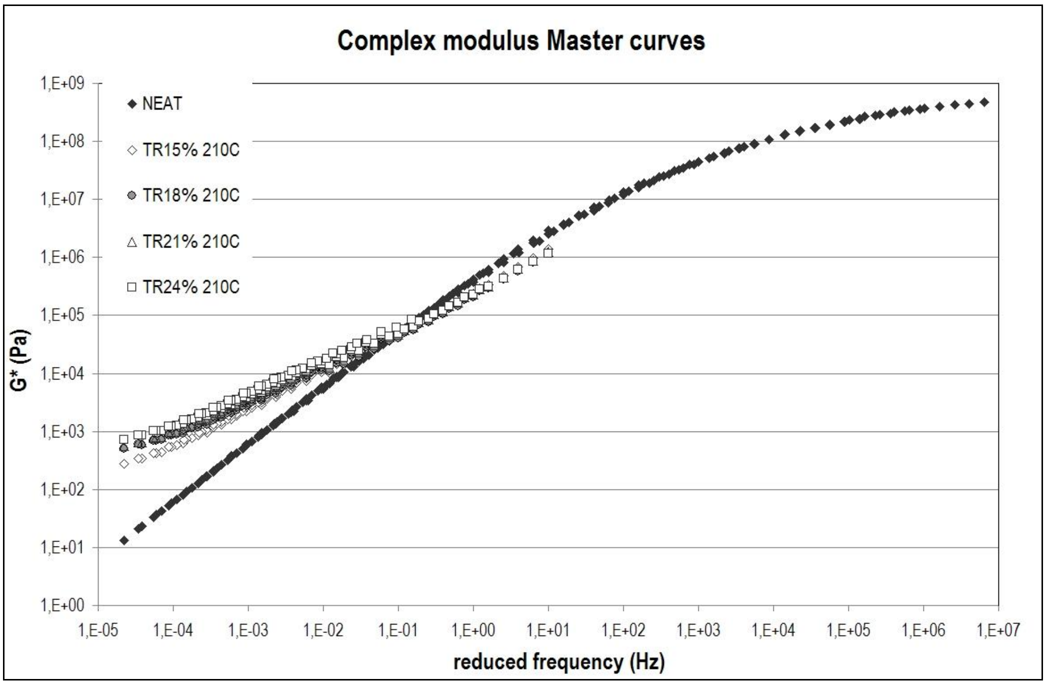


Figure 8.6. . Master curves of G∗ at 30°C of low shear TR-MBs LS 210 and neat bitumen

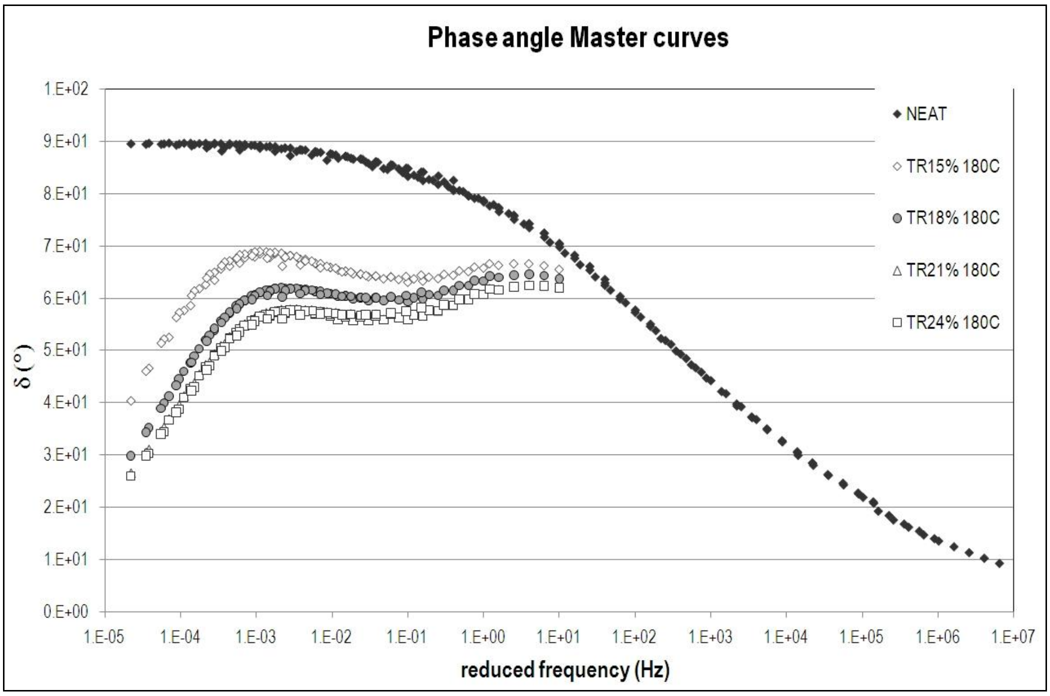


Figure 8.7. Master curves of δ at 30°C of low shear TR-MBs LS 180 and neat bitumen

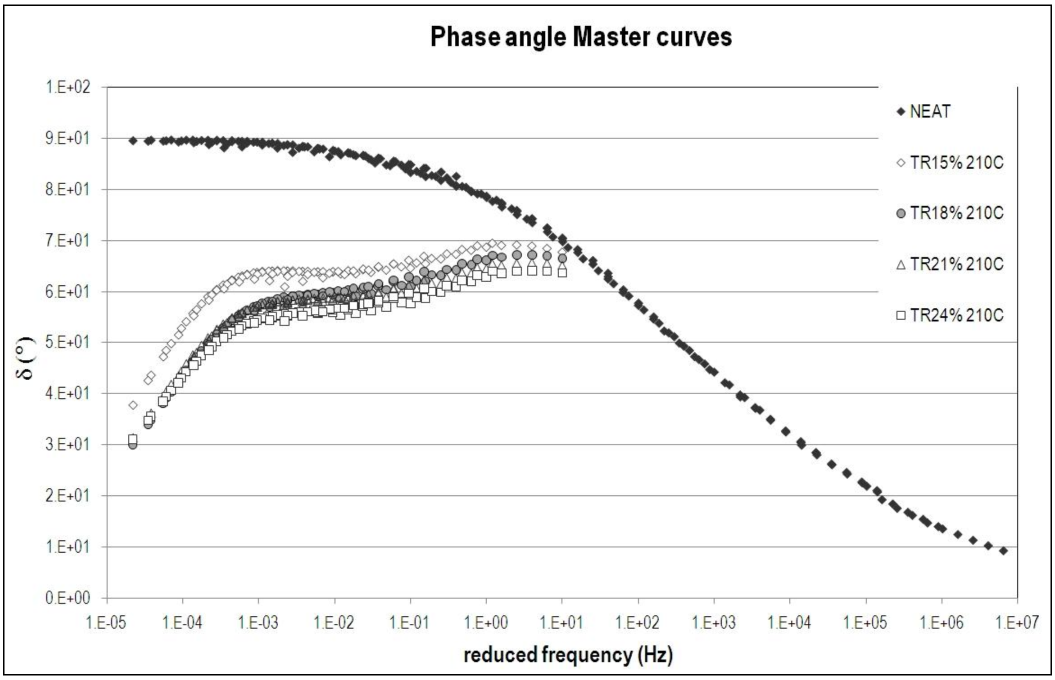


Figure 8.8. Master curves of δ at 30°C of low shear TR-MBs LS 210 and neat bitumen

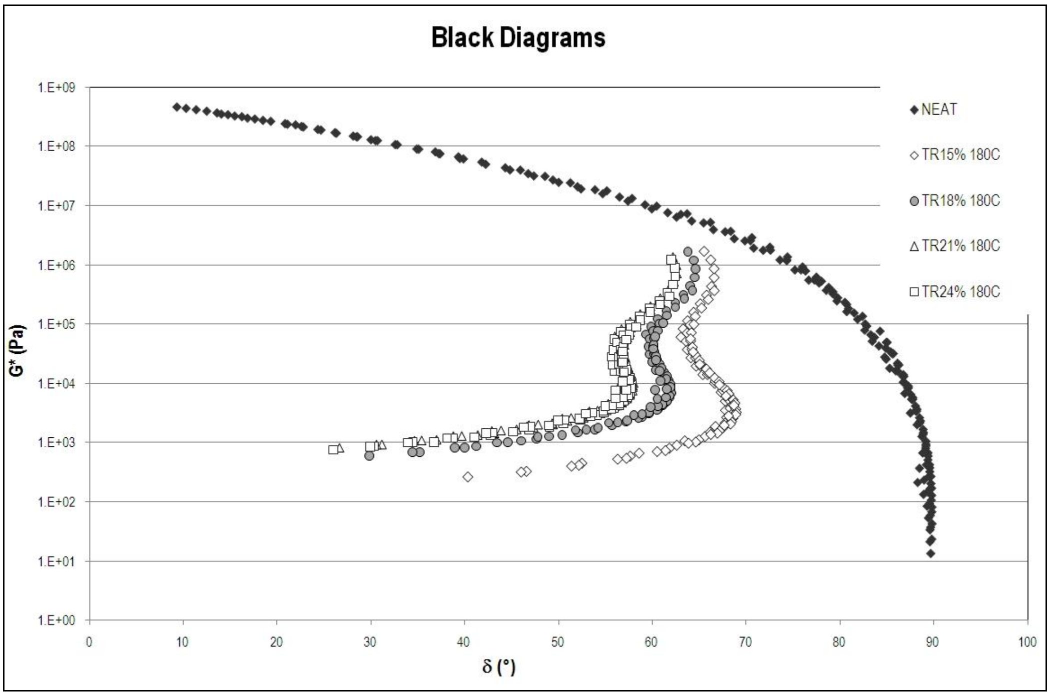


Figure 8.9. Black diagrams of low shear TR-MBs LS 180 and neat bitumen

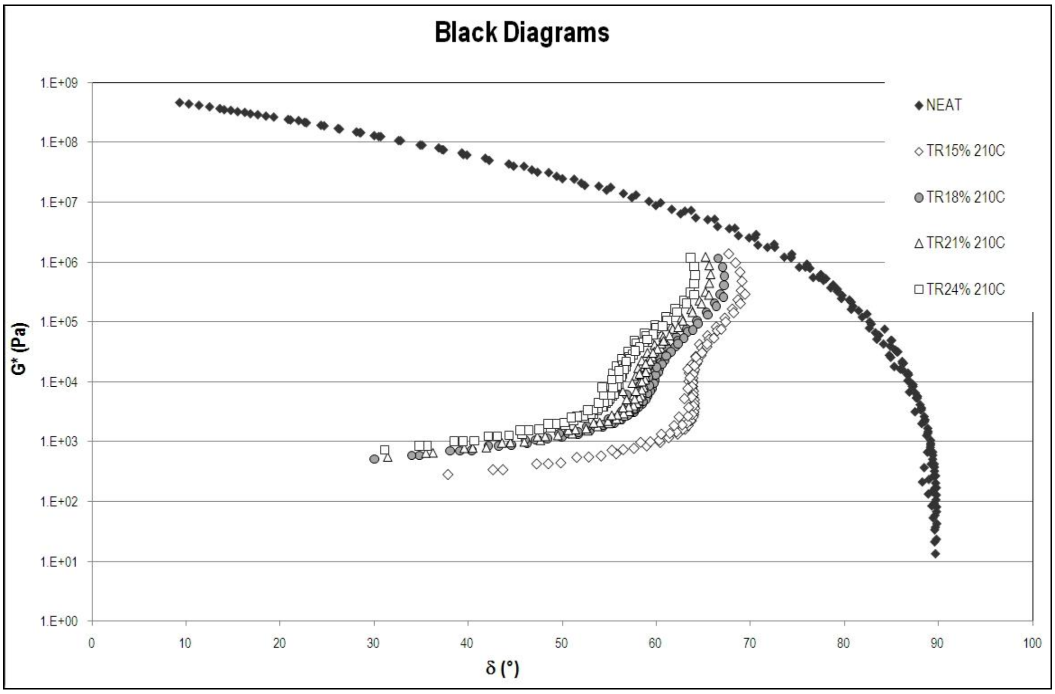


Figure 8.10. Black diagrams of low shear TR-MBs LS 210 and neat bitumen

From the evaluation of the rutting parameters, as determined via the SHRP, |G*|/sinδ, and Shenoy's parameters (§3.3.4), it is possible to notice that for both modified binders, the high critical temperature (higher value of the SHRP Performance Grade) of the un-aged neat bitumen increases from 66°C to more than 80°C when at least 15% of rubber is added (Figs.8.12 and 8.13). Shenoy's parameter |G*|/(1-(1/sinδtanδ) gives similar information and emphasises the variability of the phase angle (Figs. 9.6 and 9.7), but at temperatures above 70°C and over 18% of rubber content, it shows an incoherent trend; this is probably due to the prevalent effect of the rubber matrix at high temperatures. From this analysis it is possible to conclude that also by raising the processing temperature to 210ºC, 15% rubber content seems to be the minimum to obtain a TR-MB with good performance.

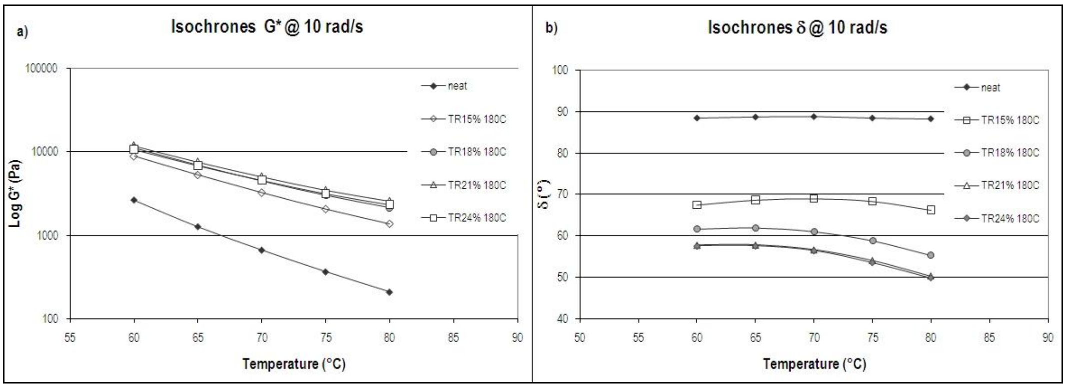


Figure 8.11. Isochronal plots of G*(a) and δ (b) of low shear TR-MBs LS 180 and neat bitumen

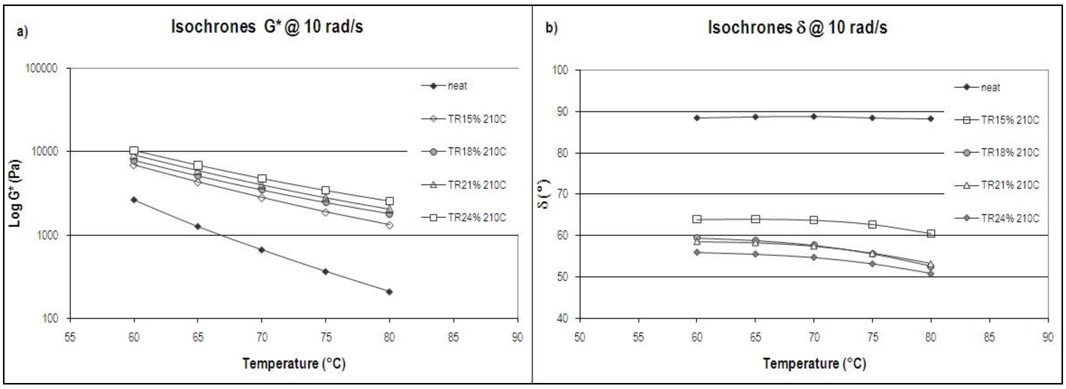


Figure 8.12. Isochronal plots of G*(a) and δ (b) of low shear TR-MBs LS 210 and neat bitumen

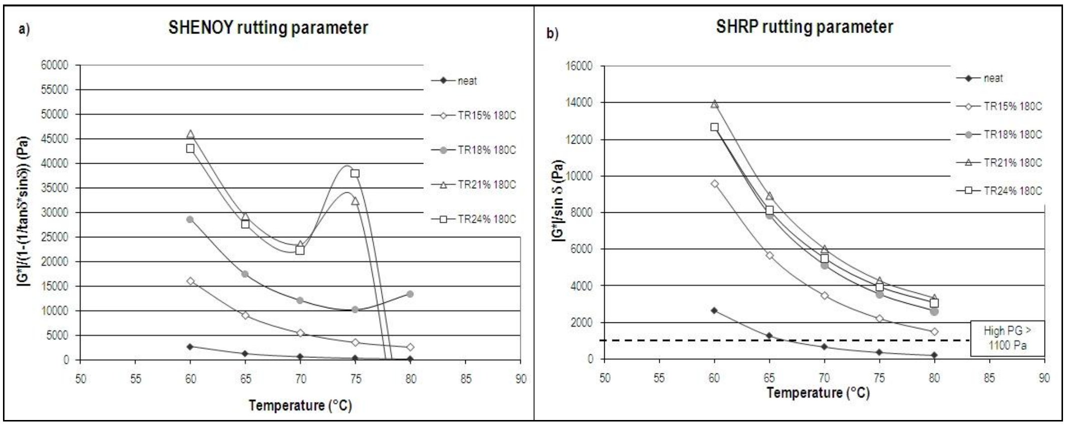


Figure 8.13. Shenoy (a) and SHRP (b) rutting parameters of low shear TR-MBs LS 180 and neat

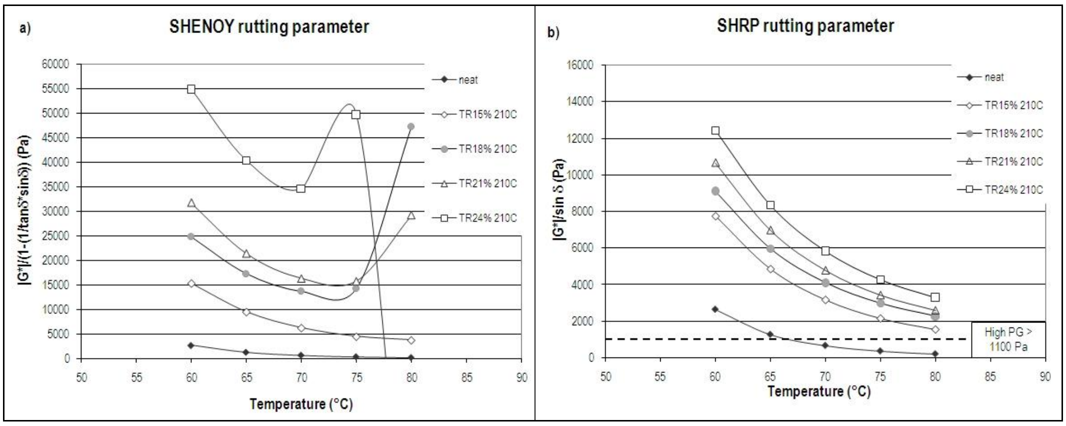


Figure 8.14. Shenoy (a) and SHRP (b) rutting parameters of low shear TR-MBs LS 210 with various rubber contents and neat bitumen

Moreover, it appears that it is not possible to appreciate any significant improvement in terms of stiffness, elastic behavior, thermal susceptibility and rutting resistance when passing from 21% to 24% tyre rubber in the blend. For these reasons and also to not work with high viscosities, for both binders, 18% was fixed as optimum rubber content to be used in the second part of the study.

8.4 Effect of temperature on High Shear blends

In the second part of the study, high shear blending protocol was used to optimize the mixing time. The blending of rubber and bitumen at high shear was carried out using the

Table 8.2: High shear mixer blending protocol

bitumen mass g	rubber mass (18% of bitumen mass) g	rubber size (30 mesh) mm	total weight g	mixing time min	mixing speed rpm	mixing temp. °C
1700	300	0-0.6	3410	120	3500-5000	180-210

high shear blending protocol (§ 8.4.1). Table 8.2 summarises the mixing parameters used in the blending procedure.

8.4.1 *Optimum blending time*

All the samples, with different mixing time, were tested by estimating the so-called apparent viscosity at 177.5°C (ASTM, 2009) that is used in the asphalt rubber production as the key parameter to assess the optimum performance.

Results are shown in Figure 8.15 in which it is clearly indicated how the reaction at 210ºC is much faster. The peak is reached within the first 20 minutes, and a clear degradation is already noticeable after 40 minutes. After that, the viscosity remains constantly at a value of about 2500 mPa.s, so lower than the stable viscosity obtained with the blend processed at 180°C. All the sample were tested with two repetitions.

The latter result is not surpring, because at 210°C the rubber is subjected to a partial depolymerization and devulcanization that clearly decrease the performance of the final blend (Abdelrahman & Carpenter, 1999).

In order to better understand these results, also a DMA at high service temperatures (30÷80°C) was performed for all the TR-MB HS samples. From the comparison of the rheological properties, assessed by Black diagrams and Master curves (Figs. 8.16, 8.17 and 8.18), it is possible to notice that on average, for both processing temperatures, all the binders show improvements in terms of stiffness and elastic properties at high testing temperatures, if compared with the neat bitumen. The most important information, provided by those diagrams, is the variability of the rheological properties relative to the mixing time and processing temperature.

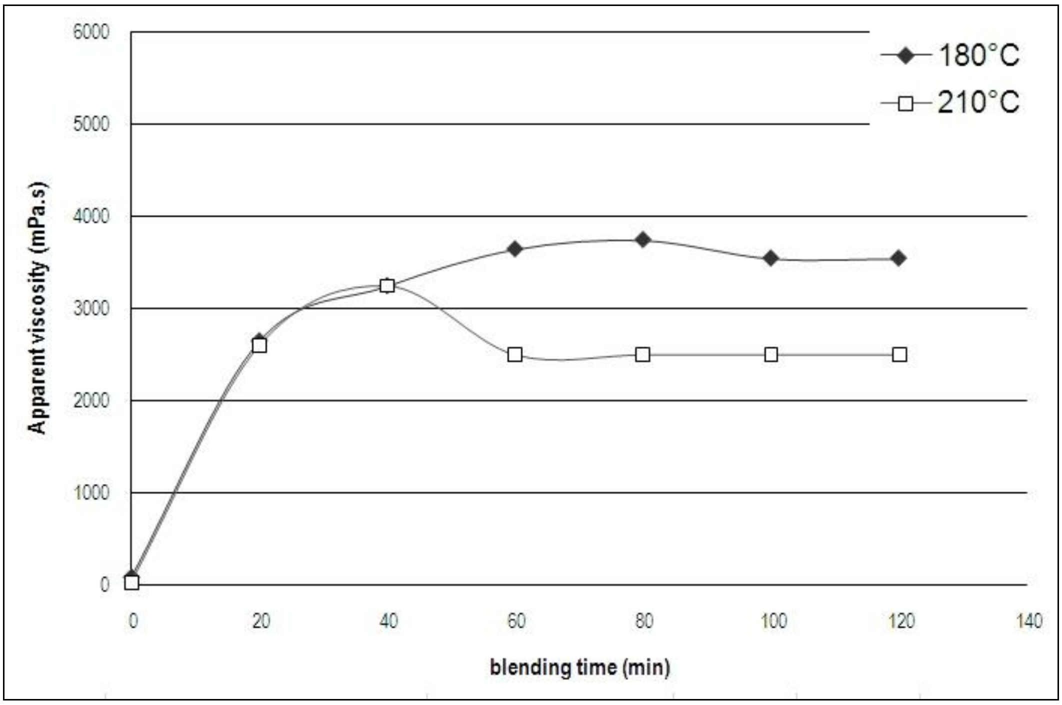


Figure 8.15. Apparent viscosity @ 177.5ºC of TR-MB HS at different time and temperatures

In fact, the TR-MB HS processed at 180°C, after it has reached its peak performance (40-80 minutes) maintains its properties, more or less constant, up to 120 minutes of mixing time. Only a low decrease of rheological properties was noticed: about 10-20% less of peak. Instead, the TR-MB HS processed at 210°C, not only reaches its peak performance in a shorter time (20-40 minutes), but after 120 minutes of high shear mixing the lose of properties is about 50-60% less of the peak. This is in terms of the lose of elastic properties as well as stiffness (Figs. 8.20 and 8.21) and anti-rutting behavior (Figs. 8.22 and 8.23). Therefore, by raising the temperature from 180°C to 210°C, significantly accelerates the reaction between tyre rubber and bitumen.

An interesting result is provided by the Shenoy’s parameter diagram which, in contrast with what was reported for the low shear blends, always shows a coherent trend. This is probably due to finest mixing provided by the high shear, which reduces crumbs agglomeration and so minimises the presence of big particles within the blend. Other information that should be underlined is the optimum blending time in high shear: for both temperatures, it is about a third of that necessary to obtain the equivalent blend in low shear mode (Tab 8.1), in agreement with what has been found by other Authors (Takallou & Sainton, 1992).

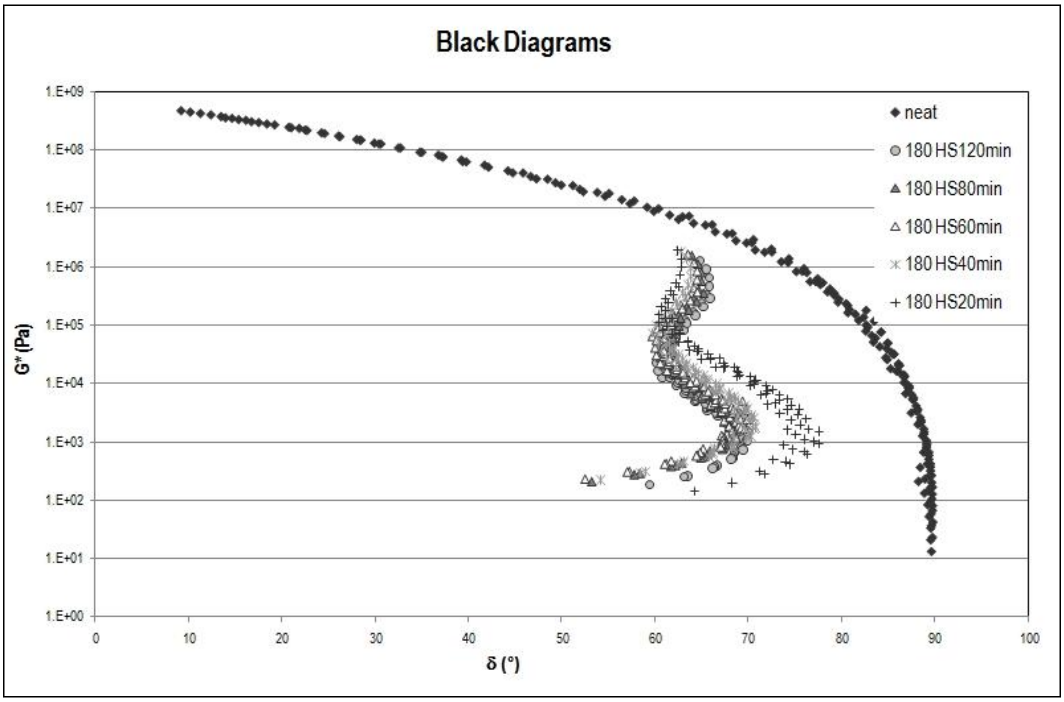


Figure 8.16. Black diagrams of: TR-MB HS180 at different blending time

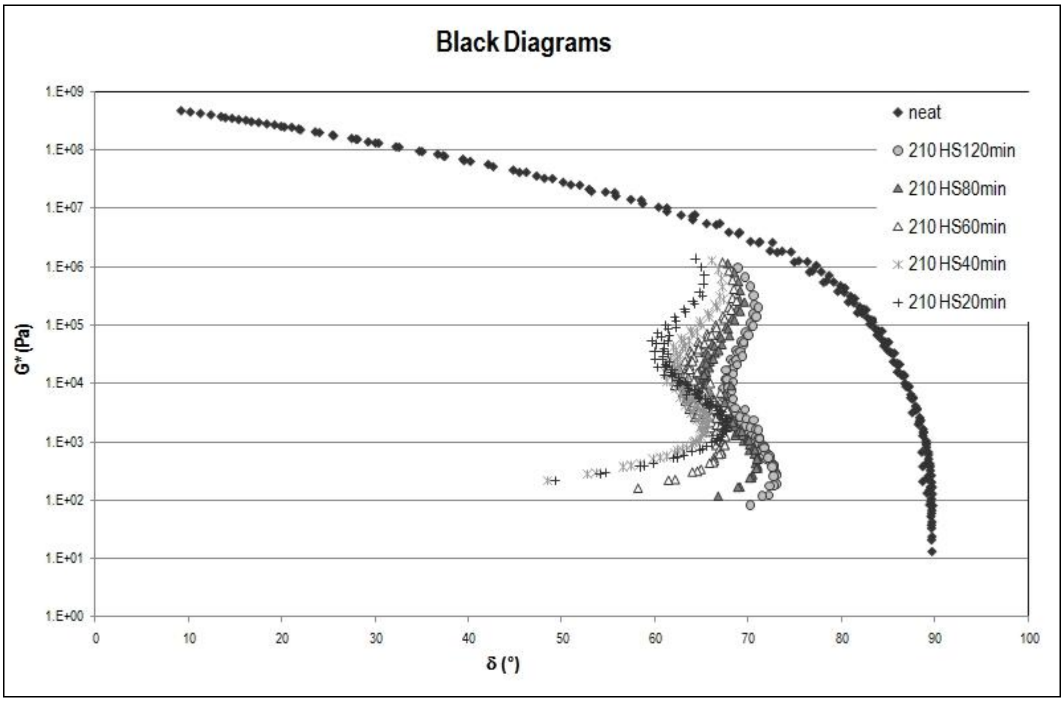


Figure 8.17. Black diagrams of: TR-MB HS210 at different blending time

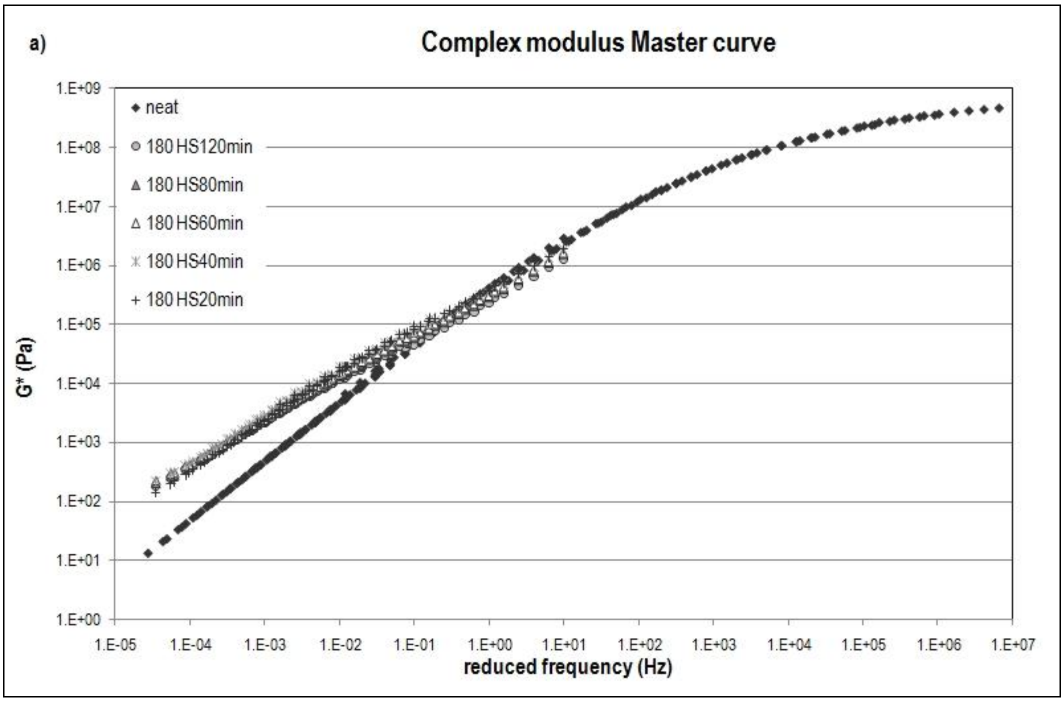


Figure 8.18a. Master curves of |G*| at 30°C of: TR-MB HS180 at different blending time

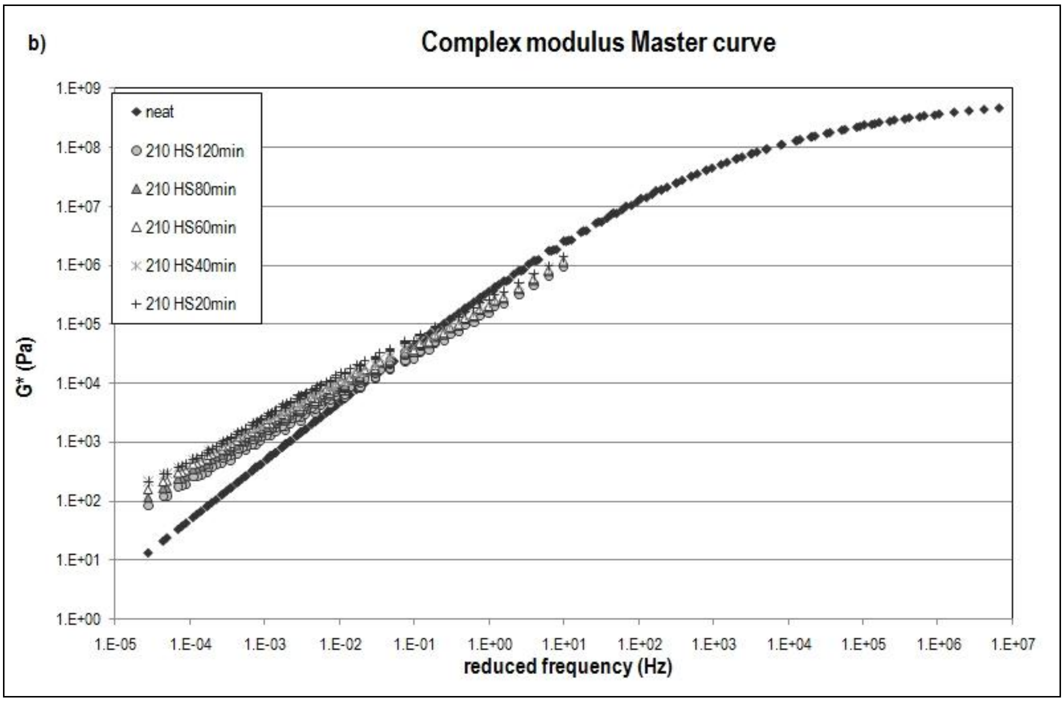


Figure 8.18b. Master curves of |G*| at 30°C of: TR-MB HS210 at different blending time

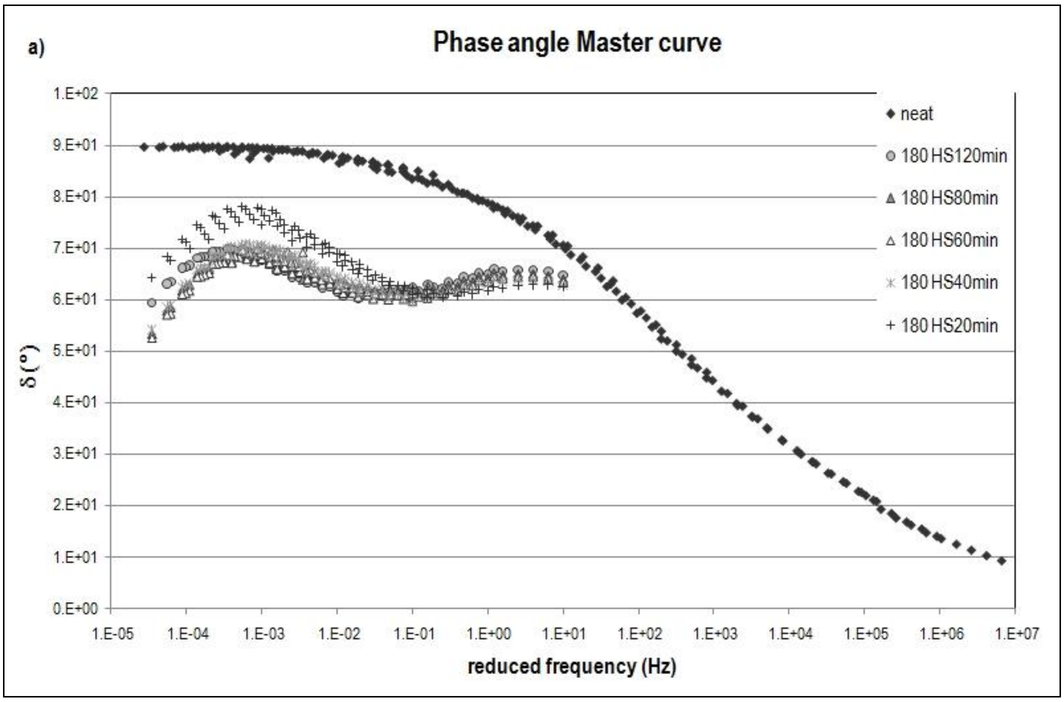


Figure 8.19a. Master curves of δ at 30°C of: TR-MB HS180 at different blending time

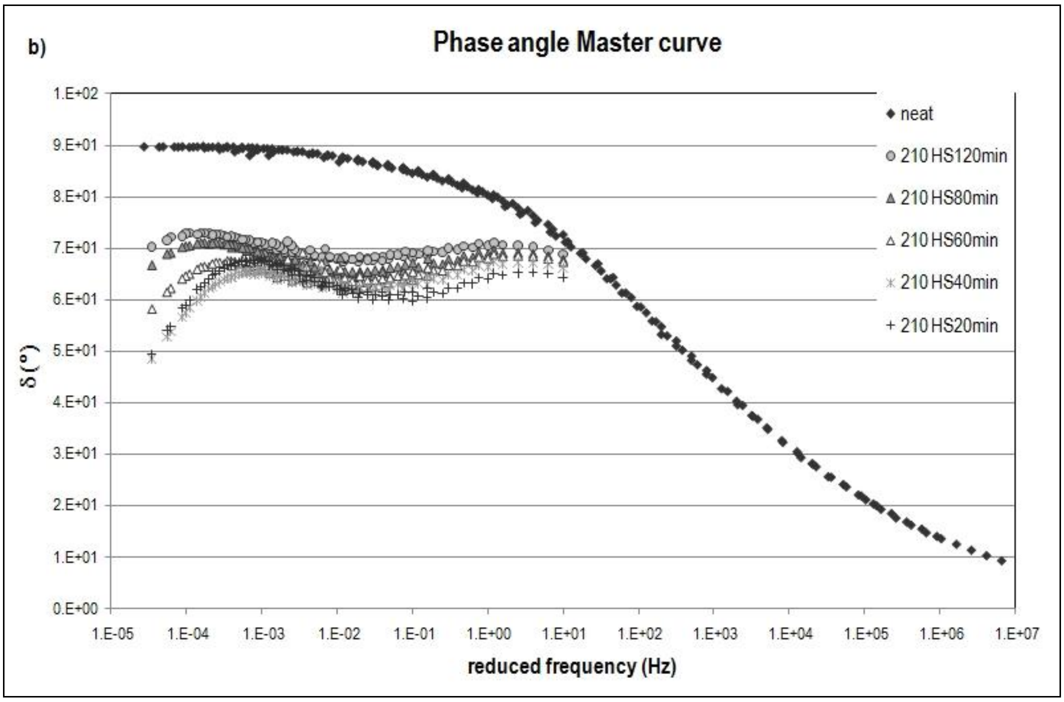


Figure 8.19b. Master curves of δ at 30°C of: TR-MB HS210 at different blending time

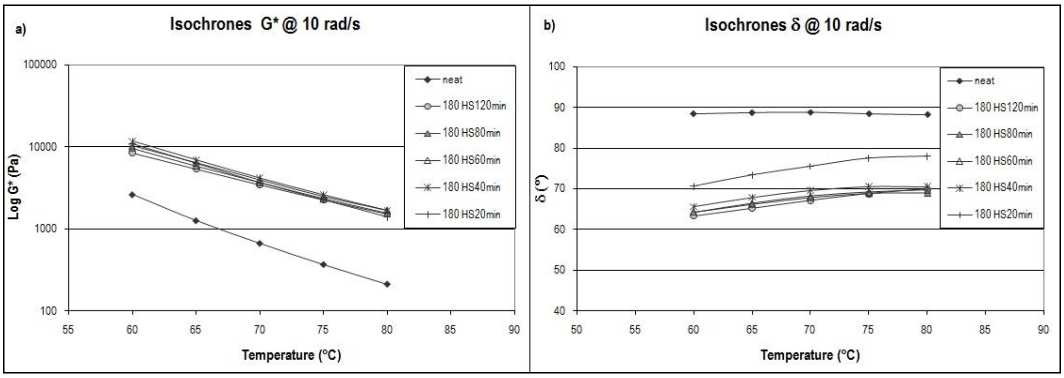


Figure 8.20. Isochronal plots of |G*| (a) and δ (b) of TR-MB HS180 at different blending time

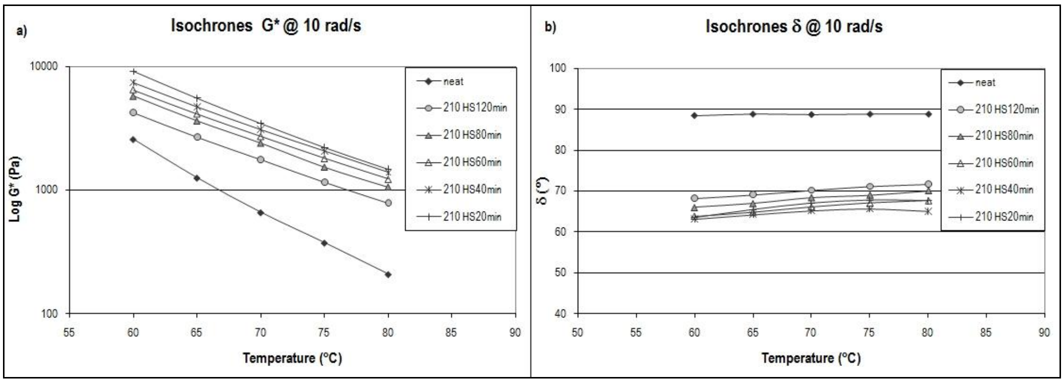


Figure 8.21. Isochronal plots of |G*| (a) and δ (b) of TR-MB HS210 at different blending time

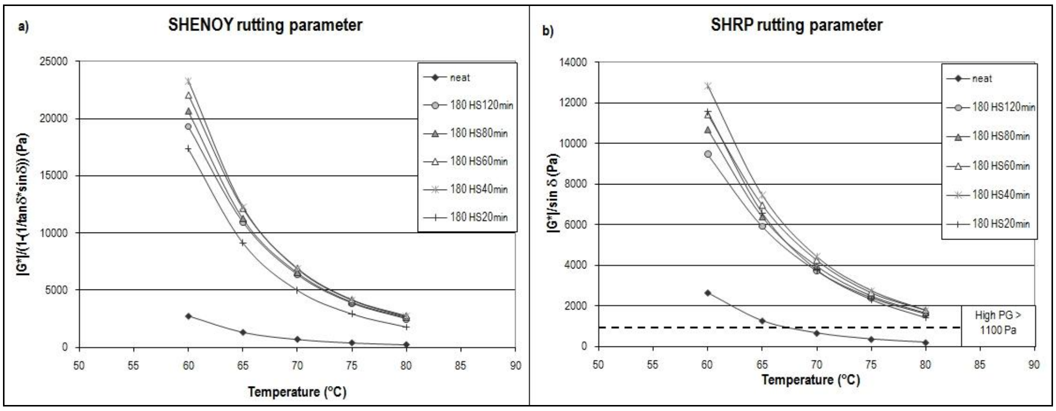


Figure 8.22. Shenoy’s (a) and SHRP (b) parameters of TR-MB HS180 at different blending time

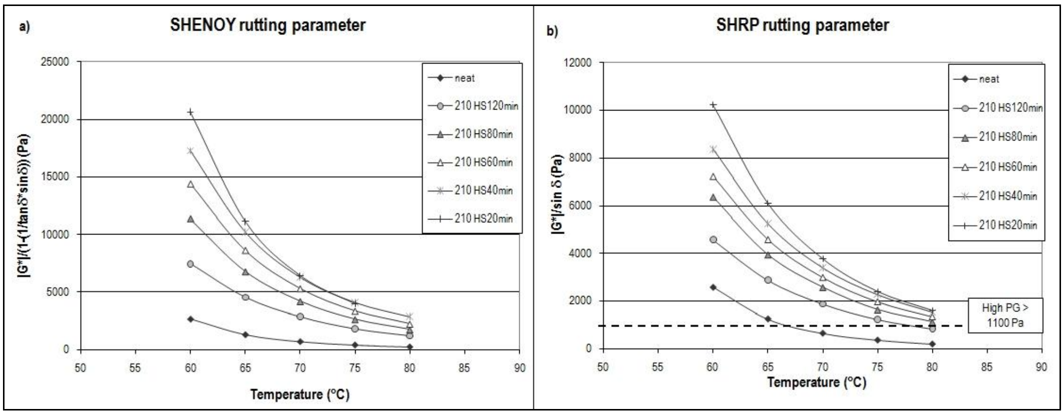


Figure 8.23. Shenoy's (a) and SHRP (b) rutting parameters of TR-MB HS210 at different blending time

8.5 Effect of Shear rate at fixed blending time

As seen in previous section (§8.4.1), by optimizing the mixing time it is possible to get the best performing blend for the selected processing conditions. It was also noticed that by processing the tyre rubber with the bitumen, in high shear, there is a certain trend of property lose with increasing the mixing time, especially at 210°C. In fact, TR-MBs HS processed for 120 minutes at 180ºC and 210ºC, both perform better than neat bitumen at the high service temperatures, but the latter shows to have lower performances, due to the partial devulcanization and depolymerization of the tyre rubber. In order to understand the influence of the shear rate in the modification process and its influence on the lose of properties with increasing the blending time, also TR-MBs LS 180 and 210, were obtained with a processing time of about 120 minutes (Figs 8.1 and 8.2).

Specific DMA at the high service temperatures (30°C - 80°C) and the consequent comparison of Black diagrams and master curves were performed. Results at the higher processing temperature (210°C) are reported below (Figs 8.24 - 8.27), while diagrams at 180°C (Figs 7.12 - 7.15) are reported in the previous chapter (§8.5.2). Comparing results at different temperatures, it is possible to assert that, at the higher processing temperature, the differences between the blends obtained in low shear and high shear are more evident. In fact, results show that TR-MB LS210 120min, obtained by processing the rubber with bitumen at 210°C with the low shear blending protocol for two hours, has very similar properties to the best performing TR-MB HS obtained at 210ºC (20-40 minutes).

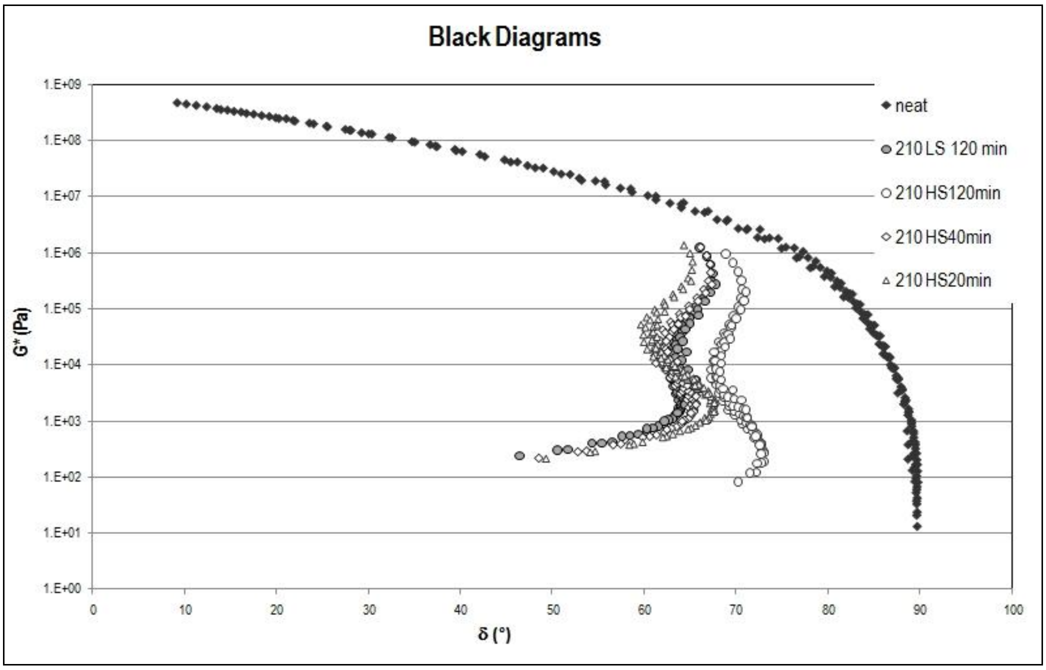


Figure 8.24. Black diagrams of TR-MB LS210 and TR-MB HS210 at different blending time

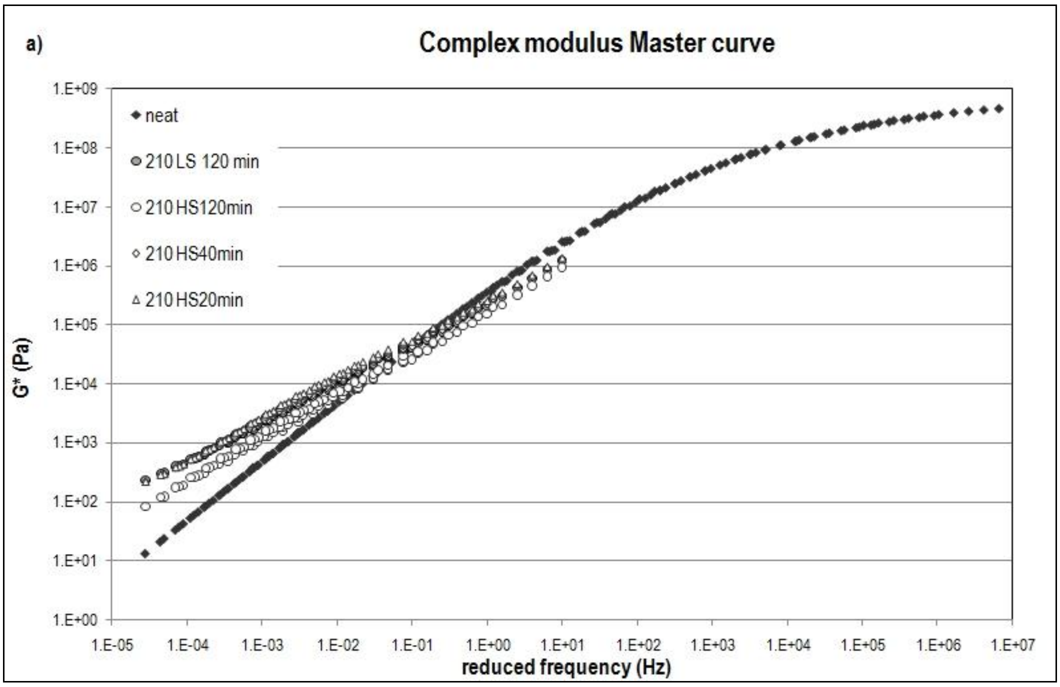


Figure 8.25a. Master curves of |G*| at 30°C of TR-MB LS210 and TR-MB HS210 at different blending time

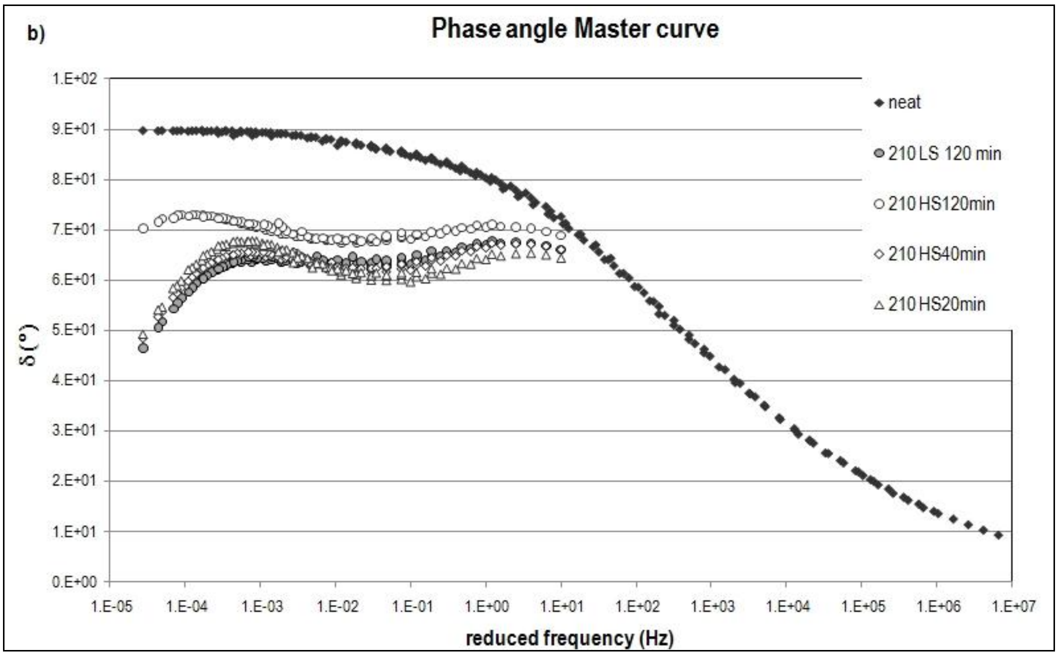


Figure 8.25b. Master curves of δ at 30°C of TR-MB LS210 and TR-MB HS210 at different time

Moreover, the TR-MB HS210 120min, obtained with the same mixing time but in high shear, has got much worse rheological properties: processing in high shear speeds up the reaction process between rubber and bitumen, especially at the higher processing temperature.

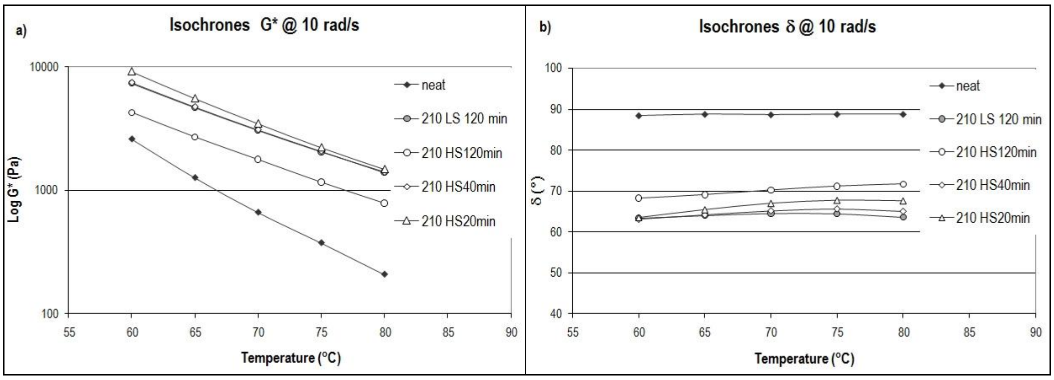


Figure 8.26. Isochronal plots of |G*| (a) and δ (b) of TR-MB LS210 and TR-MB HS210 at different blending time

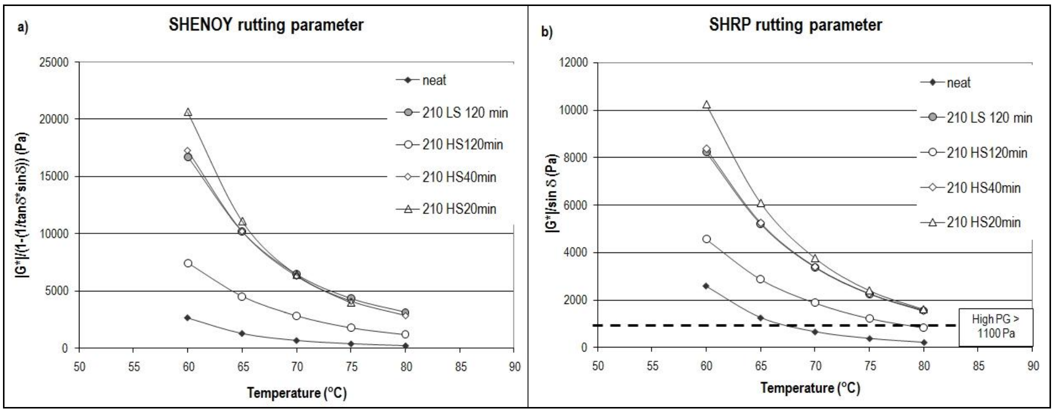


Figure 8.27. Shenoy's (a) and SHRP (b) rutting parameters of TR-MB LS210 and TR-MB HS210 at different blending time

8.5.1 Mechanical strength (shear susceptibility)

A confirmation of what has been obtained so far, it is provided by evaluating the so called "Mechanical Strength", indicated by the Antoon Paar Software (Rheoplus), consisting in performing an amplitude sweep, at 10rad/s and at 80°C on the TR-MBs produced in low shear and and high shear. These settings were chosen because 80ºC is the higher testing, which is also the closer to the high critical temperature of the modified binders (§ 9.3.2), and the frequency is the one used by SHRP to define the PG.

Neat bitumen keeps its mechanical strength, here indicated in terms of performance (G*/sinδ), constant even up to 1000% strain (Fig. 8.28). Instead, TR-MBs processed at both temperatures, begin to drop their performance (leaving the linearity region) at a lower strain than the neat bitumen, showing more shear susceptibility.

From the results it is also possible to appreciate the effect of the high shear by the smoothing of the curves - probably a symptom of a strong interaction between the phases, agreeable with enhanced interfacial adhesion (Gonzalez et.al, 2002) - and a significant reduction of the performance of the modified binders. In fact, by combining high shear and high temperature, as with TR-MB HS 210 120min, the high PG value is lower than 80ºC at any strain level: G*/sinδ < 1100 Pa

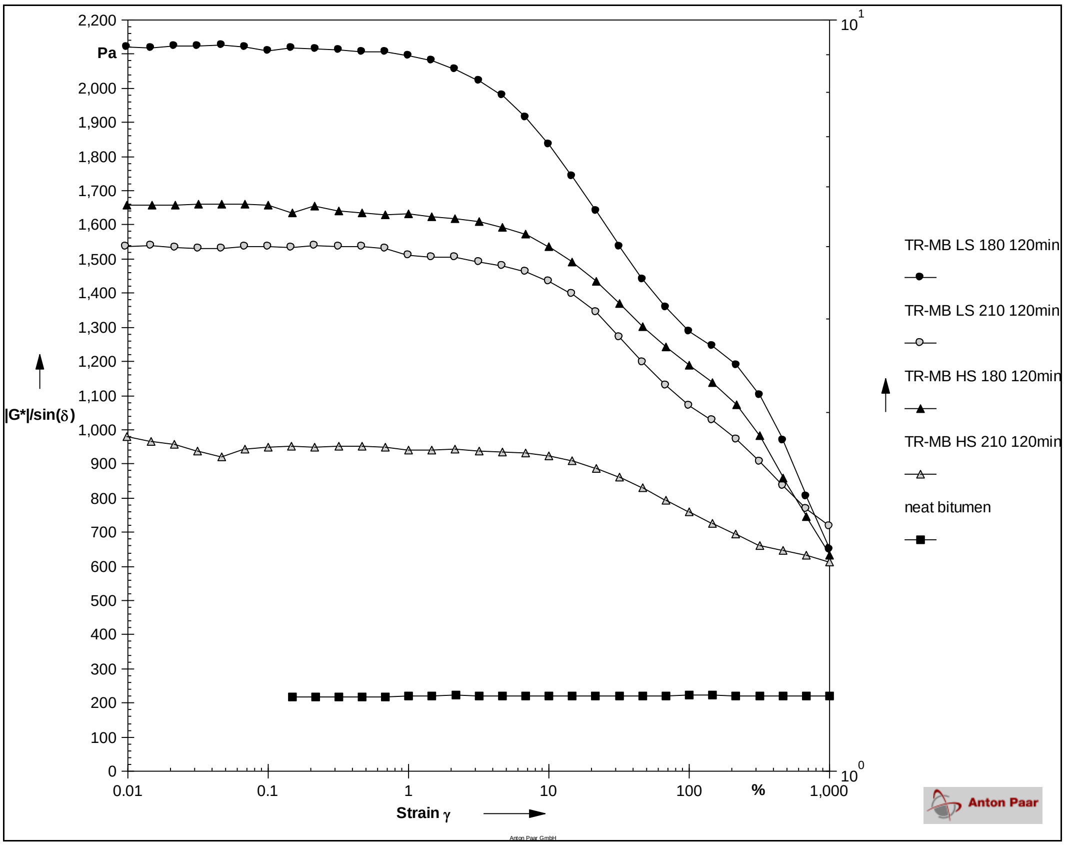


Figure 8.28. Amplitude sweep @ 80°C and 10rad/s performed on neat, PMBs and TR-MBs HS

8.6 Performance comparison with PMBs

In order to assess the performance of the binders produced in high shear, the TR-MBs were compared with the neat bitumen and two SBS polymer modified bitumens with two different levels of modification: SBS-MB Hard and SBS-MB Medium. Comparisons were made in terms of conventional and rheological properties.

8.6.1 Conventional properties

In order to assess the performance of the best performing blends, conventional physical properties were also measured. Penetration (Pen), Softening Point (SP) and Rotational Viscosity (RV) at 135°C and 160°C were measured and compared between the TR-MB binders produced in high shear, neat bitumen and the two PMBs: SBS-MB H and SBS-M.

From the conventional tests (Tab. 8.3), it can be concluded that both TR-MBs HS are harder than their base bitumen (neat) and have higher SP and Penetration index. Considering PMBs as the target, the TR-MB HS180 shows the best improvements. Indeed, it has comparable Softening point, but proves to be stiffer even than the SBS-MB Hard and too viscous for the requirements of the ASTM Standard specifications for modified bitumen (ASTM D5892, 2000). In fact, according to the ASTM standard, the viscosity at 135ºC can be a maximum of 3000 Pa.s. TR-MB HS 210 has got a much lower viscosity, it is also stiffer than PMBs, but has poor improvement in terms of its softening point.

Both TR-MBs, therefore, do not respect the ASTM standard and also due to their combination of Penetration and Softening point, they cannot be classified within the European Framework Specification of modified bitumen (EN 14023, 2005).

Therefore, already by evaluating the conventional properties, it is not possible to consider the produced tyre rubber modified bitumen as polymer modified binders. Nevertheless, it has to be noticed that both TR-MBs have the characteristics (in terms of standard requirements for Pen, SP and Apparent Viscosity) to be classified as Asphalt Rubber type I or II (ASTM D 6114, 2002).

Table 8.3 : Physical and mechanical characteristics of the binders studied

Conventional properties	**neat bitumen**	**TR-MB HS180**	**TR-MB HS210**	**SBS-MB M**	**SBS-MB H**
Penetration 25°C (mm/10) (EN 1426)	50	32	37	51	47
Softening Point (°C) (EN 1427)	51	62	55	64	85
Penetration Index	-0.96	0.38	-0.70	1.84	4.81
Apparent Viscosity at 177°C (Pa s) (ASTM D6114)	-	3.500	2.600	-	-
Viscosity at 135°C, (Pa s) (EN 13302)	0.429	5.950	3550	1.290	2.450
Viscosity at 160°C (Pa s) (EN 13302)	0.139	2.300	1.120	0.472	0.742

The classical identification tests for bitumen are easy and reliable when the binder to be characterised is neat bitumen, but when it is necessary to classify modified binders, it is really difficult to make comparisons only based on conventional classification. For this reason, in the next section, all the binders have been also characterised through rheological tests, with which was possible to characterise the binder by investigating their thermal, frequency, shear susceptibility as well as the mechanical properties, within the whole range of service temperatures (0 - 80ºC).

8.6.2 Rheological properties

The rheological properties of the blends were assessed, by performing a DMA across a whole range of service temperatures (0-80ºC). Particular care was taken with regards to the gap settings; 1.5mm, for the 25mm plates, was shown to give the most reliable results for the modified binders, while 1mm gap was maintained for the neat bitumen.

The frequency dependence of complex modulus and phase angle for the modified binders has been assessed by producing Black diagrams (Fig. 9.26) and master curves at a reference temperature of 30°C (Fig. 9.27a,b). Isochronal plots at 10 rad/s were also produced to show the temperature dependency of the binders (Fig. 9.28a,b), while Shenoy’s and SHRP rutting parameters were calculated to be able to compare the performances at high service temperatures. (Fig. 9.35a,b). A comparison regarding the complex modulus of both the SBS-MBs and both the TR-MBs indicates that the behavior of the binders is pretty similar over the whole range of considered frequencies.

Making a comparison with the original base bitumen, all the modified binders show clear improvements, having a lower frequency (temperature) susceptibility and being stiffer at low frequencies (high temperatures), but softer at high frequencies (low temperatures) (Fig. 8.30a and 8.31a). This last result is due to the presence of the polymer network which affects the rheological properties of the modified binders, with a slight plateau on the complex modulus curves at low frequencies which infers less rigidity in the material at high frequencies (low temperatures). The plateau is even more evident on the phase angle master curves, where it is noticeable how the modification process significantly reduces the phase angle, at medium/low frequencies (temperatures), so allowing to significantly increase the elastic properties (Fig. 8.30b and 8.30b).

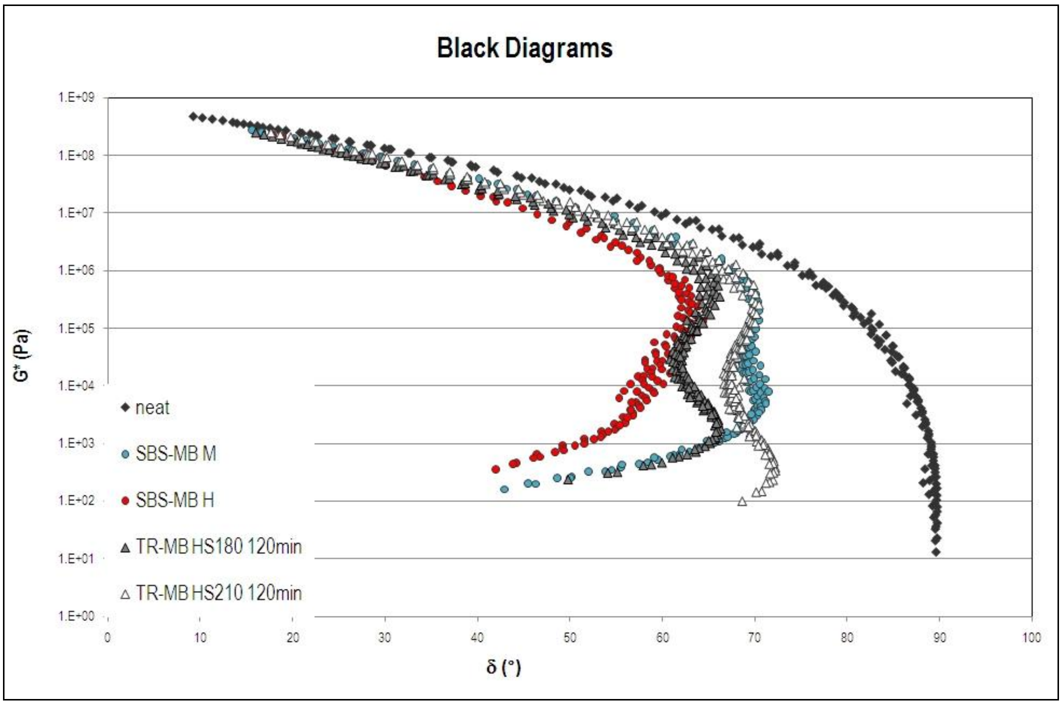


Figure 8.29. Black diagrams of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

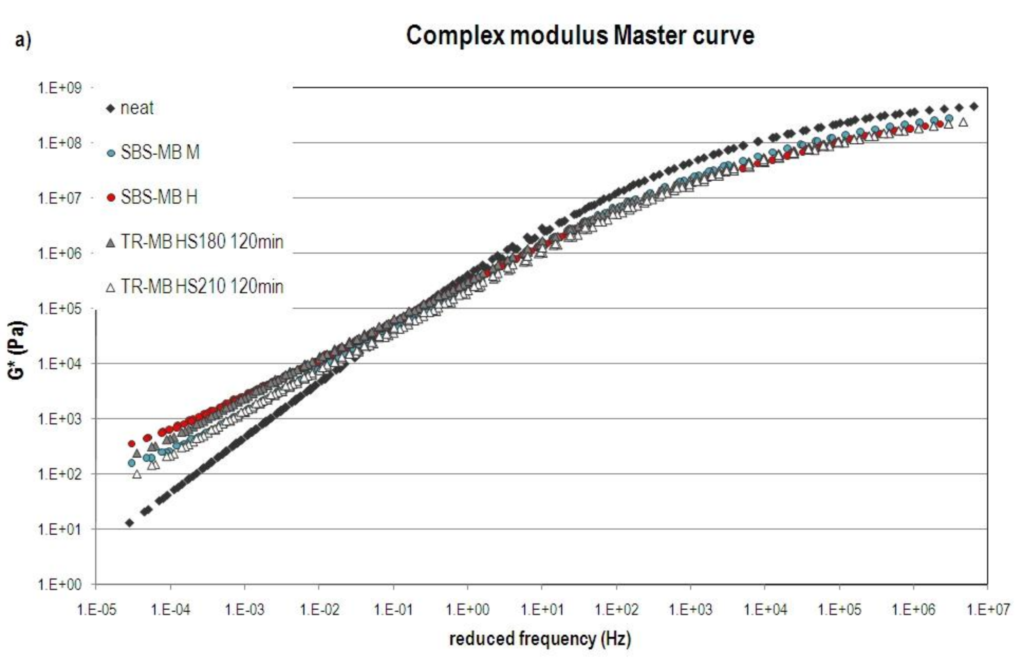


Figure 8.30a. Master curves of |G*| at 30°C of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

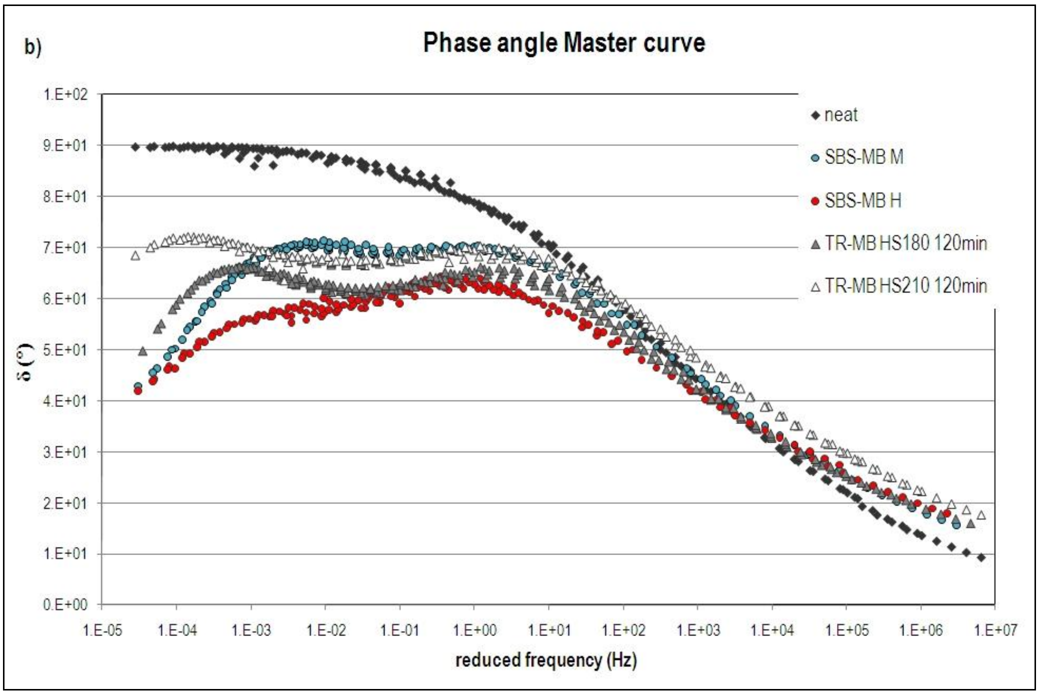


Figure 8.30b. Master curves of δ at 30°C of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

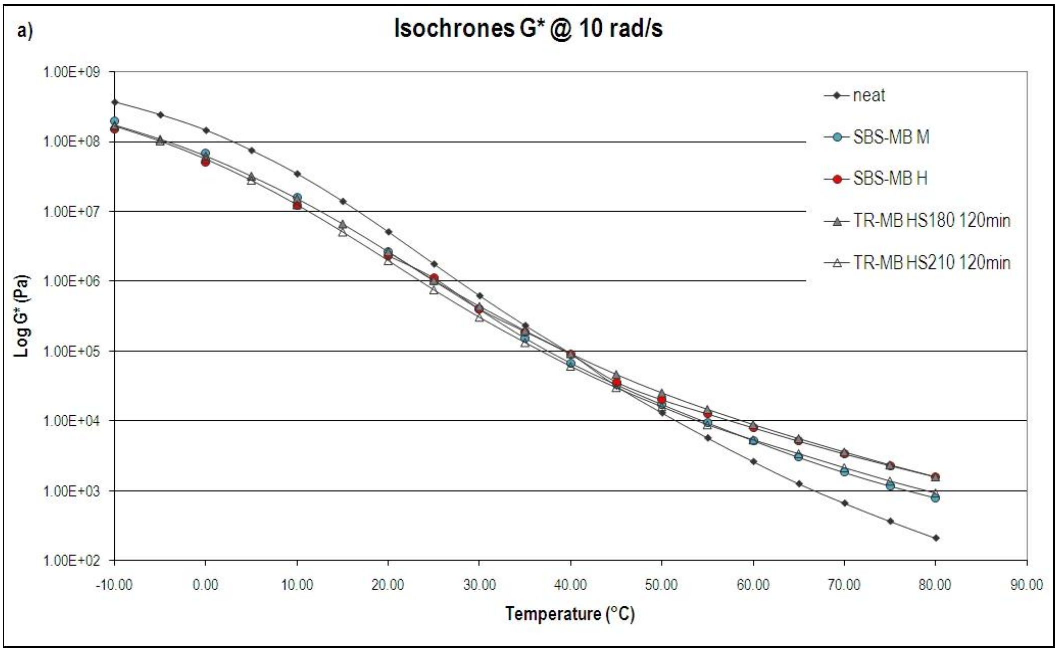


Figure 8.31a Isochronal plots of |G*| at 10rad/s of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

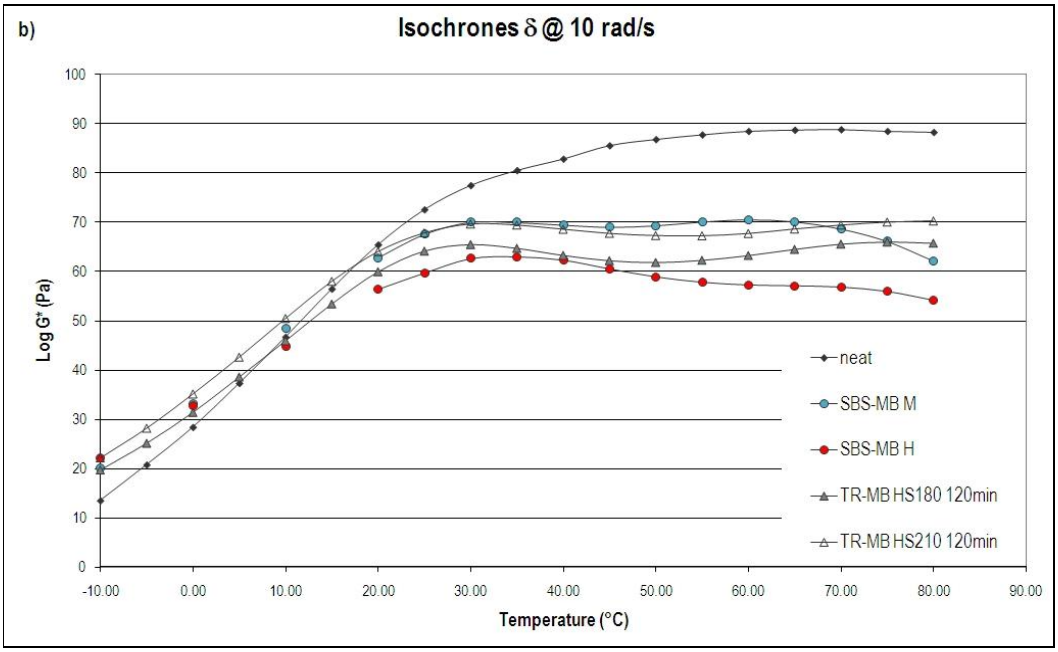


Figure 8.31b. Isochronal plots of δ at 10rad/s of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

An overall analysis of the master curves and isochronal plots in Figs. 8.30 and Figs 8.31, demonstrates that: between the two TR-MBs processed for two hours in high shear, TR-MB HS180 is stiffer and more elastic, at high temperatures and that it has got a rheological behavior almost comparable even with the PMB with a high level of modification: SBS-MB H. The TR-MB HS210 has the same temperature susceptibility but it is softer and less elastic than the TR-MB HS180 and for this reason, it has rheological properties comparable only with the PMB with a medium level of modification.

Mechanical strength (shear susceptibility)

Comparison between the binders was performed also by checking the previously defined mechanical strength (§ 8.5.1). Results show the ability of this kind of test of giving, not only a quick estimation of the performance, but also an understanding of the rheological homogeneity of binders. A good example is given by the TR-MBs HS produced at 210ºC, which has less performance than the TR-MB HS 180, but it is visibly a more homogeneus

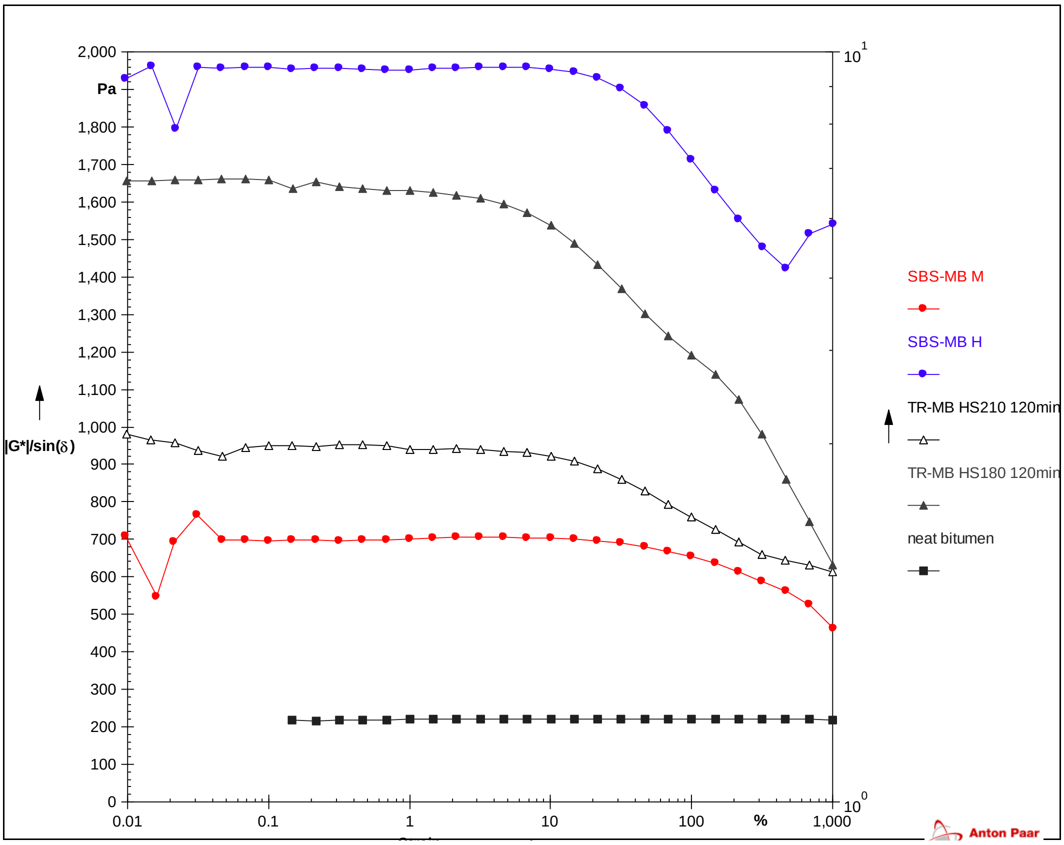


Figure 8.32. Amplitude sweep @ 80°C and 10rad/s performed on neat, PMBs and TR-MB HS at 180 and 210ºC

material and it is also easier to handle. Figure 8.32 shows that SBS-MB H and TR-MB HS 180 are the best performing binders. TR-MB HS 180, is also able to keep its high PG value over 80ºC up to really high strain level (more than 100%), but it show a really high shear susceptibility.

Instead, the TR-MB HS 210 has got worse rheological properties than TR-MB HS 180, but it seems to have better performance than the SBS-MB Medium and it also shows comparable shear susceptibility.

Finally, another interpretation of the results that should be noted comes from the G*/sinδ value showed at the highest applied strain: 1000%. As it is possible to see in figures 8.28 and 8.32, these results seem to give an estimation of the modification kind that is independent from the selected processing conditions and it is property of the selected modifier. At a strain level of 1000%, all the tested TR-MBs have comparable performance (similar value of G*/sinδ), no matter what have been the processing conditions in terms of temperature and applied stress. As a result, the G*/sinδ of TR-MBs at 1000% strain, results in a lower value than the SBS-MB with high level of modification, but higher than the SBS-MB Medium and neat bitumen.

8.6.3 Best performing blends

In order to understand what is the level of performance reached by the best performing blends at selected temperatures, but also to assess what are the performance of the "over-processed" blends in terms of mixing time, the comparison with the two commercially used PMBs was extended.

Results emphasis again the importance of preliminary investigations to optimise the mixing time, and the properties of the final product, especially at high processing temperatures. In fact, while both the TR-MBs HS180 have properties comparable with the PMB with high level of modification (SBS-MB H), the TR-MB HS210 processed for 120 minutes, is similar to the PMB with a medium level of modification: SBS-MB M. Isochronal plots in Figures 8.37a,b and the evaluation of the rutting parameters (Figs. 8.38a,b) give another demonstration of how the best performing TR-MB HS 210 (40 minutes) have similar stiffness, elastic properties, thermal susceptibility and rutting resistance as the best performing TR-MB HS obtained at 180ºC. Moreover, both of them have comparable rheological properties with regards to the PMB with a high level of modification (SBS-MB H).

As final considerations, in this case the SHRP and Shenoy's parameters, provide results with different resolutions. The latter one seems to be able to provide a more adequate measurement of the rutting resistance of the modified binders, probably because it is more influenced by the phase angle variability than the SHRP's |G*|/sinδ.

Finally, as far as the optimisation of the blending time in high shear at 180°C and 210°C is concerned, a blending time of a minimum 40-80 minutes for the former, and 20-40 minutes for the latter, provide the best performing blends. Results are in accordance with the previous rotational viscosity measurements. (Fig.8.15). Nevertheless, the final blends: TR-MB HS180 and TR-MB HS210, obtained after 120 minutes of high shear mixing, are still well performing binders and the former has better performance than the latter.

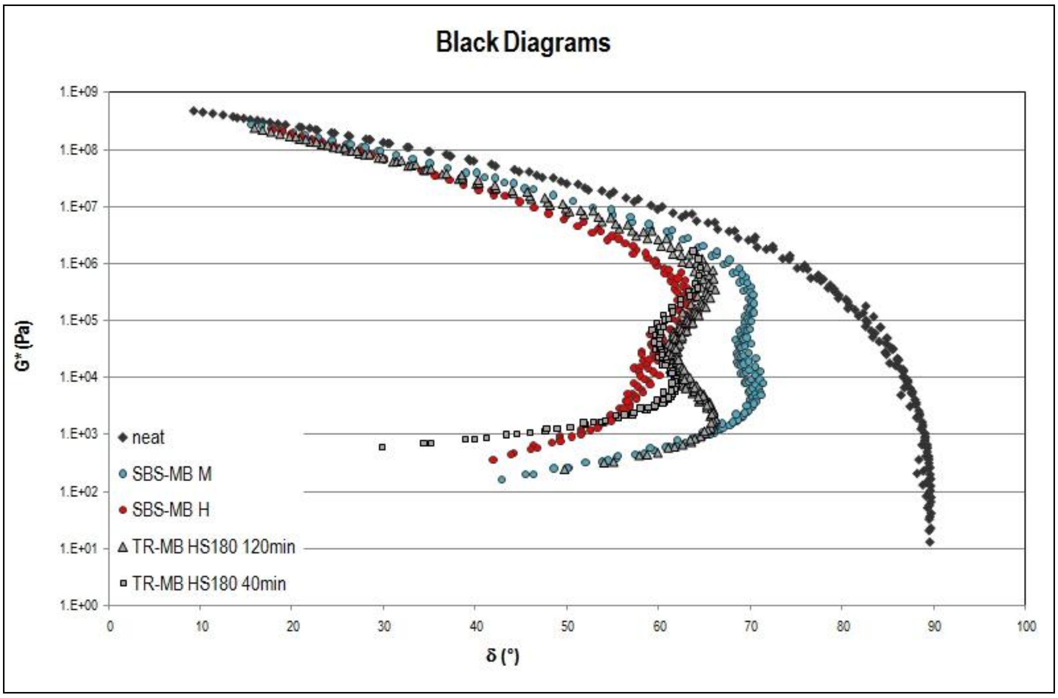


Figure 8.33. Black diagrams of neat bitumen, PMBs and TR-MB HS210 and TR-MB LS210

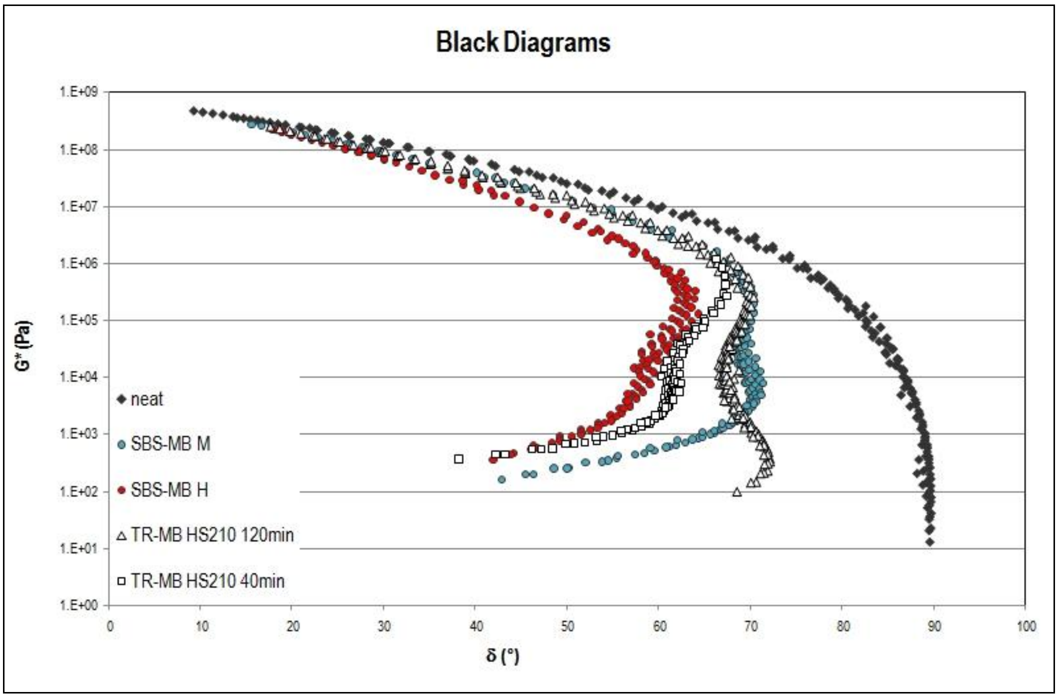


Figure 8.34. Black diagrams of neat bitumen, PMBs and TR-MB HS210 and TR-MB LS210

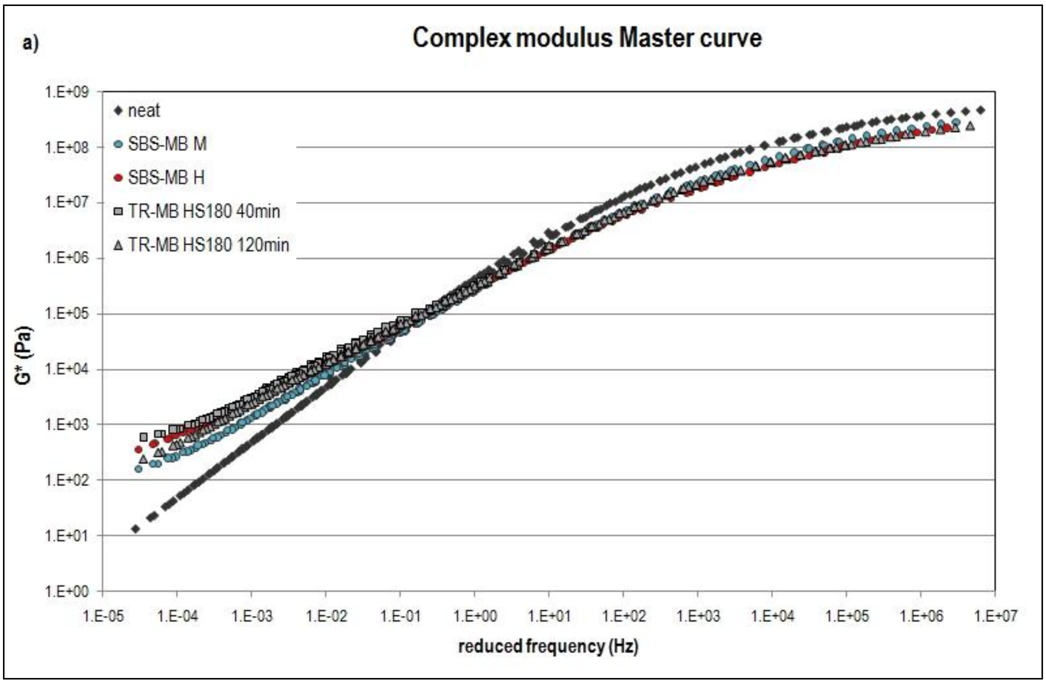


Figure 8.35a. Master curves of |G*| at 30°C of neat bitumen, PMBs and TR-MB HS180 and TR-MB LS180

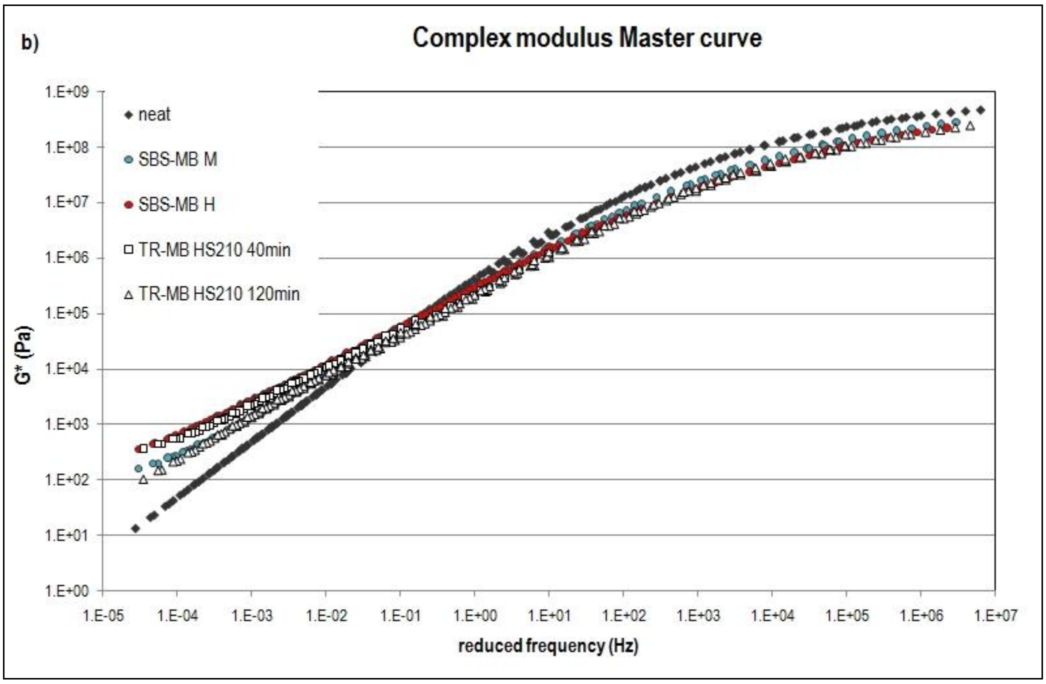


Figure 8.35b. Master curves of |G*| at 30°C of neat bitumen, PMBs and TR-MB HS210 and TR-MB LS210

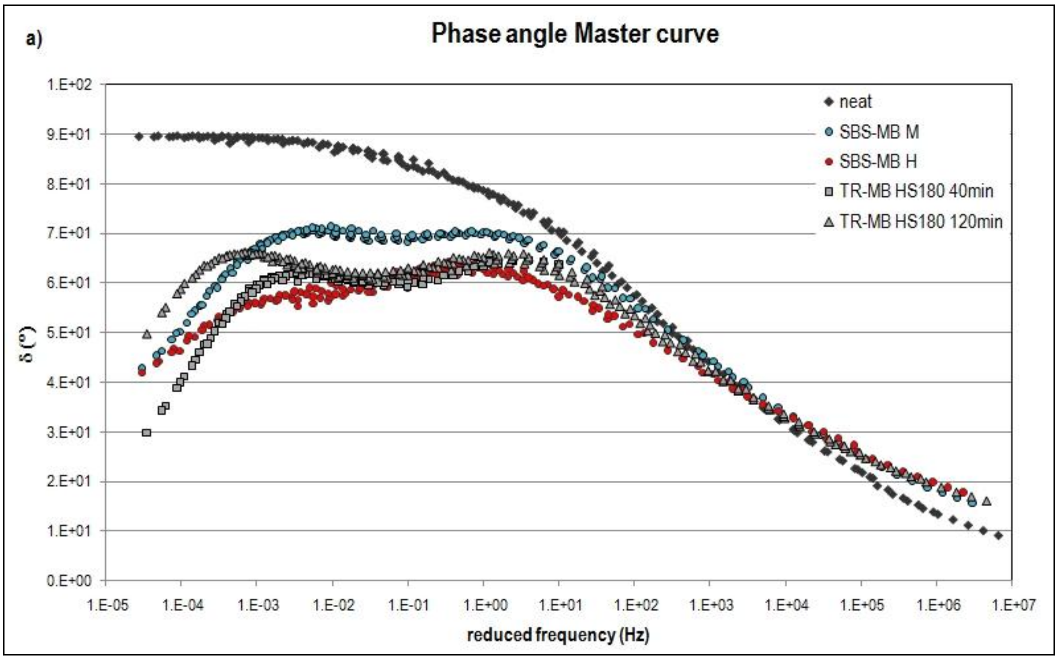


Figure 8.36a. Master curves of δ at 30°C of neat bitumen, PMBs and TR-MB HS180 and TR-MB LS180

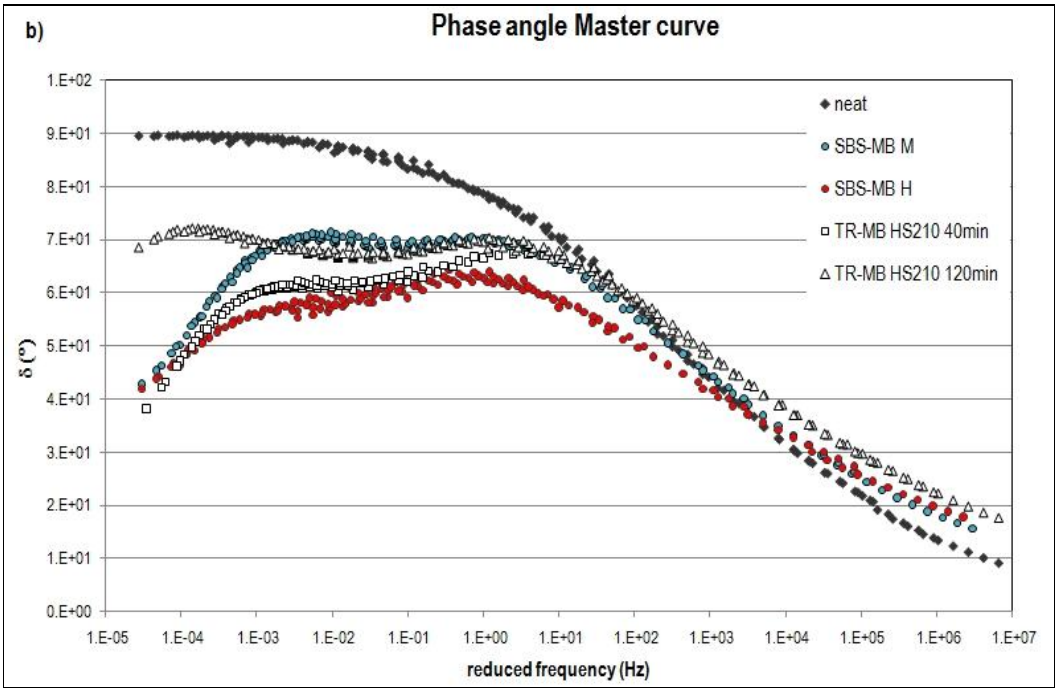


Figure 8.36b. Master curves of δ at 30°C of neat bitumen, PMBs and TR-MB HS210 and TR-MB LS210

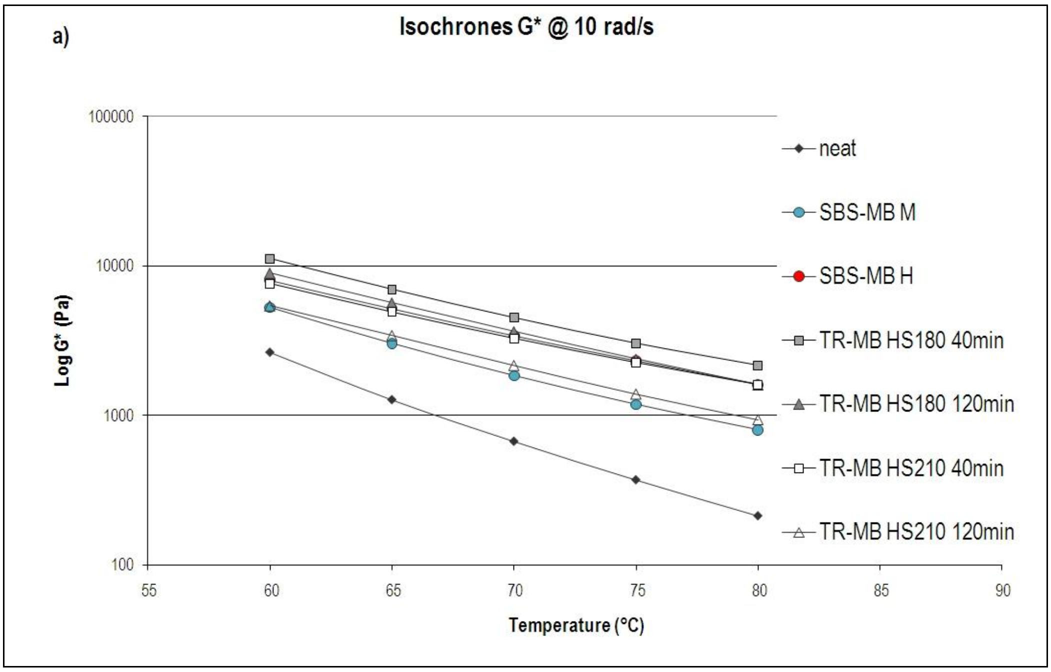


Figure 8.37a Performance comparison by isochronal plots of |G*| of all TR-MBs HS, PMBs and neat

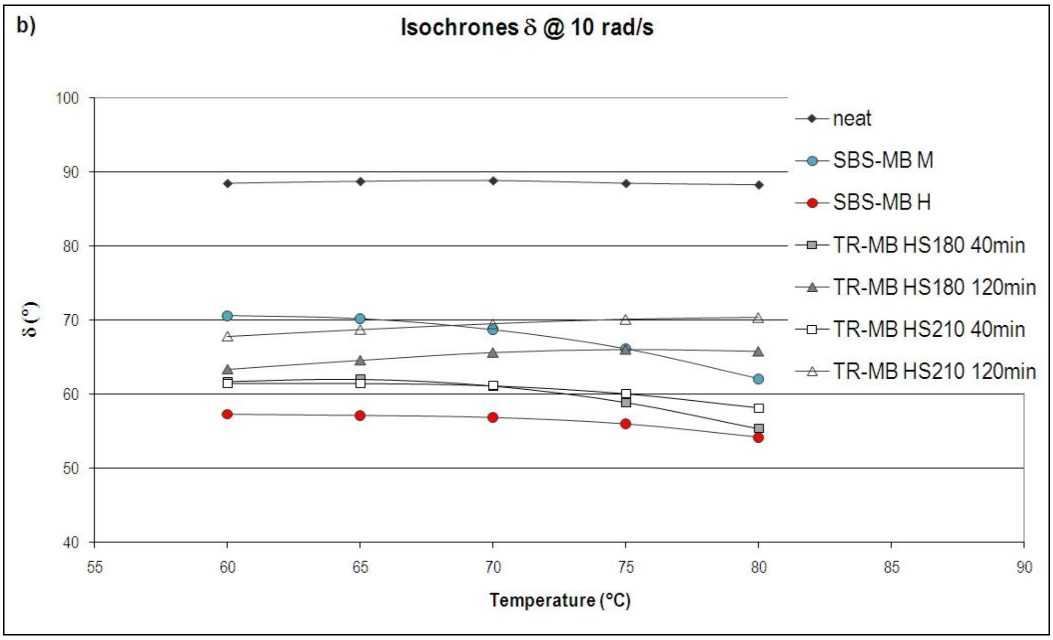


Figure 8.37b Performance comparison by isochronal plots of δ of all TR-MBs HS, PMBs and neat

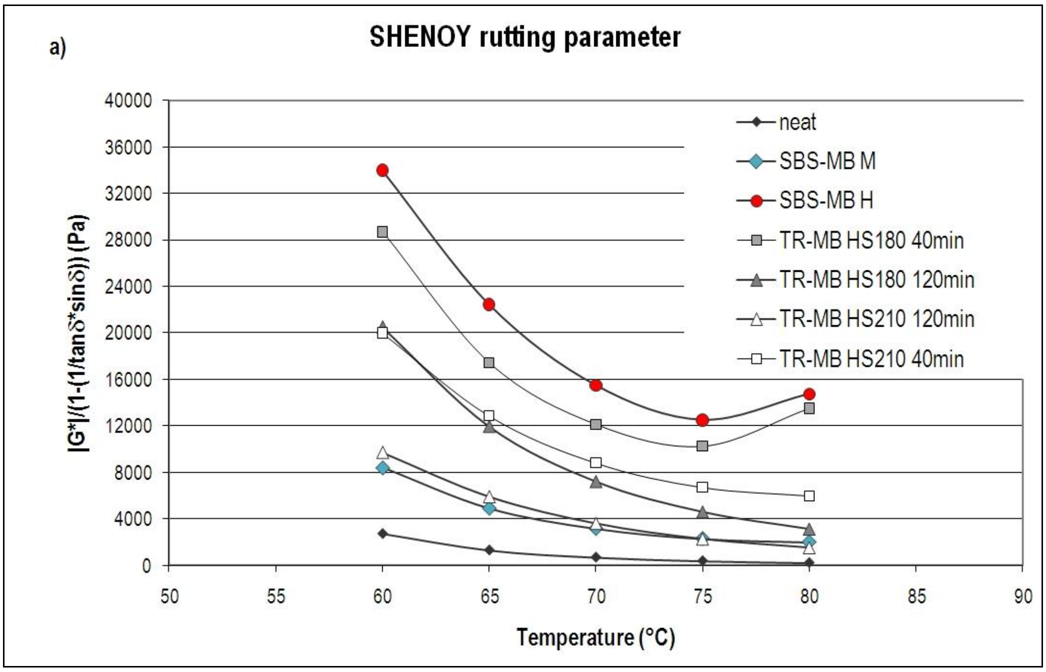


Figure 8.38a. Performance comparison by Shenoy parameter of TR-MBs HS, PMBs and neat

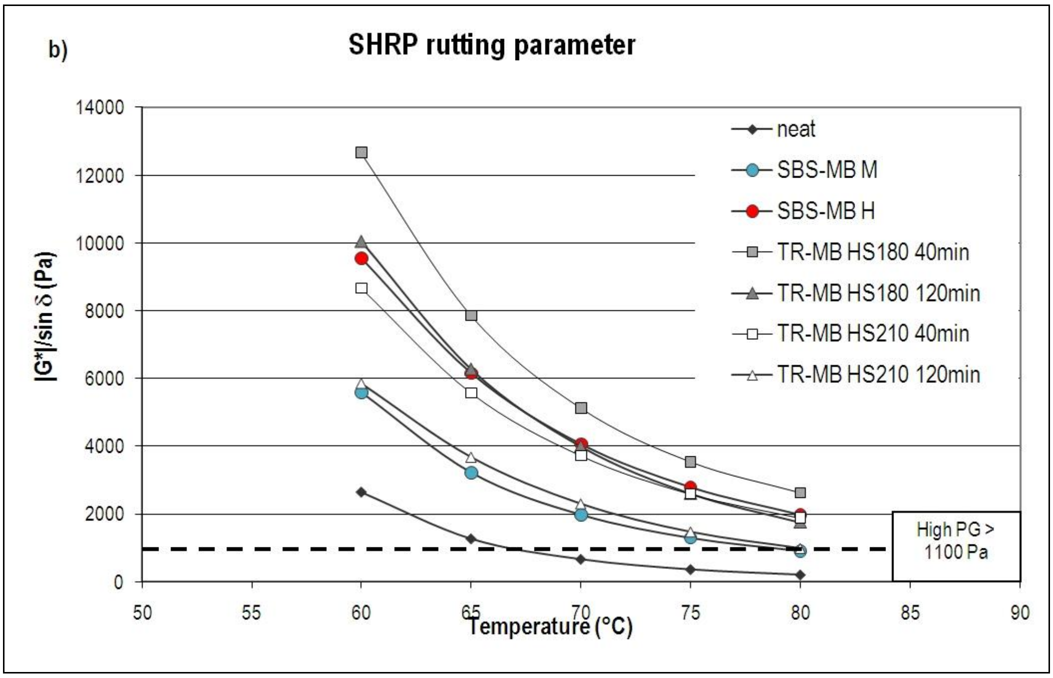


Figure 8.38b. Performance comparison by SHRP parameter of TR-MBs HS, PMBs and neat

The best performing TR-MB HS210 (20-40 min), obtained by processing the rubber with bitumen in high shear at 210ºC, has very similar properties to the best performing TR-MB HS obtained at 180ºC (40-80 minutes).These results confirm how the reaction process between rubber and bitumen is speed up by the higher processing temperature and it highlights, again, the importance of the optimisation of the mixing time relative to the selected processing temperature.

8.7 Processing conditions effects on blend stability

This section of the project was focused on the effect of the processing temperature on the stability of the blends. Therefore, TR-MBs produced after 120 minutes of high shear were subjected to storage stability analysis, as well as the two PMBs with different levels of modification (SBS-MB M and SBS-MB H), which were used as references of a storage stable binders.

8.7.1 Storage stability analysis (SSA)

All the modified bitumens have been subjected to a hot storage test based on the relative European Standard UNI EN 13399, but modified due to the fast phase separation of the rubber. The procedure consisted of filling drinking cans of 330ml (three for each binder) with pre-heated modified binder (180°C) and then, once the tubes had been closed, placing them in a vertical orientation in an oven at 180°C. After three different periods (1,4 and 24 hours), one tube for each binder was taken out of the oven and cooled down to ambient (room) temperature before placing in a freezer at -20°C. After that, the samples were cut into thirds and the top and bottom sections were saved for further analysis by softening point tests and rheological characterisation with DMA.

As obtained in the previous sections (§5.3.2) Softening point results (Table 8.4) show that the phase separation of the rubber starts to be relevant after a few hours. The results do not show a clear trend, in fact TR-MB produced at 210ºC seems to have a higher separation rate after 4 hours, but after 24 hours of hot storage, it is the TR-MB HS180 which shows the higher difference of Softening points between the top and bottom sections.

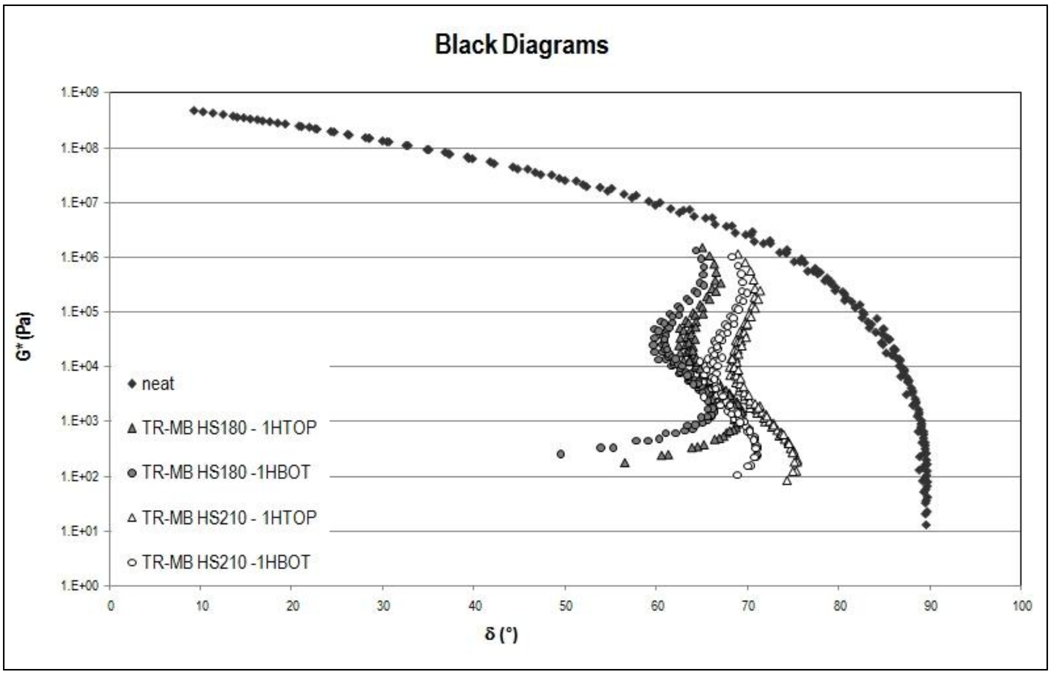


Figure 8.39a. Black diagrams of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 1h of hot storage @ 180ºC

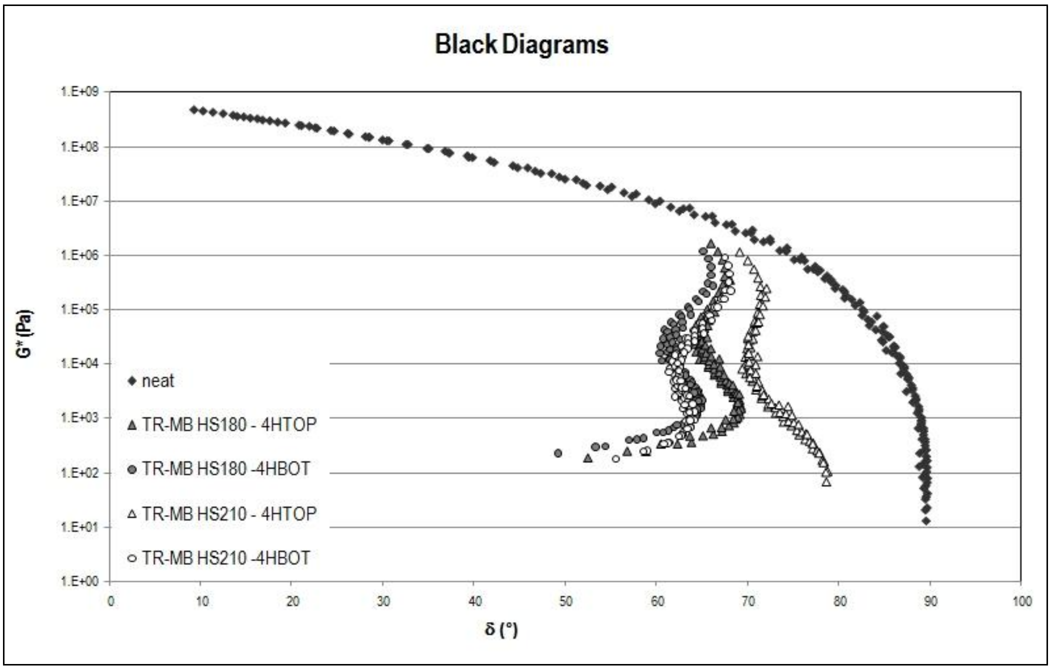


Figure 8.39b. Black diagrams of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 4h of hot storage @ 180ºC

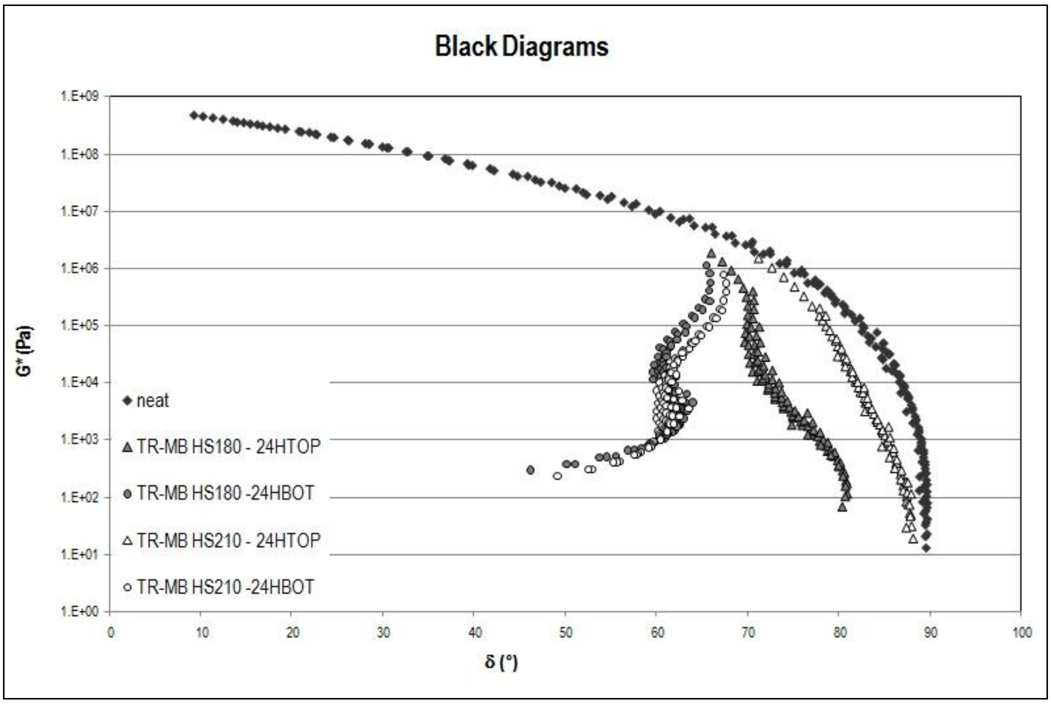


Figure 8.39c. Black diagrams of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 24h of hot storage @ 180°C

Table 8.4: Softening points of the TR-MBs HS before and after hot storage

Softening point (UNI EN 1427)	TR-MB HS 180		TR-MB HS 210			
	°C					
	top	bottom	top	bottom	ΔSP	
before hot storage	62.0		55.0			
after 1h of hot storage	61.0	63.0	54.0	55.0	2.0	1.0
after 4h of hot storage	59.0	61.5	55.0	59.0	2.5	4.0
after 24h of hot storage	50.0	63.0	50.0	59.0	13.0	9.0

It also has to be noted that performing the ring and ball test with such heterogeneous material is almost never problem-free, compared to testing neat bitumen. Again, when it is necessary to classify modified binders, it is really difficult to make comparisons only based on conventional classification, also because probably they're not suitable for this kind of binders. For this reason, all the binders have also been characterized through rheological tests.

DMA was performed by frequency sweep tests at the high service temperatures (30 - 80ºC) with conditions shown in Section 7.4. The results of these analyses, here showed in terms of Black diagrams, clearly show the differences between the two TR-MBs. After 1 hour (Fig. 8.39a) both of them show almost no separation, but already after four hours (Fig. 8.39b) TR-MB HS 210 demonstrates a very high difference of performance between the top and bottom sections. The rubber tends to settle towards the bottom and the Black diagram of the top part tends to have the properties of the base bitumen (neat). After 24 hours, (Fig. 8.39c) the TR-MB HS180 also shows a big gap between the upper and lower sections, but it is not comparable with the loss in properties of the TR-MB HS210 which shows rheology of the top section really close to the neat bitumen. Figures 8.40a and 8.40b, confirm that the loss of properties regards the top part of the sample and it is a decrease of both stiffness and elastic behavior. Also to evaluate the storage stability of the tyre rubber modified bitumens, the PMBs were taken as a reference; comparison in terms of conventional and rheological properties were carried out.

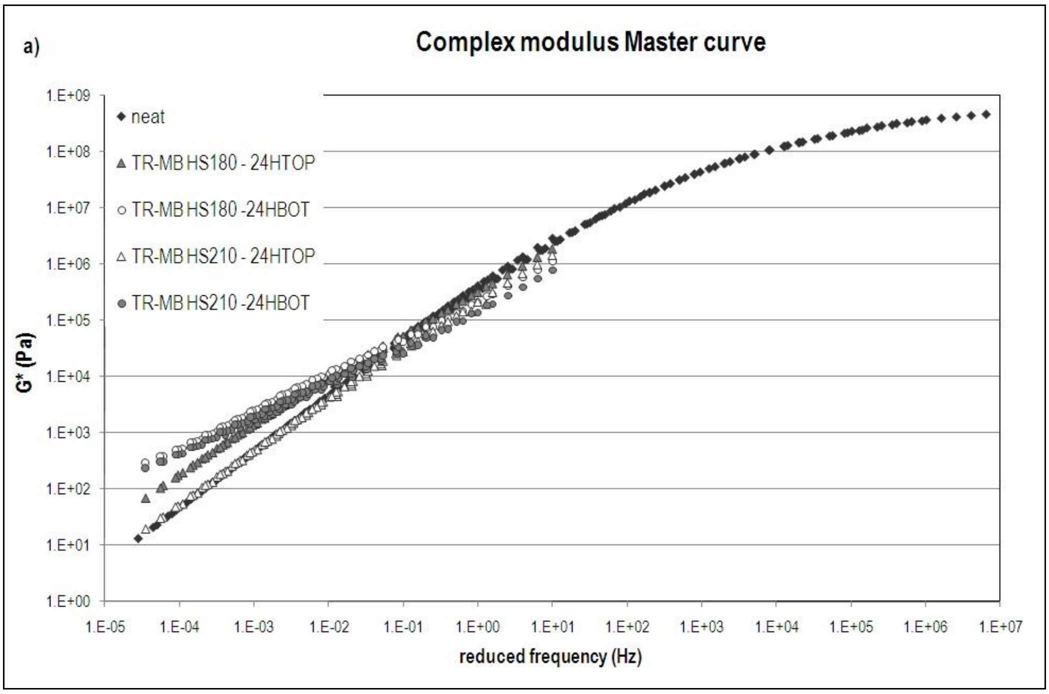


Figure 8.40a. Master curves of |G*| at 30°C of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 24h of hot storage @ 180ºC

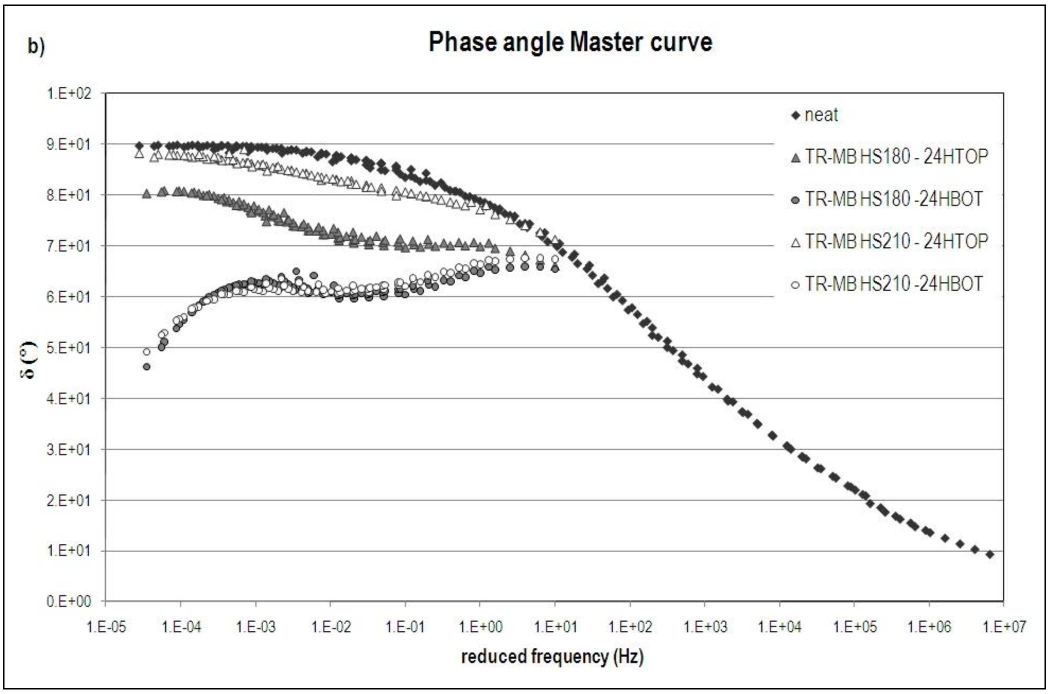


Figure 8.40b. Master curves of δ at 30°C of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 24h of hot storage @ 180ºC

The results of these analyses confirm, as expected, that also after 24 hours the SBS-MBs has got a much better stability than TR-MBs, in terms of both softening points (UNI EN 13399 prescribes a maximum ΔSP of 5ºC) (Tab 8.5) and rheology (Fig. 8.42).

Table 8.5: Softening points of the TR-MBs HS and SBS-MSs after 24 h of hot storage

Softening point (EN 1427)	Before hot storage	After 24 hours of hot storage @ 180°C		
		top	bottom	ΔSP
	°C			
TR-MB HS 180	62.0	50.0	63.0	13.0
TR-MB HS 210	55.0	50.0	59.0	9.0
SBS-MB Medium	64.0	66.5	66.0	0.5
SBS-MB Hard	85.0	86.0	84.0	2.0

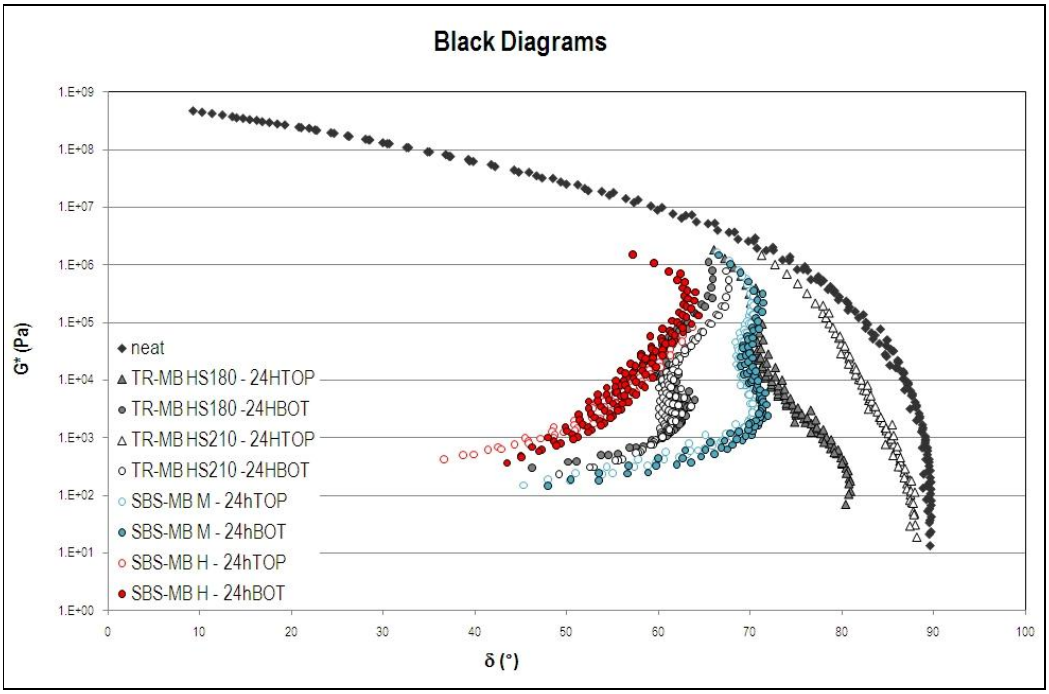


Figure 8.41. Black diagrams of top and bottom parts of TR-MB HS180 and TR-MB HS210 and PBMs after 24h of hot storage @ 180ºC

In order to have an easily determinable parameter, which could represent a value of the storage stability, two different separation indices, proposed by Lu (Lu et al, 1999) and Abhlerdam (Attia & Abdelrahman, 2009), were calculated and compared to summarise the hot storage stability of the modified binders. The separation index (I_s) indicated by Lu, compares the complex modulus of lower and upper part of the sample as follows:

$$\text{Lu}, I_s = \log \frac{G*_{bottom}}{G*_{top}}$$

Modified bitumens without phase separation during hot storage show I_s values close to zero. In lieu of the G*, Abdelrahman suggested to compare the SHRP rutting parameter of the bottom or lower part of the sample (whichever is the higher) with the average of these two values, as follows:

$$\text{Abdelrahman}, I_s = \frac{\max\left(G*_{bottom}, G*_{top}\right) - avg\left(G*_{bottom}, G*_{top}\right)}{avg\left(G*_{bottom}, G*_{top}\right)}$$

In order to find the most suitable measure of the Hot Storage Stability (HSS), both calculation methods described above were used with three parameters: G*, SHRP and Shenoy's rutting parameters. All the parameters were calculated from the raw data of the performed DMA, at the highest service temperature of 60ºC and the frequency of 10 rad/s (used to calculate the SHRP's rutting parameter). Results were compared and reported in the form of diagrams (Figs 9.42a,b):

By looking at the Abhlerdam's separation indices (Fig. 9.42a), it is possible to notice a similar trend for all the parameters. Comparing the calculations made with G* and the SHRP's parameter, almost no differences are appreciable. Instead, the I_s calculated by using the Shenoy's parameter, in which the phase angle variability has more influence than in the SHRP's parameter, emphasis the difference in HSS between the two tyre rubber modified bitumens and the SBS-MBs. Moreover, it is only the I_s calculated with the Shenoy's parameter that confirms the result of the ring-and-ball test (ΔSP) which shows that the SBS-MB Medium is slightly more stable than the SBS-MB with high level of modification (SBS-MB H).

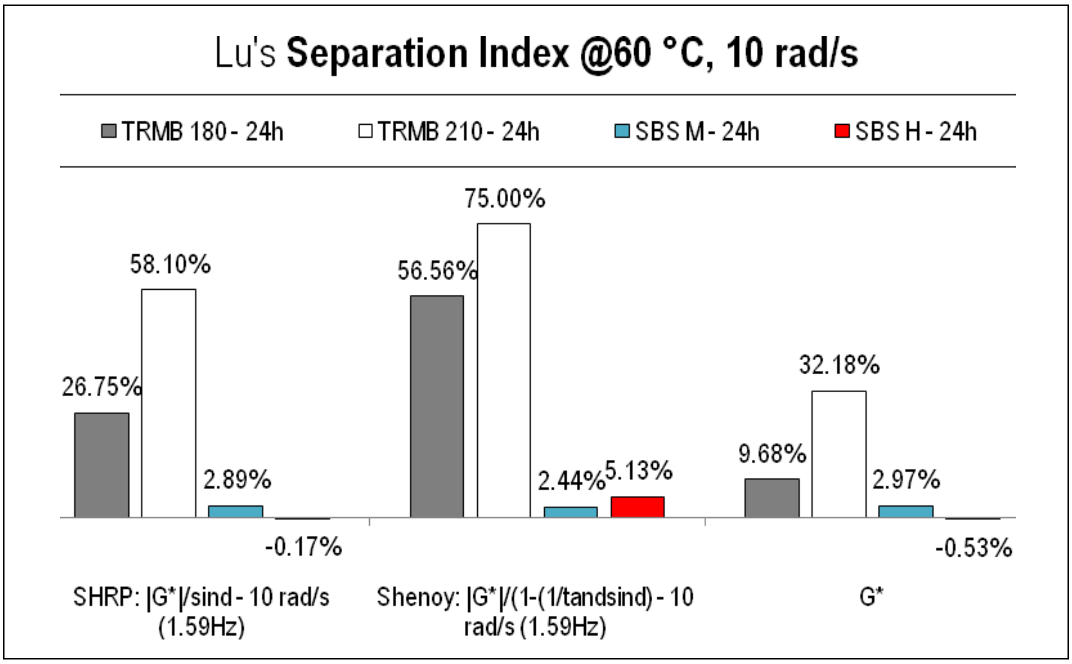


Figure 8.42a. Analysis of the separation indecies (Lu) of the modified binder after 24h of hot storage @ 180ºC

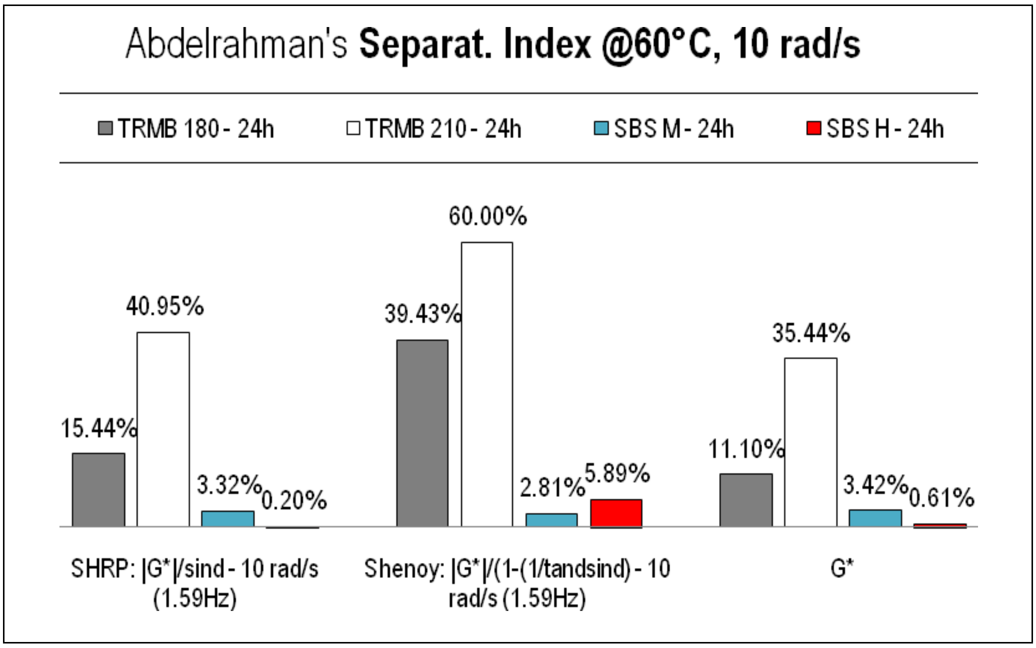


Figure 8.42b. Analysis of the separation indecies (Abhelerdam) of the modified binder after 24h of hot storage @ 180ºC

Similar considerations can be made for the Lu's separation indices (Fig. 8.42a), which demonstrate again the differences shown by the calculation with the Shenoy's parameter, but they also show clear differences between the indices calculated with G* and the SHRP's parameter. This happens probably because with the Lu's method there is no comparison with a "dummy" binder with average properties, in fact the parameters of the lower and upper sections of the sample are directly correlated. Moreover, the Lu's I_s, allows to find also negative value of the index, which permits to identify the part of the sample richer of polymer. In fact, in some case also surfactants are used to modify bitumen, therefore when PMBs are tested it is not possible to establish a priori which is the polymer-rich-phase.

Considering all the above mentioned information, it is possible to conclude that between those analysed in Figures 8.42a and 8.42b, the most suitable rheological index to assess the hot storage stability of modified binder, seems to be Lu's index calculated with the Shenoy's parameter.

8.8 Summary of results

The aim of this section was to understand the combined effect of processing temperature and shear rate, on performance and hot storage stability of tyre rubber modified bitumen (TR-MB). Two temperatures: 180ºC and 210ºC, and two blending protocols: low shear LS (§ 7.2.1) and high shear HS (§7.2.2) have been considered and results coming from their combination compared. The study was performed by choosing the most suitable base bitumen according to its chemical properties (SARA analysis). Once the base bitumen was selected, a low shear protocol was used to assess the level of modification of the TR-MBs binders when varying the rubber content and the processing temperature. Once optimum rubber content was chosen, the high shear protocol was used to assess the optimum mixing time and the storage stability of the produced binders. DMAs were used to assess rheology and performance of all the TR-MBs.

Finally, two commercially-used SBS modified binders, respectively with medium and high level of modification, were used for comparison with the produced TR-MBs. The PMBs were taken as a target and their rheology was studied to understand how the curing process of the TR-MBs can be improved.

Effect of processing temperature: optimum rubber content

Optimisation of the tyre rubber content, to be added to the selected bitumen, was performed with the low shear protocol. Results, show that higher processing temperature, 210ºC, does not change the optimum rubber content. Therefore, for both processing temperatures, 18% was fixed as rubber content to produce the TR-MBs in high shear.

Effect of processing temperature: optimum processing time

TR-MB processed in high shear at 180°C, reaches the peak performance after 40-80 minutes, and after 120 minutes it has a loss of performance of about 10-20%. Instead, the TR-MB processed in high shear at 210°C, not only reaches its peak performance in a shorter time (20-40 minutes), but after 120 minutes of high shear mixing the loss of performance is about 50-60% less of the peak.

Optimum blending time in high shear seems to be related to the one in low shear, which can be used to predict the former. In fact, for both temperatures, the optimum time in high shear results to be about a third of that necessary to obtain the equivalent blend in low shear mode (Tab 8.1), as obtained by other researcher (Takallou & Sainton, 1992).

Effect of processing temperature: storage stability

Hot storage stability analysis of the TR-MBs, performed by looking only at softening points, did not show a coherent trend. However by considering the longer hot storage time, TR-MB HS180 seemed to be the less stable. Instead, by performing a DMA it has been clarified that TR-MB produced at 210ºC, has a higher separation rate than the one produced at 180ºC. For these reasons, the Lu's index modified by using the Shenoy's parameter, is proposed as a rheological index to assess the storage stability of modified binders.

Effect of the shear rate

TR-MBs in low shear and high shear were both produced at 180ºC and 210 ºC, with a processing time of 120 minutes, and maintaining the same proportions between the raw materials. As a result, the processing of the TR-MBs in high shear speeds up the reaction process between rubber and bitumen. This result is even accelerated when raising the processing temperature to 210°C. This result is explainable if it considered that high shear mixing (3000-4000 RPM with a duplex head) disperses the polymer within the bitumen matrix and reduce its size, while the low shear blending (200 RPM with the Brookfield's spindle) is performed with a tool (spindle) which is made to measure viscosity and therefore to disturb the sample as little as possible.

Nevertheless, high shear mixing helps to get TR-MBs less heterogeneous and less shear susceptible than those obtained through low shear mixing. With regards to hot storage stability, in literature (§ 4.3.3) has been widely demonstrated that high shear mixing helps to homogenize the blend and has a positive effect on their stability at high storage temperature.

From these results, it is possible to affirm that raising the processing temperature from 180°C to 210°C, significantly speeds up the reaction between tyre rubber and bitumen and it also reduces the peak/apparent viscosity in both low shear and high shear. Nevertheless, by choosing the correct rubber content and the appropriate mixing time, also at high processing temperature, 210ºC, it is possible to produce well performing Tyre Rubber Modified Bitumens with a high level of modification.

Moreover, TR-MB processed at 210ºC resulted to be easier to handle and less shear susceptible than TR-MB processed at 180ºC. However processing at such high temperature negatively influences the storage stability of the TR-MB.

Therefore, it is possible to think about an optimum blend by using high shear and high processing temperature, as an intermediate step of the modification process. This has the aim of handling a well performing material, which has reasonable viscosity and shear susceptibility. Then, by reducing the temperature, also below the usual value of 177°C, and also reducing the shear rate to a simple agitation and optimising the mixing time, it will probably be possible to obtain an even better material.

9. Conclusions and Recommendations for future researches

The adoption of the Tyre Rubber Modified Bitumens (TR-MBs) technologies presents several economic, environmental and practical issues. However, this study shows that TR-MBs have also several benefits and it is therefore strongly advised to consider these technologies as a first option to the binders currently used in road pavements all over Europe.

In order to widely adopt TR-MBs in Europe, it has to be evaluated if it is convenient to use the standard wet process technology, which proved widely to provide several benefits, but implies high initial costs for the modification of the existing asphalt plants, or to invest more in the development of the wet process-NO agitation. In both cases laboratory analyses, of raw materials and final blends, are necessary to optimise the modification process and the performance of the final product.

For these reasons, this research have been focused firstly, on assessing the benefits of the TR-MB by performing a detailed investigation of their rheological properties and then by trying to have a better understanding, and a better control, of the interaction process occurring by modifying the bitumen with tyre rubber.

In this section it is indicated what has been found to be of fundamental importance in the literature review and from the overall analysis of the rheology and curing of the Tyre

Rubber Modified Bitumens (TR-MBs). At last, those statements are completed with recommendations for future research.

9.1.1 Rheological characteristics of TR-MBs

The main conclusions that can be drawn from the rheological research undertaken in this thesis are:

- The Superpave Performance Grade (PG) and the detailed rheological properties of various Tyre-Rubber Modified Bitumens (TR-MB) have been compared with those of of commercially available SBS Polymer Modified Bitumens (SBS-MBs). The results have shown that TR-MBs can have similar PG and rheological properties expected of an elastomeric polymer modified bitumen. Moreover, All the TR-MBs have shown considerable improvements in terms of their rheological and physical properties compared to the base binders used for their production.

- Although TR-MBs show comparable behavior with SBS-MBs over a wide range of frequencies and temperatures, concerns still exist over the storage stability of the tyre rubber blend, with both rheological and morphological evidence of phase separation occurring already after 3-5 hours of high temperature storage.

- Traditional characterisation methods are not suitable for this kind of materials. In fact, conventional tests present difficulties in performing the tests and show unreliable results. Contrarily, Dymanic Mechanical Analysis, by means of DSR, has shown to have great repeatability and to be a very useful tool to characterise the modified bitumen and to control the modification process of TR-MBs.

- In this work, it is believed that a good level of modification for a TR-MB is achieved only when three conditions are all verified: phase angle is constantly lower then 70°C, secondly when phase angle master curves and isochronal plot reach a plateau at low frequencies; at last when TR-MB show a high critical temperature over 80°C (measured with SHRP or Shenoy’s parameter).

- Current methods to establish stability of binders, at high storage temperatures, are based on evaluation of conventional properties. This research stated that conventional properties could lead to erroneous evaluations, also in this case. DMA, have demonstrated to be a very useful tool to understand the phase separation process of unstable binders.

- Lu’s index (Lu, 1999) calculated with the Shenoy’s parameter, showed to be the most suitable rheological index to assess the hot storage stability of modified binders, by means of DSR tests.

- In the whole research, DMA has found to be a fundamental tool to characterise binders and to be suitable also for modified binders. In order to rely on these measurements consistent data is necessary. For this reason, tests have to be performed with high accuracy and precision, in terms of material handling, equilibrium time, gap setting and correct geometry. Moreover, in order to have good repeatability it is mandatory to ensure a constant maintenance of the equipment.

9.1.2 Curing of TR-MBs

The main conclusions that can be drawn from the study of the curing conditions related to the production of TR-MBs are the following:

Laboratory procedures

- Laboratory mixing procedure undertaken by using a hot plate, to heat up and maintain a constant temperature within the binder, showed to be not reliable. Differences of even 15°C were noticed between the top and bottom sections of the container. The problem has been solved by adapting a thermostatic bath as a processing vessel. This made it possible to accurately control the processing temperature, during the modification with high shear stress, though high amount of materials were needed (~ 3 Kg of bitumen).

- A new protocol, called Low Shear Protocol (LSP), has been defined in order to control the modification process of bitumen with tyre rubber, without wasting material and time. LSP consisted in mixing the raw materials, by adapting a Brookfield viscometer as a low shear mixer and then by testing the sample with DSR. Only few hours, and very limited consumption of material, are needed to make blend and also characterise its rhoelogy. LSP proved to provide a correct indication of the reaction occurring when mixing bitumen with tyre rubber and also to be a very handy tool to assess optimum rubber content and mixing time, for a selected combination of bitumen and tyre rubber.

- Optimum blending time in high shear seems to be related to the one in low shear, which can be used to predict the former. The optimum time in high shear results to be about a third of that necessary to obtain the equivalent blend in low shear mode.

- Therefore, it is concluded that for the laboratory “production” of the TR-MBs, it is better to use the high shear mixing in order to enhance compatibility between the materials and reduce the time of mixing, but the low shear protocol was shown to be a really useful tool for the “predicition” of the rheological properties of the blends. In fact, due to its easy handling, LSP allowed finding the optimimum mixing time and the optimum tyre rubber content, to be added to the selected bitumen to produce a well performing TR-MB.

- Polymer Dispersion Analysis, by means of optical microscope, resulted to be a useful tool to evaluate differences between storage stable binders and TR-MBs. However, to evaluate the effect of different processing conditions on the structure of the tyre rubber-bitumen blends, optical microscope, with 40x of magnification, have not been helpful.

- Mechanical strength (shear susceptibility), consisting in an amplitude sweep at 10 rad/s at higher testing temperature (80°C), showed to be a useful tool to evaluate the level of heterogeneity of the TR-MBs and to also have a fast estimation of the performance of the tested binders.

Selection of the most suitable materials

- It is possible to obtain well performing TR-MBs from a wide range of base bitumen. In fact, by carefully selecting the processing conditions and eventually using oil extenders, it is possible to have enough oil fractions to let the rubber swell and react within the bitumen, by maintaining a good workability of the TR-MBs (fair value of viscosity). Of course, starting from a very soft base bitumen limitates the usage of oil extenders that can be harmful at high temperatures and could have a detrimental effect on the modification in terms of the materials stability (§ 6.4.2). However, bitumen with high rate of oils fraction are not always available, in that case laboratory analyses are crucial to find the correct process to obtain well performing blends. The definitions of handy protocols, as those indicated in this research, are therefore very helpful tools which allow defining the optimum processing conditions by optimising time and resources.

- Specifications adopted in the states where TR-MBs are intensively use, usually prescribe to use soft bitumen (higher than 80/100) as base for modificationwith tyre rubber. What has been found in this research, indicates that selecting the base bitumen only by physical properties doesn’t allow optimising viscoelastic properties and storage stability of the TR-MBs. Deeper investigations on the compatibility between rubber, base bitumen and other eventual components are necessary to optimise the final product, especially when the Wet process-NO agitation is used.

- Estimation of the sole asphaltenes content of base bitumen, is not enough to optimise viscoelastic properties of TR-MBs. In order to have a base which could provide enough oils fraction for the swelling of the rubber by keeping a fair value of final viscosity, it is necessary to assess the oils fractions content. SARA analysis through Low pressure chromatography based on the method B of the standard ASTM D6114, allowed to find the oils fractions with reliable results and very good repeatability. Although, a very long time and high amount of solvents are necessary.

- The role of the oil extender in the modification process has been investigated. As a results, the addition of flux effects the physical properties of the TR-MBs by softening the modified binder that has got, therefore, reduced viscosity and enhanced low temperature properties. The rheological analysis highlights that even if the base binders contain flux, it has got the same black diagrams as that of the base bitumens: The finger print does not change.

- Several studies in literature (§ 4.3.3) have indicated that compatibility between tyre rubber and bitumen could be improved by using tyre rubber with the following characteristics: high content of natural rubber (typically from trucks) and with particle size as little as possible.

- Comparison between the rheological properties of TR-MBs and those offered by commercially used SBS-MBs shows that only by choosing the correct rubber content, and optimising the mixing time, it possible to produce a tyre rubber modified bitumen with an high level of modification.

Processing conditions

- **Temperature**. It is the key parameter of the interaction process between tyre rubber and bitumen. In the standard wet process, 180-190°C is the most common processing temperature. Wet process-NO agitation requires higher temperatures. Therefore, the effect of raising the processing temperature from 180°C to 210°C has been investigated and the following occurs:
  - increasing the processing temperature from 180°C to 210°C, significantly speeds up the reaction between tyre rubber and bitumen and
  - it also reduces the peak/apparent viscosity in both low shear and high shear.
  - higher processing temperature, 210ºC, does not have a great influence on the optimum content of tyre rubber.

  - If correct rubber content and the appropriate mixing time are selected, also at high processing temperature, 210ºC, it is possible to produce TR-MBs with a high level of modification.
  - TR-MB processed at 210ºC resulted to be easier to handle and less shear susceptible than TR-MBs processed at 180ºC.

  - However processing at such a high temperature negatively influences the storage stability of the TR-MBs.

- **Shear rate.** The wet process is a low shear process (Shatanawi, 2010). Instead, Wet process-No agitation, requires high shear stress and continuous blending system. Therefore, in this research a comparison between blend produces in high shear (3000-4000 RPM with Silverson mixer) and low shear (200 RPM with Brookfiled viscometer) has been investigated and the following occurs:
  - Processing TR-MBs in high shear, speeds up the reaction process between rubber and bitumen. This result is explainable if it considered that high shear mixing disperses the polymer within the bitumen matrix and reduce its size.
  - high shear mixing helps to get TR-MBs less heterogeneous and less shear susceptible than those obtained through low shear mixing.
  - With regards to the hot storage stability, in literature (§ 4.3.3) it has been widely demonstrated that high shear mixing helps to homogenize the blend and has a positive effect on their stability at high storage temperature.

- **Processing Time**. Comparison between the rheological properties of TR-MBs and those offered by commercially used SBS-MBs shows that only by optimising the mixing time, it possible to produce well performing TR-MBs. Long interaction time, at high temperature, leads to properties decrease.

9.1.3 Reccomendations for future research

- Further studies are necessary in order to know if the proportions between the SARA fractions of a bitumen can be good indicators of the compatibility between bitumen and tyre rubber. The literature review indicates that thermodynamic analysis, by means of phase diagrams, can be also a powerful tools that seems to be able to provide a better understanding of the interaction process between bitumen and polymers and could also be a good indicator to assess compatibility and storage stability of the blends.

- In order to assess durability and to validate anti-rutting behaviour of the TR-MBs, ageing effect has to be further analysed. In fact, apart from the estimation of the Performance Grade, the evaluation of ageing effect on TR-MBs has not been included in this thesis.

- Would be of great interest to evaluate if it is possible to find a correlation between the homogeneity (shear susceptibility) of the tyre rubber blends, evaluated by means of rheological tests, and their storage stability. This will make it possible to assess storage stability of the binders only by means of DSR and without the need for long waiting times to perform the Storage Stability test.

- In order to use Wet process – NO agitation, storage stability of the TR-MBs have to be improved. In order to achieve this goal, future research should focus the attention on first assessing and, if necessary, improving the compatibility between bitumen and tyre rubber and secondly, by using additives or other modifiers, to stabilise the blend with accurate selection of the processing conditions. Another interesting option to improve compatibility, could involve some kind of pre-processing of the tyre rubber.

- Several of the benefits of rubberised asphalt mixture obtained through the standard wet process come out from the higher binder content accepted by the rubberised mixture. This probably depends on the higher viscosity of the TR-MBs, while Wet process-NO agitation leads to TR-MBs with lower viscosity. Therefore future research has to assess if this new technology allows benefits to be obtained comparable to those proved by using of the standard wet process.

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List of Figures

Chapter 1

Figure 1.1. Histroy and Geography of the ELT management in Europe (ETRMA stat, 2010)

Figure 1.2. Country specific implementation & ELT managment companies (ETRMA stat, 2010)

Figure 1.3. Annual trends of sales on the European tyre replacement market (ETRMA stat, 2010)

Chapter 2

Figure 2.1. Distillation of bitumen (courtesy of Total)

Figure 2.2. Composition of varium petroleum crude oils (concentrations in vol %) (Siracusa et al. 2010)

Figure 2.3. LPC process

Figure. 2.4. SEC process.

Figure. 2.5. Example of IEC equipment

Figure. 2.6. Example of HPLC equipment

Figure 2.7. Example of a bitumen Chromatogram (Isacsson & Lu, 1997).

Figure 2.8. Colloidal nature of bitumen (Read & Whiteoak, 2003)

Figure 2.9. Modello colloidale dei bitumi SOL e GEL. (Lesueur D.,2009).

Figure 2.10. Colloidal structures against temperature (Lu et al, 1999).

Figure 2.11. Separazione del bitume in diverse frazioni in relazione delle classi di solubilità. (Lesueur, 2009)

Figure 2.12. Possible structure of the Asphaltenes (Read & Whiteoak, 2003).

Figure 2.13. Possible structure of Aromatics (Read & Whiteoak, 2003)

Figure 2.14. Possible structure of Saturates (Read & Whiteoak, 2003)

Figure 2.15. Separation of bitumen in strong and weak acids, strong and weak bases and neutrals trough IEC (Anderson et al., 1994-SHRP 367)

Figure 2.16. Separation of bitumen in acids, bases, amphoterics and neutrals trough IEC (Anderson et al., 1994-SHRP 367).

Figure 2.17. Separation into SARA and IEC fractions of some SHRP bitumens. Amphoteric were quantified for only 4 of them (after 24 Lesuer)

Figure 2.18. Typical viscosity of a binder over its working temperature range.

Figure 2.19. Prediction of PG for different crude oil blends (PavementInteractive.org, 2010)

Figure 2.20. Structure of bituminous binders working groups (Southern, 2007)

Figure 2.21. List of candidate empirical tests to classify bituminous binders (Southern, 2007)

Figure 2.22. List of candidate performance-realted test methods to classify bituminous binders (Southern, 2007)

Chapter 3

Figure 3.1. Mechanical response of a viscoelastic material (Airey, 1997)

Figure 3.2. Linear viscoelastic response of bitumen

Figure 3.3. Van der Poel's nomograph (Read & whiteoak, 2003)

Figure 3.4. Measured stiffness versus Van der Poel's nomograph predicted Stiffness (SHRP 367, 1994)

Figure 3.5. SHRP equipments and criteria

Figure 3.6. Brookfield rotational viscometer (PavementInteractive.org, 2010).

Figure 3.7. Close-up of the BBR beam on its supports (PavementInteractive.org, 2010).

Figure 3.8. DTT equipment (PavementInteractive.org, 2010).

Figure 3.9. RTFO equipment (PavementInteractive.org, 2010).

Figure 3.10. PAV equipment (PavementInteractive.org, 2010).

Figure 3.11. Dynamic Shear Rheometer testing geometry

Figure 3.12. DSR and testing geometries used to characterise bituminous binders

Figure 3.13. DSR cone and plate geometry

Figure 3.14. DSR parallel plates geometry

Figure 3.15. Strain sweep used to determine linear region (SHRP 370, 1994)

Figure 3.16. Linear viscoelastic strain limit as a function of complex modulus for unaged and aged asphalts (SHRP 370, 1994)

Figure 3.17. Vectorial representation of the relationship between the Complex Shear modulus and its components, (PavementInteractive, 2010)

Figure 3.18. Dymanic oscillatory stress-strain functions and geometry (Lu & Isacsson, 1997)

Figure 3.19. Typical trends of isochronal plots of bitumen for G* and δ

Figure 3.20. Typical trends of isochronal plots of bitumen for G* and δ

Figure 3.21. Time-Temperature Superposition Principle

Figure 3.22. Typical trends of G* and δ mastercurves

Figure 3.23. Example of WLF Shifting factor curve

Figure 3.24. The correlation between SHRP binder rutting parameter and the average mixture rutting parameter, by using modified binders . (NCHRP 459, 2001)

Figure 3.25. Burgers model and its response. (NCHRP 459, 2001)

Figure 3.26. Results of the accumulated strain under repeated creep testing for three PG 82 binders at 1 s loading and 9 s recovery (70°C, 300 Pa). (NCHRP 459, 2001)

Figure 3.27. The correlation between NCHRP binder rutting parameter and the average mixture rutting parameter, by using modified binders. (NCHRP 459, 2001)

Figure 3.28. Plot of the accumulated strain versus the SHRP and Shenoy's parameter parameter at 70°C for three binders identically graded as PG 82-22 (Bahia et al., 2001)

Figure 3.29. Correlations between various rutting-related binders tests for unmodified binders (Bitval, 2006)

Figure 3.30. Correlations between various rutting-related binder tests for modified binders (Bitval, 2006)

Chapter 4

Figure 4.1. Temperature susceptibility of an ideal thermoplastic binder. (Brule', 2007)

Figure 4.2. EVA – molecular structures and aspect.

Figure 4.3. SBS – molecular structures, compatibility with bitumen and aspect.

(TradeKorea.com, 2011)

Figure 4.4a. Effect of aromaticity of maltenes on the characteristics of SBS-modified bitumens.(Van Beem & Brasser, 1973)

Figure 4.4b. Different morphologies of SBS modified bitumen by changing the base bitumen (Airey, 2003)

Figure 4.5. Typical Polymer Blending Plant (Holleran et al., 2011)

Figure 4.6. Effect of polymer-modification on the colloidal structure of a bitumen: original bitumen (A) and the corresponding PMB with increased asphaltenes content in the matrix (B) (Lesuer, 2009)

Figure 4.7. Effect of asphaltene content on the storage stability of EVA-modified binders (Brule', 2007).

Figure 4.8. Typical phase diagram for binary mixtures miscible in all temperatures (a) that segregate upon heating, (b) that segregate upon cooling, (c) that segregate upon heating and cooling (d,e). The composition of the segregated phases (Φ_a and Φ_b) is governed by the spinoidal curve (f) (Masson et al., 2003)

Figure 4.9. Translation of the spinoidal along the temperature axis due to a change in SBS content and its effect on equilibrium concentration (Masson et al., 2003)

Figure 4.10. Black diagrams for base bitumen, EVA and SBS PMBs (Airey, 2002)

Figure 4.11. Complex modulus master curve at 25ºC for base bitumen, EVA and SBS PMBs (Airey, 2002)

Figure 4.12. Phase angle master curve at 25ºC for base bitumen, EVA and SBS PMBs (Airey, 2002)

Figure 4.13. Isochronal plot at 1 Hz for base bitumen, EVA and SBS PMBs (Airey, 2002)

Figure 4.14. Raw material used in tyre

Figure. 4.15a Life cycle of End of Life Tyres (Rahman, 2004)

Figure 4.15b. Shredded tyre (left) and crumb rubber (right) (CWC 1998)

Figure 4.15c. Different processes and technologies in application of tyre rubber in asphalt (Heitzman, 1992).

Figure 4.16. Schematic diagram of wet process (Airey, 2002)

Figure 4.17. Schematic diagram of McDonald's wet process

Figure 4.18. Example of Portable Asphalt Rubber production unit: 1) Mixing unit

Figure 4.19. Example of Portable Asphalt Rubber production unit: 2) Reaction tank

Figure 4.20. Schematic diagram of the dry process

Figure 4.21. Bitumen rubber interaction phenomenon (Abdelrahaman, 2006)

Figure 4.22. Micrographs of tyre rubber modifed bitumen morphology changing over time (Pereira & Pais, 2008)

Figure 4.23. Typical changes in viscosity alues fro bitumen rubber at different temperatures over time (AsAc, 2007)

Figure 4.24. Distributive mixing and Dispersive mixing (Chung, 2000)

Figure 4.25. Viscosity of four TR-MBs differing by CRM source and content: Source 1 cryogenic/passenger; Source 4 ambient/truck (Shatanawi, 2008)

Figure 4.26 SEM micrographs of Ambient CRM (left) and Cryogenic CRM at 30x magnification (Shatanawi, 2008)

Figure 4.27. Comparison of Penetration and American Viscosity bitumen grades

Figure 4.28. Asphalt Rubber Production plant (left) and Weigh Hopper for CRM proportioning. (Caltrans, 2006)

Figure 4.29. Austroads laboratory procedure for Crumb rubber modified binders (AP-T42, 2006)

Figure 4.30. Typical costs for scenario used by USA state highway agencies

(Hicks & Epps, 2003)

Figure 4.31. Maintainance cost (left) and User cost comparison betwen conventional bituminous mixes (AC) and Asphalt Rubber mixes (ARAC) (Suk Jung et al., 2002)

Figure 4.32. Terminal blend Tyre Rubber system

Figure 4.33. Performance Graded Tyre Rubber Modified Binder (PCCAS, 2008)

Figure 4.34. TR-MB from Wet process (left) and Wet Process-NO agitation (right)

(PCCAS, 2008)

Figure 4.35. Production of NO agitation TR-MB as proposed by Attia & Abdelrahman (2009)

Chapter 5

Figure 5.1. Grading curve of the tyre rubber crumbs

Figure 5.2a. Master curves of complex modulus at 25ºC of base bitumen and base binder

Figure 5.2b. Master curves of phase angle at 25ºC of base bitumen and base binder

Figure 5.2c. Black diagram of base bitumen and base binder

Figure 5.2d. Isochronal plots of complex modulus and phase angle at 0.4 Hz of base bitumen and base binder

Figure 5.3a Master curves of complex modulus at 25ºC of the modified binders and base binder

Figure 5.3b Master curves of phase angle at 25ºC of the modified binders and base binder

Figure 5.3c Black diagram of the modified binders

Figure 5.3d. Isochronal plots of complex modulus and phase angle at 0.4 Hz of the modified binders

Figure 5.4a Black diagrams of base binder and SBS-MB before and after the hot storage.

Figure 5.4b Black diagrams of base binder and SBS-MB before and after the hot storage.

Figure 5.5. Fluorescent microscopic images of the top and bottom sections of the SBS-MB and polymer dispersion before and after hot storage

Figure 5.6a Black diagrams of base binder and TR-MB before and after 3h hot storage.

Figure 5.6b Black diagrams of base binder and TR-MB before and after 5h hot storage.

Figure 5.7 Fluorescent microscopic images of the top and bottom sections of the TR-MB showing the polymer dispersion before and after hot storage

Chapter 6

Figure 6.1a. Master curves of |G*| and δ at 25 ºC for the base bitumens

Figure 6.1b. Black diagram for the base bitumens

Figure 6.1c. Isochronal plots of |G*| and δ at 0.4 Hz for the base bitumens

Figure 6.3a. Master curves of |G*| and δ at 25 ºC for bitumen B and binder Bf

Figure 6.3b. Black diagram for bitumen B and binder Bf

Figure 6.3c. Isochronal plots of |G*| and δ at 0.4 Hz for bitumen B and binder Bf

Figure 6.4. Overview of the performance properties of all the binders

Figure 6.4. Master curves of complex modulus at 25 ºC for all the TR-MBs

Figure 6.5. Master curves of phase angle at 25 ºC for all the TR-MBs

Figure 6.6. Black diagrams for all the TR-MBs

Figure 6.7. Isochronal plots of complex modulus and phase angle at 0.4 Hz for all the TR-MBs

Figure 6.8. Polymeric dispersion analysis of the top and bottom sections of “TR-MB A” and “TR-MB Af”

Figure 6.9. Black diagrams of base bitumen A and TR-MB A before and after hot storage; a) 3h hot storage, b) 5h hot storage

Figure 6.10. Black diagrams of base binder Af and TR-MB Af before and after hot storage; a) 3h hot storage, b) 5h hot storage

Figure 6.13. Polymeric dispersion analysis of the top and bottom sections of “TR-MB B” and “TR-MB Bf”

Figure 6.11. Black diagrams of base bitumen B and TR-MB B before and after hot storage; a) 3h hot storage, b) 5h hot storage

Figure 6.12. Black diagrams of base binder Bf and TR-MB Bf before and after hot storage; a) 3h hot storage, b) 5h hot storage

Figure 6.13. Diagram of temperature variability of top and bottom sections of the sample, due to the usage of the hot plate method

Chapter 7

Figure 7.1. Thermostatic vessel and covering metal rings

Figure 7.2. SARA analyses results

Figure 7.3 Triangular representation of the different bitumen families.

Figure 7.4 Isolines of the dispersion factor

Figure 7.5. Gradation curve of the tyre rubber used, as obtained via mechanical grinding

Figure 7.6. Results of constant monitoring using the Brookfield Viscometer as a low shear mixer

Figure 7.7. Black diagrams of low shear TR-MBs with various rubber contents and neat bitumen

Figure 7.8a. Master curves of G*at 30°C of low shear TR-MBs with various rubber contents and neat bitumen

Figure 7.8b. Master curves of δ at 30°C of low shear TR-MBs with various rubber contents and neat bitumen

Figure 7.9a. Isochronal plots of G*of low shear TR-MBs with various rubber contents and neat bitumen

Figure 7.9b. Isochronal plots of δ of low shear TR-MBs with various rubber contents and neat

Figure 7.10a. Shenoy rutting parameters of low shear TR-MBs with various rubber contents and neat

Figure 7.10b. SHRP rutting parameters of low shear TR-MBs with various rubber contents and neat bitumen

Figure 7.11. Apparent viscosity of TR-MB HS at different blending time

Figure 7.12. Black diagrams of: TR-MB HS at different blending time, TR-MB LS and neat

Figure 7.13a. Master curves of G at 30°C of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

Figure 7.13b. Master curves of δ at 30°C of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

Figure 7.14a. Isochronal plots of G* of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

Figure 7.14b. Isochronal plots of δ of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

Figure 7.15a. Shenoy rutting parameters of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

Figure 7.15b. SHRP rutting parameters of: TR-MB HS at different blending times, TR-MB LS and neat bitumen

Figure 7.16. Assesing optimum rubber content thorugh analysis of Black diagrams

Figure 7.17a. Assesing optimum rubber content thorugh analysis of Master curves of G*at 30°C

Figure 7.17b. Assesing optimum rubber content thorugh analysis of Master curves of δ at 30°C

Figure 7.18a. Master curves of G* at 30°C of : TR-MB HS40, TR-MB HS120, PMBs and neat

Figure 7.18b. Master curves of δ at 30°C of : TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

Figure 7.19. Black diagrams of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

Figure 7.20a. Isochronal plots of G* of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

Figure 7.20b. Isochronal plots of δ of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

Figure 7.21a. Shenoy rutting parameters of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

Figure 7.21b. SHRP rutting parameters of: TR-MB HS40, TR-MB HS120, PMBs and neat bitumen

Chapter 8

Figure 8.1. Results of the Low Shear mixing at 180°C using the Brookfield Viscometer

Figure 8.2. Results of the Low Shear mixing at 210°C using the Brookfield Viscometer

Figure 8.3. Amplitude sweep @ 80°C and 10rad/s performed on neat and TR-MB LS

Figure 8.5. . Master curves of G∗ at 30°C of low shear TR-MBs LS 180 and neat bitumen

Figure 8.6. . Master curves of G∗ at 30°C of low shear TR-MBs LS 210 and neat bitumen

Figure 8.7. Master curves of δ at 30°C of low shear TR-MBs LS 180 and neat bitumen

Figure 8.8. Master curves of δ at 30°C of low shear TR-MBs LS 210 and neat bitumen

Figure 8.9. Black diagrams of low shear TR-MBs LS 180 and neat bitumen

Figure 8.10. Black diagrams of low shear TR-MBs LS 210 and neat bitumen

Figure 8.11. Isochronal plots of G*(a) and δ (b) of low shear TR-MBs LS 180 and neat bitumen

Figure 8.12. Isochronal plots of G*(a) and δ (b) of low shear TR-MBs LS 210 and neat bitumen

Figure 8.13. Shenoy (a) and SHRP (b) rutting parameters of low shear TR-MBs LS 180 and neat bitumen

Figure 8.14. Shenoy (a) and SHRP (b) rutting parameters of low shear TR-MBs LS 210 with various rubber contents and neat bitumen

Figure 8.15. Apparent viscosity @ 177.5ºC of TR-MB HS at different time and temperatures

Figure 8.16. Black diagrams of: TR-MB HS180 at different blending time

Figure 8.17. Black diagrams of: TR-MB HS210 at different blending time

Figure 8.18a. Master curves of |G*| at 30°C of: TR-MB HS180 at different blending time

Figure 8.18b. Master curves of |G*| at 30°C of: TR-MB HS210 at different blending time

Figure 8.19a. Master curves of δ at 30°C of: TR-MB HS180 at different blending time

Figure 8.19b. Master curves of δ at 30°C of: TR-MB HS210 at different blending time

Figure 8.20. Isochronal plots of |G*| (a) and δ (b) of TR-MB HS180 at different blending time

Figure 8.21. Isochronal plots of |G*| (a) and δ (b) of TR-MB HS210 at different blending time

Figure 8.22. Shenoy's (a) and SHRP (b) parameters of TR-MB HS180 at different blending time

Figure 8.23. Shenoy's (a) and SHRP (b) rutting parameters of TR-MB HS210 at different blending time

Figure 8.24. Black diagrams of TR-MB LS210 and TR-MB HS210 at different blending time

Figure 8.25a. Master curves of |G*| at 30°C of TR-MB LS210 and TR-MB HS210 at different blending time

Figure 8.25b. Master curves of δ at 30°C of TR-MB LS210 and TR-MB HS210 at different time

Figure 8.26. Isochronal plots of |G*| (a) and δ (b) of TR-MB LS210 and TR-MB HS210 at different blending time

Figure 8.27. Shenoy's (a) and SHRP (b) rutting parameters of TR-MB LS210 and TR-MB HS210 at different blending time

Figure 8.28. Amplitude sweep @ 80°C and 10rad/s performed on neat, PMBs and TR-MBs HS

Figure 8.29. Black diagrams of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

Figure 8.30a. Master curves of |G*| at 30°C of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

Figure 8.30b. Master curves of δ at 30°C of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

Figure 8.31a Isochronal plots of |G*| at 10rad/s of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

Figure 8.31b. Isochronal plots of δ at 10rad/s of neat bitumen, PMBs and TR-MBs HS produced at 180ºC and 210ºC

Figure 8.32. Amplitude sweep @ 80°C and 10rad/s performed on neat, PMBs and TR-MB HS at 180 and 210ºC

Figure 8.33. Black diagrams of neat bitumen, PMBs and TR-MB HS210 and TR-MB LS210

Figure 8.34. Black diagrams of neat bitumen, PMBs and TR-MB HS210 and TR-MB LS210

Figure 8.35a. Master curves of |G*| at 30°C of neat bitumen, PMBs and TR-MB HS180 and TR-MB LS180

Figure 8.35b. Master curves of |G*| at 30°C of neat bitumen, PMBs and TR-MB HS210 and TR-MB LS210

Figure 8.36a. Master curves of δ at 30°C of neat bitumen, PMBs and TR-MB HS180 and TR-MB LS180

Figure 8.36b. Master curves of δ at 30°C of neat bitumen, PMBs and TR-MB HS210 and TR-MB LS210

Figure 8.37a Performance comparison by isochronal plots of |G*| of all TR-MBs HS, PMBs and neat

Figure 8.37b Performance comparison by isochronal plots of δ of all TR-MBs HS, PMBs and neat

Figure 8.38a. Performance comparison by Shenoy parameter of TR-MBs HS, PMBs and neat

Figure 8.38b. Performance comparison by SHRP parameter of TR-MBs HS, PMBs and neat

Figure 8.39a. Black diagrams of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 1h of hot storage @ 180ºC

Figure 8.39b. Black diagrams of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 4h of hot storage @ 180ºC

Figure 8.39c. Black diagrams of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 24h of hot storage @ 180ºC

Figure 8.40a. Master curves of |G*| at 30°C of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 24h of hot storage @ 180ºC

Figure 8.40b. Master curves of δ at 30°C of top and bottom parts of TR-MB HS180 and TR-MB HS210 after 24h of hot storage @ 180ºC

Figure 8.41. Black diagrams of top and bottom parts of TR-MB HS180 and TR-MB HS210 and PBMs after 24h of hot storage @ 180ºC

Figure 8.42a. Analysis of the separation indecies (Lu) of the modified binder after 24h of hot storage @ 180ºC

Figure 8.42b. Analysis of the separation indecies (Abhelerdam) of the modified binder after 24h of hot storage @ 180ºC

Figure 9.39. Separation indecies of the modified binder after 24h of hot storage @ 180ºC

Figure B.1. Superpave binder specification taken from NAPA's Virtual Superpave Laboratory and AASHTO MP 1

List of Tables

Chapter 1

Table 1.1. End of Life Tyres recovery rate for 2009 (metric tonnes) (ETRMA, 2010)

Table 1.2. Evolution of the ELT recovery in Europe since 1996 (ETRMA stat, 2010)

Chapter 2

Table 2.1. Penetration and viscosity graded bitumens (Airey, 1997)

Chapter 3

Table 3.1. Raw data and rheological parameters for oscillatory tests (Mezger, 2002)

Chapter 4

Table 4.1. Generic types of modifiers currently used for paving applications (NCHRP 459, 2001).

Table 4.2. Effect of temperature on natural rubber (Rahman, 2004)

Table 4.3. Comparison of passenger car and truck tyres in the EV (ETRA, 2004)

Table 4.4 Comparison between Ambient and Cryogenic Ground Rubber

Table 4.5 Comparison between Ambient and Cryogenic Ground Rubber

Table 4.6. Typical gradation of the CRM to be used in the Wet Process (Hicks, 2002)

Table 4.7. Specification for Asphalt Rubber (ASTM D6114)

Table 4.8. Caltrans Specification for Rubberised bitumen (Caltrans, 2006)

Table 4.9. SABITA requirements for rubber crumbs for modifying bitumen (AsAc, 2007)

Table 4.10. SABITA Properties of bitumen rubber surfacing seals and asphalt (AsAc, 2007)

Table 4.11. SABITA Typical temperature/time limits for bitumen rubber (AsAc, 2007)

Chapter 5

Table 5.1. Properties of the tyre rubber crumbs
Table 5.2. Sieving of the tyre rubber crumbs
Table 5.3. Blending protocol
Table 5.4. Overview of the grading procedure
Table 5.5. Physical properties of the base bitumen and base binder
Table 5.6. Rotational viscosity of the base bitumen and base binder @ 100 and 160ºC
Table 5.7. Performance properties of base bitumen and base binder
Table 5.8. Rotational viscosity of modified bitumens @ 100 and 160ºC
Table 5.9. Performance properties of SBS-MB and TR-MB
Table 5.10. Softening points before and after hot storage
Table 5.11. Separation index (Lu et all, 1999) of the modified binders after hot storage periods

Chapter 6

Table 6.1. Blending protocol for TR-MB A and TR-MB B
Table 6.2. Blending protocol for TR-MB Af and TR-MB Bf
Table 6.3. Properties of base bitumen A and base bitumen B
Table 6.4. Physical properties of base binder Af and base binder Bf
Table 6.5. Performance grading of bitumen A and binder Af
Table 6.6. Performance grading of “bitumen B” and “binder Bf”
Table 6.7. Rotational viscosity @ 100 and 160ºC
Table 6.8. Performance grading of “TR-MAB A” and “TR-MAB Af”
Table 6.9. Performance grading of “TR-MAB B” and “TR-MAB Bf”
Table 6.10. Softening points of TR-MB A and TR-MB Af before and after hot storage
Table 6.11. Softening points of TR-MB B and TR-MB Bf before and after hot storage

Chapter 7

Table 7.1. SARA analyses results
Table 7.2. Colloidal parameters
Table 7.3. Physical properties of the bitumens selected as potential bases for modification

Table 7.4. Physical and chemical properties of the selected base bitumen (UB01)

Table 7.5. Low shear mixer blending protocol (Brookfield viscometer with spindle 27)

Table 7.6. High shear mixer blending protocol

Table 7.7. Physical and mechanical characteristics of the binders studied

Chapter 8

Table 8.1. Results of the monitoring of the Low Shear mixing procedure at 180°C and 210°C

Table 8.2. High shear mixer blending protocol

Table 8.3. Physical and mechanical characteristics of the binders studied

Table 8.4. Softening points of the TR-MBs HS before and after hot storage

Table 8.5. Softening points of the TR-MBs HS and SBS-MSs after 24 h of hot storage

APPENDIX A - SARA Analysis

Bitumen fractioning through liquid chromatography performed by following an internal protocol based on ASTM D6114 specification

1) SAMPLE PREPARATION

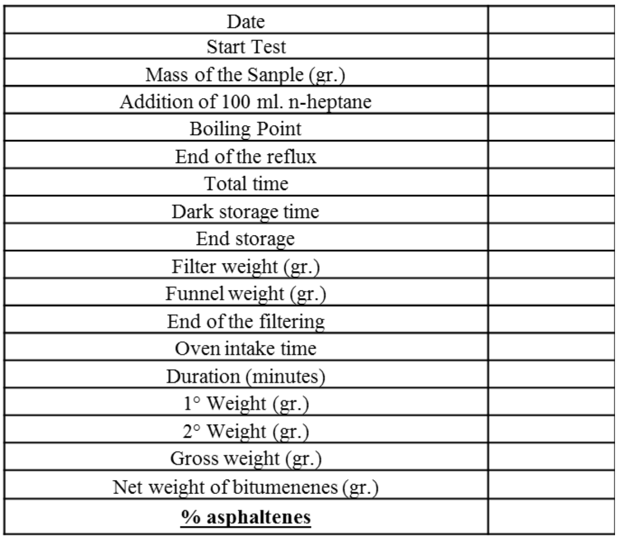
2,5 g of bitumen

100 ml of n-heptane

2) SEPARATION OF ASPHALTENES

A - condensation column

B - filtering



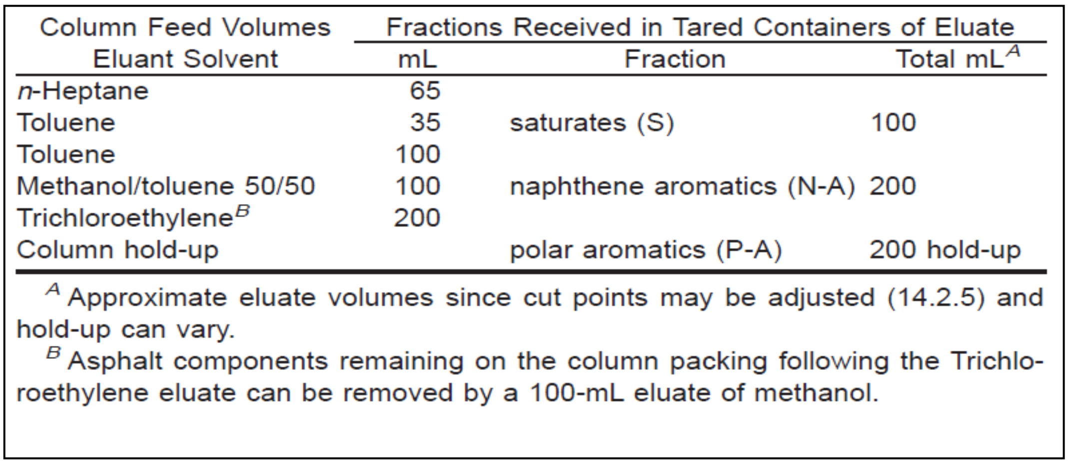
Date	
Start Test	
Mass of the Sanple (gr.)	
Addition of 100 ml. n-heptane	
Boiling Point	
End of the reflux	
Total time	
Dark storage time	
End storage	
Filter weight (gr.)	
Funnel weight (gr.)	
End of the filtering	
Oven intake time	
Duration (minutes)	
1° Weight (gr.)	
2° Weight (gr.)	
Gross weight (gr.)	
Net weight of bitumenenes (gr.)	
% asphaltenes	

C - weightening

$$\%A = \frac{(A - B)}{M} \times 100$$

A – Filter Weight + Weight of asphaltenes;
B – Filter Weight;
M – Mass of the Sample.

3) SEPARATION OF THE MALTENSE



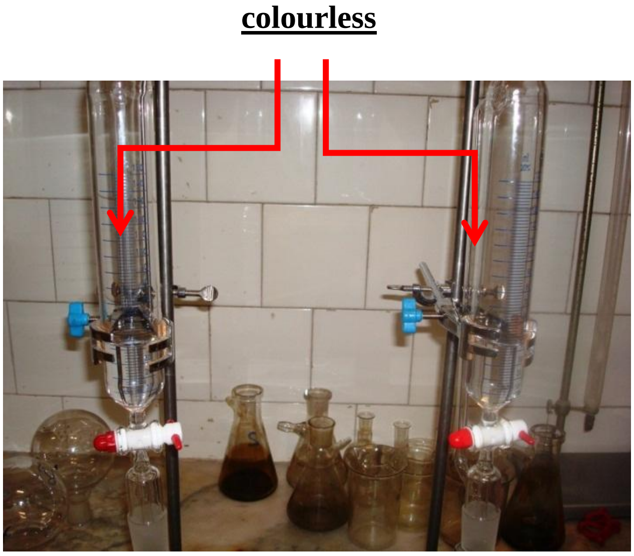
Column Feed Volumes	Fractions Received in Tared Containers of Eluate		
Eluant Solvent	mL	Fraction	Total mL[A]
n-Heptane	65		
Toluene	35	saturates (S)	100
Toluene	100		
Methanol/toluene 50/50	100	naphthene aromatics (N-A)	200
Trichloroethylene[B]	200		
Column hold-up		polar aromatics (P-A)	200 hold-up

[A] Approximate eluate volumes since cut points may be adjusted (14.2.5) and hold-up can vary.

[B] Asphalt components remaining on the column packing following the Trichloroethylene eluate can be removed by a 100-mL eluate of methanol.

separation schedule (ASTM D6114)

3a) SATURATES

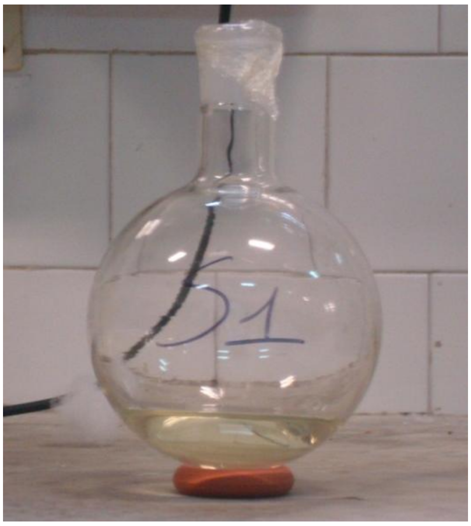


Sample:

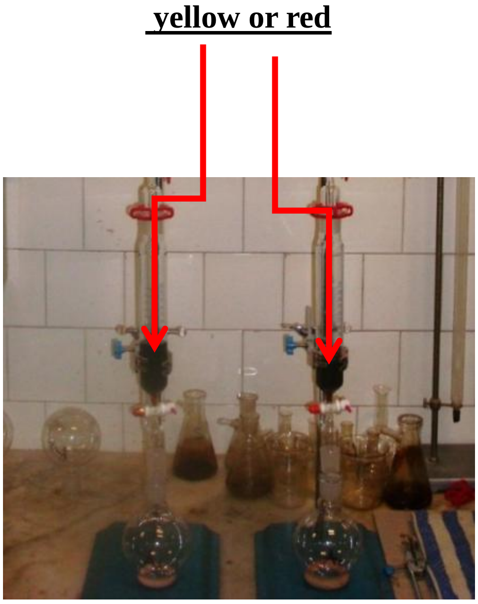
Date: ____________________

Chromatographic column	
n-Heptane (65ml)	V
Toluene (35ml)	V
Toluene (100ml)	
Methanolo/Toluene (50/50ml)	
Trichloroethylene (100ml)	
Trichloroethylene (100ml)	
Start Test	
Weight of Saturates container (gr.)	
Weight of Aromatics container (gr.)	
Weight of Resins container (gr.)	
Exit Saturates	
Saturates (ml.)	
Exit Aromatics	
Aromatics (ml.)	
Exit Resins	
Resins (ml.)	
End Test	

average time 1 hour



3b) AROMATICS

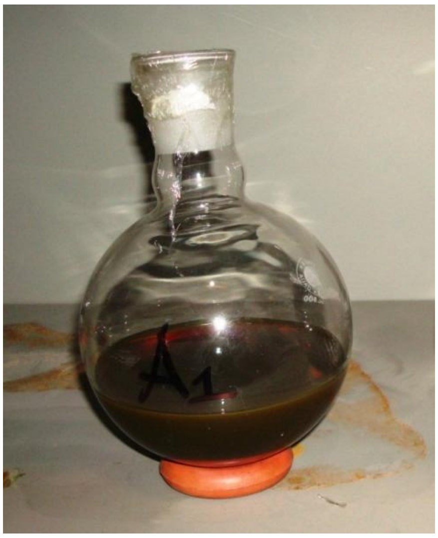


Sample:

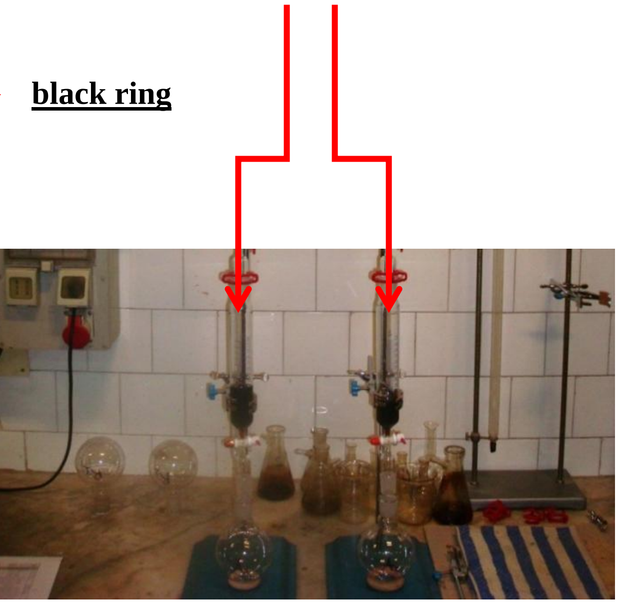
Date: ____________________

Chromatographic column	
n-Heptane (65ml)	V
Toluene (35ml)	V
Toluene (100ml)	V
Methanolo/Toluene (50/50ml)	V
Trichloroethylene (100ml)	
Trichloroethylene (100ml)	
Start Test	
Weight of Saturates container (gr.)	
Weight of Aromatics container (gr.)	
Weight of Resins container (gr.)	
Exit Saturates	
Saturates (ml.)	
Exit Aromatics	
Aromatics (ml.)	
Exit Resins	
Resins (ml.)	
End Test	

average time 1,5 hour



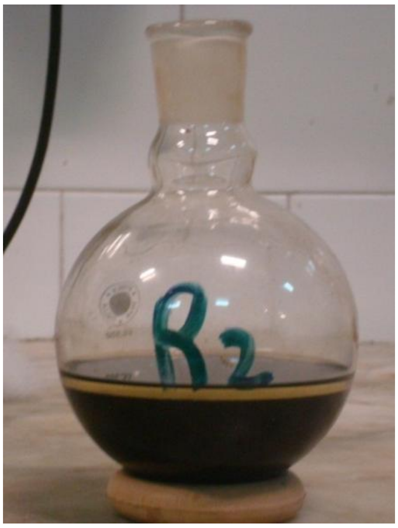
3c) RESINS



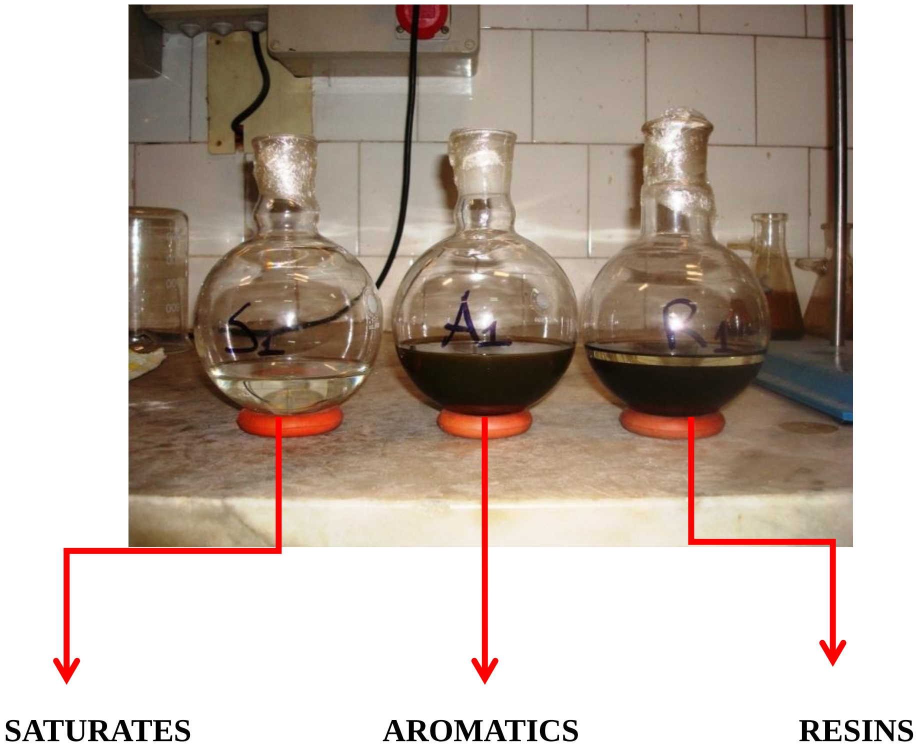
Sample:
Date:

average time 3,5 hour

Chromatographic column	
n-Heptane (65ml)	V
Toluene (35ml)	V
Toluene (100ml)	V
Methanolo/Toluene (50/50ml)	V
Trichloroethylene (100ml)	V
Trichloroethylene (100ml)	V
Start Test	
Weight of Saturates container (gr.)	
Weight of Aromatics container (gr.)	
Weight of Resins container (gr.)	
Exit Saturates	
Saturates (ml.)	
Exit Aromatics	
Aromatics (ml.)	
Exit Resins	
Resins (ml.)	
End Test	



4) SOLVENT REMOVAL



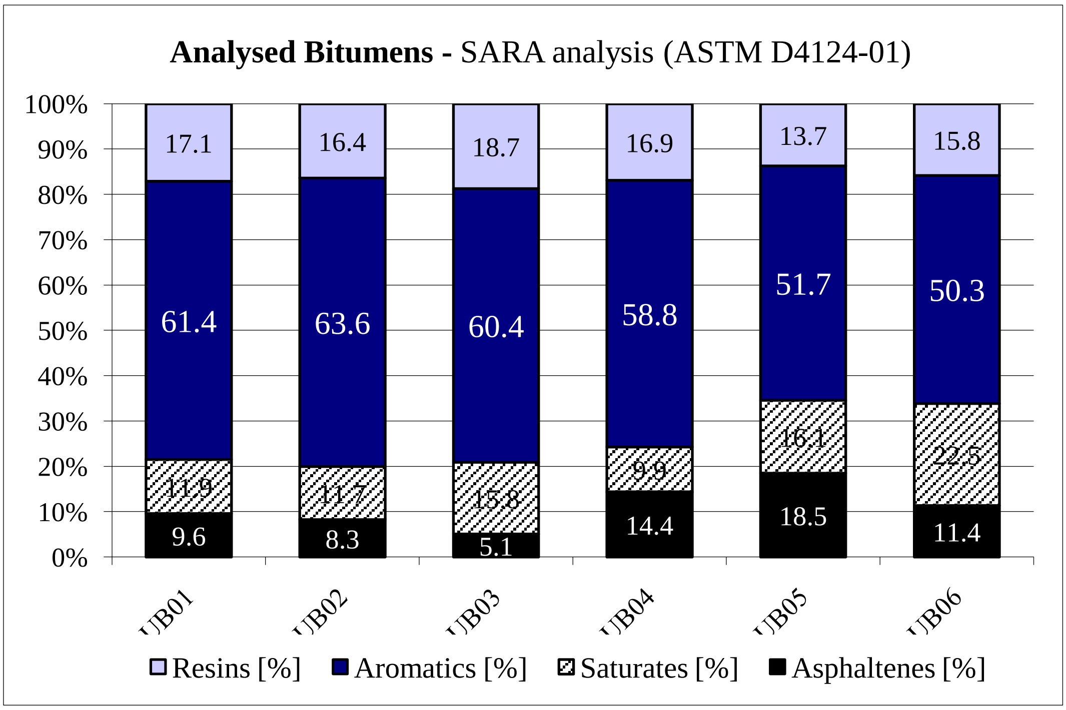
Rotovapor

5) FINAL RESULTS

	1° Weight	2° Weight	Weight (constant mass)
Gross weight of Saturates container (gr.)			
Gross weight of Aromatics container (gr.)			
Gross weight of Resins container (gr.)			

$$\%F = \frac{(A - B)}{M} \times 100$$

A - Mass of the container and fraction
B - Mass of the container;
M - Mass of the sample.


Analysed Bitumens - SARA analysis (ASTM D4124-01)

APPENDIX B - SHRP Grading Procedure

Step by Step procedure to determine SHRP Performance Grade of binders

B.1 Grading procedure overview

This practice describes the procedure to determine the performance grade of an unknown asphalt binder according to the AASHTO designations. In the first part of the report will be furnished some preliminary informations about necessary documents to keep present, time planning, materials and laboratory tips in order to avoid time wasting and to improve laboratory productivity. As well known, the performance grading is made by testing the binder in three different aging conditions: unaged, short term aged (RTFO aged) and long term aged (PAV aged). As explained in table 2.1, performing the tests with the un-aged and RTFO aged binder permits to get the high performance grade (high PG). Completing the sequence, by testing the PAV aged binder, makes possible to get even the low performance grade (low PG) (Fig. B.1).

Summary of practice

In the following section every step of this summary will be discussed in details. In this part of the report will be furnished an overview of the whole procedure and some preliminary informations in order to avoid time wasting and to improve laboratory productivity.

Table B.1. Summary of grading procedure

high PG
Un-aged binder: The tank [as-received] sample of asphalt binder is tested to determine: • the flash point in °C [T 48], • viscosity at 135°C [T316], • the shear modulus [G*] and phase angle [T 315] RTFO aged binder: • The asphalt binder is aged in the Rolling Thin-Film Oven [T 240] • and the residue is tested to determine the mass loss [T 240], • the shear modulus [G*] and phase angle [T 315]
low PG
PAV aged binder: • The residue from the rolling thin-film oven is aged in the Pressurized Aging Vessel [R 28] • and this residue is tested to determine the shear modulus [G*] and phase angle [T 315], • the creep stiffness [S] and slope, *m*, of the log creep stiffness versus log time relationship at different instants of load [T 313] • the failure stress in Direct Tension [T 314], • and in postprocessing the Critical Cracking Temperature [PP 42]

Necessary documents

The content of this report is a summary of the test containing practical lab advices but it does not contains the complete procedures for every test and should not be used as absolute reference to perform the test. The complete procedure can be found in the following documents of AASHTO:

Table B.2 list of all the necessary AASHTO standards

AASHTO Standards:	
M 320-05	Performance-Graded Asphalt Binder referenced tables with all the specifications for grading an asphalt binders by performance
R 29-02	Grading or Verifying the Performance Grade of and Asphalt Binder procedure for determining the high PG of an asphalt binder. *N.B. the low PG determination procedure showed in this standard is superseded*
PP42-02 [2003]	Determination of Low-Temperature Performance Grade (PG) of Asphalt Binders procedure for determining the low PG of an asphalt binder.
T 48	Flash and Fire Points by Cleveland Open Cup the same specifications are contained in the ASTM standard D 42 *N.B. Another flash point standard exists, it is the Flash-Point by Pensky-Martens Closed Cup Tester (AASHTO T72 or ASTM D43), but the one reported in this list is the more common for asphalt cement used in HMA*
T 316-04	Viscosity Determination of Asphalt Binder Using Rotational Viscometer. the same specifications are contained in the ASTM standard D 4402

• T 315-05	Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)
• T 240-03	Effect of heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test) the same specifications are contained in the ASTM standard D 2872-97
• R 28-02	Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)
• T 313-05	Determining the Flexural Creep Stifness of Ashpalt Binder using the Bending Beam Rheometer (BBR)
• T 314-02	Determining the Fracture Proprties of Ashpalt Binder in Direct tension (DT)

Estimation of binder quantities

In order to establish the grade of an unknown binder, approximately 700 g of asphalt binder is the minimum required to perform all the tests with the necessary replicates. This estimation is based on what is reported in the standard [R 29-02] and from the laboratory experience of the writer. In the following table the previous binder quantity estimation is summarised in details:

Table B.3. Binder quantity estimation by tests

Test	*Binder quantity per sample*	*Num. of samples*	*Total*
Flash point	~150 g	1	~150 g
Rotational viscosity	~10 g	1/2/3	~30 g
DSR tests	~2.5 g per vial	6 (2 every aging kind)	~15 g
BBR tests	35 g	6 (2 every temperature)	210 g
DT test	15 g	18 (6 every temperature)	270 g
		Total quantity approximated per excess	*~675 g*

Table B.4. Binder quantity estimation by ageing

aging	*Test*	*Binder quantity per sample*	*Num. of samples*	*Total*
un-aged	Flash point	~150 g	1	~150 g
	Rotational viscosity	~10 g	1/2/3	~30 g
	DSR tests	~2.5 g per vial	2	~5 g
			Total amount of un-aged binder:	*~185 g*
short-term aged (after RTFO)	DRS tests	~2.5 g per vial	2	~5 g
long-term aged (after PAV)	DRS tests	~2.5 g per vial	2	~5 g
	BBR tests	35 g	6 (2 every temperature)	210 g
	DT test	15 g	18 (6 every temperature)	270 g
			Total amount of aged binder:	*~490 g*

LAB TIP:

Basing on laboratory experience is recommended to use a bigger amount of binder, it means that when is possible it's suggested to use 1000g as total amount of bitumen to be tested.

Estimation of total time necessary to establish the PG

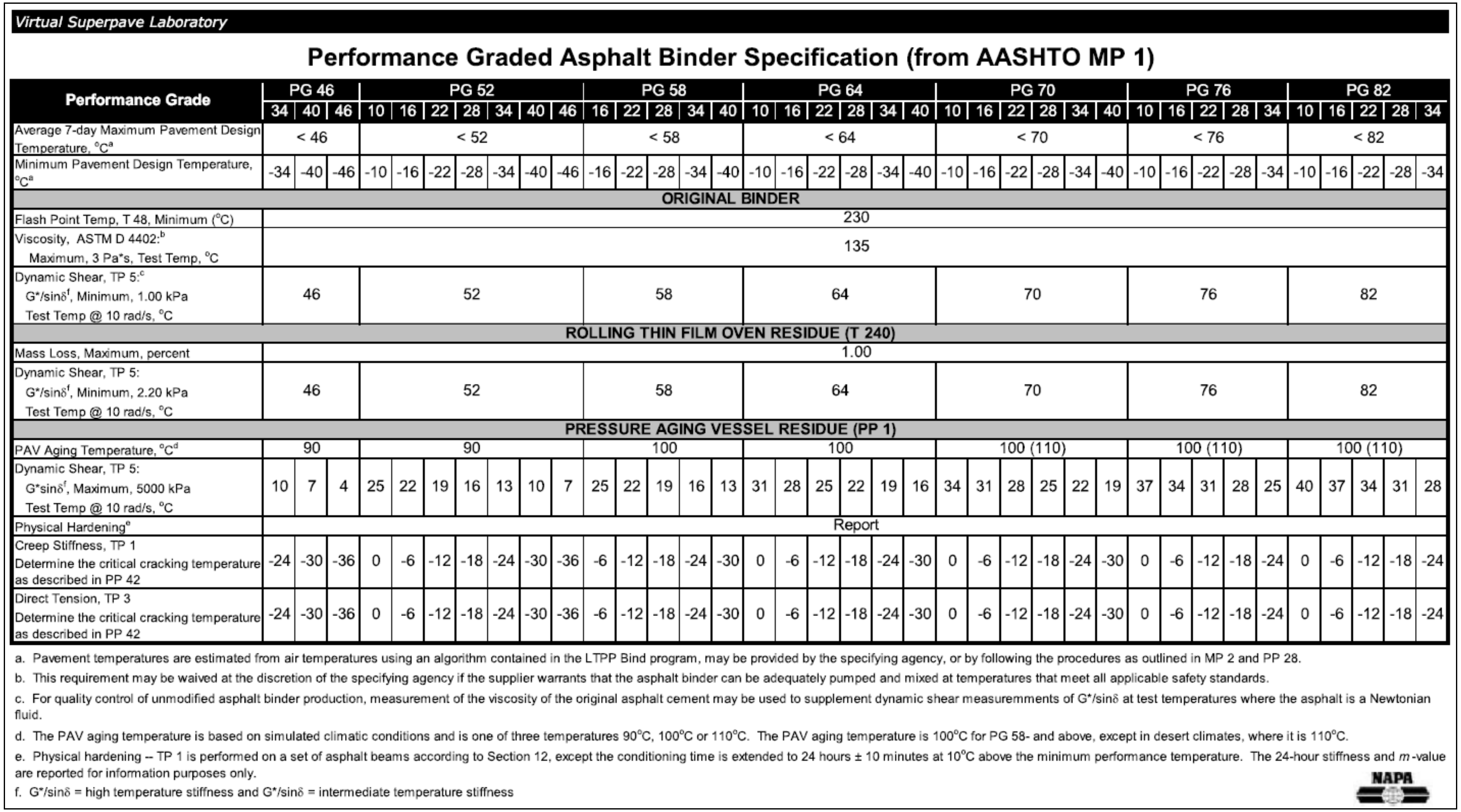
In terms of the total time to undertake all the tests, it depends on various factors such as: testing experience, obtained results, number of replicated tests and availability of the equipment. According to the standard [R 29-02], if the analysis is started at the beginning of a morning work shift, all testing and analysis should be completed during the afternoon of the next day. This schedule includes the 20 hours needed for PAV conditioning and considers high laboratory productivity creditable to the fact that samples are aged and analysed in parallel. Though, this schedule does not include the time necessary to get the low grade that, with a rough estimation, is estimable in almost another day of work. In conclusion, to perform all the tests, analyse the data and establish the performance grade of an asphalt binder, *at least 3 days of work are necessary*.

Performance Grade Specification

The Table below is the standard summary table presented in the AASHTO MP 1 specification for performance graded asphalt binder. The following items may help to decipher this table:

The top several rows (all the rows above the "original binder" row) are used to designate the desired PG grade. For instance, if the average 7-day maximum pavement design temperature is greater than 52°C but less than 58°C then "< 58" column should be used. The temperatures directly under the "< 58" cell are selected based on the minimum pavement design temperature in °C. No matter what the desired PG binder specification, the same tests are run. The PG specification (e.g., PG 58-22) just determines the temperature at which the tests are run.

Tests are run on the original binder (no simulated aging), RTFO residue (simulated short-term aging) and PAV residue (simulated long-term aging) in order to fully characterize the asphalt binder throughout its life. Notice that often the same test is run on different simulated binder ages. For instance, the dynamic shear test is run on all three simulated binder ages. The tests run on the binder are listed in the left-hand column. They are not necessarily listed by their common names but the applicable AASHTO test procedure is listed. For instance, "Flash Point Temp. T 48, Minimum (oC)" means that the flash point is measured according to AASHTO T 48 and that the value in the adjacent column represents the minimum allowable in degrees Centigrade.



Virtual Superpave Laboratory

Performance Graded Asphalt Binder Specification (from AASHTO MP 1)

Performance Grade	PG 46			PG 52							PG 58					PG 64						PG 70						PG 76					PG 82				
	34	40	46	10	16	22	28	34	40	46	16	22	28	34	40	10	16	22	28	34	40	10	16	22	28	34	40	10	16	22	28	34	10	16	22	28	34
Average 7-day Maximum Pavement Design Temperature, °C[a]	< 46			< 52							< 58					< 64						< 70						< 76					< 82				
Minimum Pavement Design Temperature, °C[a]	-34	-40	-46	-10	-16	-22	-28	-34	-40	-46	-16	-22	-28	-34	-40	-10	-16	-22	-28	-34	-40	-10	-16	-22	-28	-34	-40	-10	-16	-22	-28	-34	-10	-16	-22	-28	-34
ORIGINAL BINDER																																					
Flash Point Temp, T 48, Minimum (°C)	230																																				
Viscosity, ASTM D 4402:[b] Maximum, 3 Pa*s, Test Temp, °C	135																																				
Dynamic Shear, TP 5:[c] G*/sinδ[f], Minimum, 1.00 kPa Test Temp @ 10 rad/s, °C	46			52							58					64						70						76					82				
ROLLING THIN FILM OVEN RESIDUE (T 240)																																					
Mass Loss, Maximum, percent	1.00																																				
Dynamic Shear, TP 5: G*/sinδ[f], Minimum, 2.20 kPa Test Temp @ 10 rad/s, °C	46			52							58					64						70						76					82				
PRESSURE AGING VESSEL RESIDUE (PP 1)																																					
PAV Aging Temperature, °C[d]	90			90							100					100						100 (110)						100 (110)					100 (110)				
Dynamic Shear, TP 5: G*sinδ[f], Maximum, 5000 kPa Test Temp @ 10 rad/s, °C	10	7	4	25	22	19	16	13	10	7	25	22	19	16	13	31	28	25	22	19	16	34	31	28	25	22	19	37	34	31	28	25	40	37	34	31	28
Physical Hardening[e]	Report																																				
Creep Stiffness, TP 1 Determine the critical cracking temperature as described in PP 42	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	0	-6	-12	-18	-24
Direct Tension, TP 3 Determine the critical cracking temperature as described in PP 42	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	0	-6	-12	-18	-24

a. Pavement temperatures are estimated from air temperatures using an algorithm contained in the LTPP Bind program, may be provided by the specifying agency, or by following the procedures as outlined in MP 2 and PP 28.

b. This requirement may be waived at the discretion of the specifying agency if the supplier warrants that the asphalt binder can be adequately pumped and mixed at temperatures that meet all applicable safety standards.

c. For quality control of unmodified asphalt binder production, measurement of the viscosity of the original asphalt cement may be used to supplement dynamic shear measuremments of G*/sinδ at test temperatures where the asphalt is a Newtonian fluid.

d. The PAV aging temperature is based on simulated climatic conditions and is one of three temperatures 90°C, 100°C or 110°C. The PAV aging temperature is 100°C for PG 58- and above, except in desert climates, where it is 110°C.

e. Physical hardening -- TP 1 is performed on a set of asphalt beams according to Section 12, except the conditioning time is extended to 24 hours ± 10 minutes at 10°C above the minimum performance temperature. The 24-hour stiffness and *m*-value are reported for information purposes only.

f. G*/sinδ = high temperature stiffness and G*/sinδ = intermediate temperature stiffness

NAPA

Figure B.1. Superpave binder specification taken from NAPA's Virtual Superpave Laboratory and AASHTO MP 1

APPENDIX C - DSR testing protocol

Testing protocol to determine the rheological properties of bituminous binders with the Antoon PAAR Physyca MCR 101 Dynamic Shear Rheometer

In order to obtain a rheological characterisation of all the binders, various rheological tests, mainly dynamic mechanical analysis (DMA), over a wide range of temperatures, amplitudes, stresses and frequency were performed within this project.

In order to rely on these measurements consistent data are necessary, for this reason in this appendix are explained the undertaken preliminary operations to ensure reliable data from DSR rheological testing.

Material handling and samples preparation

In order to test materials with low influence of external factors, mainly ageing due long time exposure at high temepratures (160°C), all binders were stored in vials of 10ml and placed in fridge at 5°C. Any vial has been heated for a maximum of 3 times, for 10-15 minutes per time, depending on the binders. For each test, samples were prepared by means of a hot pour method, based on Alternative 1 of the AASHTO TP5 Standard. The gap between the upper and lower plates of the DSR was set to a height of 50 μm plus the required testing gap at the mid-point of the testing temperature range. Once the gap has been set, a sufficient amount of hot bitumen (160ºC) was poured on the lower plate of the DSR to ensure a slight excess of material appropriate to the chosen testing geometry. The upper plate of the DSR was then gradually lowered to the required nominal testing gap. The bitumen that was squeezed out between the plates was then trimmed flush to the edge using a hot blade (pouring method). Finally, the gap was closed until there was a slight bulge around the circumference of the testing geometry.

Assessing temperature equilibrium time

Bitumen is a good thermal insulator and is also highly temperature susceptible. In order to make accurate measurements it is important firstly, that the whole sample is at the same temperature and secondly, that the temperature is accurately controlled. DSRs used in this research had different temperature control system, water bath for the Bohlin and double Peltier system for the Antoon Paar Physica MCR 101. Both of them showed to control the the temperature even under 0.1 °C. In order to ensure that before testing, the whole sample was at the same temperature, as suggested by the other researchers (Anderson et al. 1994), the rheological characteristics have been monitored by applying a torque at constant frequency and changing the temperature from 25°C to 80°, with 25mm plates, and from 25°C to -10°C with 8mm plates.

With this procedure has been possible to assess 12 and 15 minutes (720 and 900 sec) as optimum equilibrium time to achieve constant value of complex modulus and phase angle.

Machine compliance

Machine compliance is a phenomen can could affect results when testing sample at extremes conditions, in terms of temperature and torque levels. Its extent depends on both the rheometer and the plate diameter and gap. The problem is measuring small displacements which contain contributions from both the binder and the machine using a particular measuring geometry. As the stiffness of the binder increases, the strain in the binder decreases until a point is reached where torsional movements in the machine itself become significant. The instrument and software assumes the torsional movement is

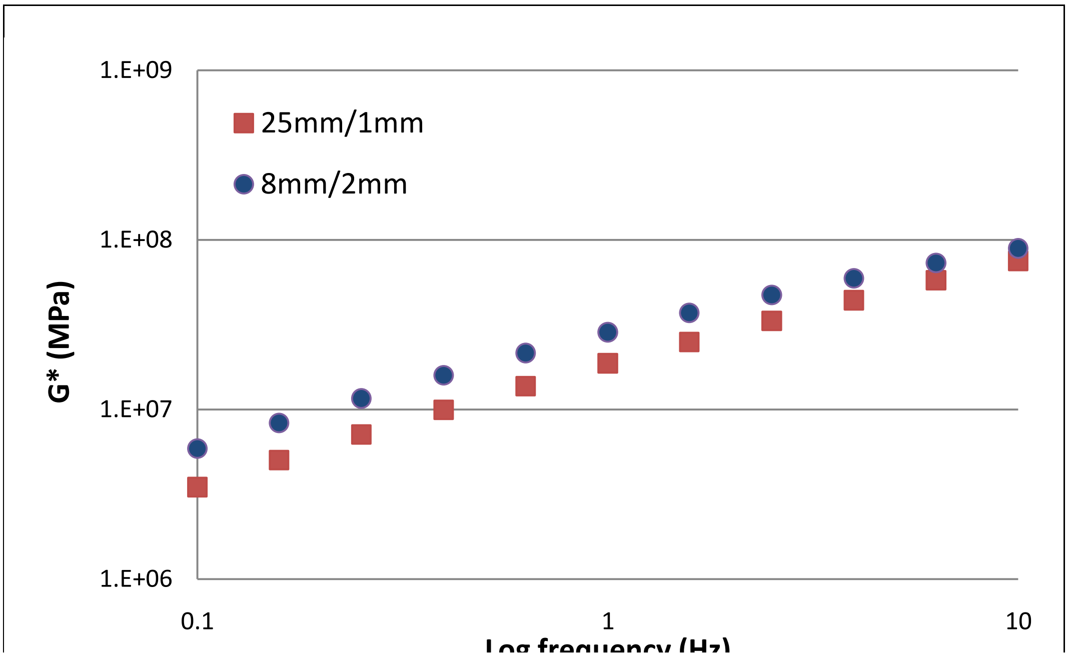


Figure C.1. Machine compliance affecting test of a neat bitumen at 15°C

entirely due to the binder and, where this is not the case, this will result in a lower measured stiffness (Fig. C.1).

In order to ensure that machine compliance do not affected results on this research, especially at low tempeartures, applied torque have been monitored to check that maximum torque was not exceeded (150.000 μNm for the Antoon Paar MCR 101).

Linearing viscoelastic region

To analyse the binder samples in this study it was necessary to determine the strain level which corresponds to the linear viscoelastic region. Theoretically, the linear viscoelastic region exists in the strain level range from 0 percent to some maximum percent strain level.In reality the measurable linear viscoelastic region exists from a strain level range of slightly above 0 percent, a minimum strain level, to a maximum percent strain level. This range was determined by specifying several different strains and observing the strain response. The strain level for measurement was chosen to be the minimum strain level at which measurable linear viscoelastic behavior occurred. This minimum strain level was found to be highly sample dependent and ranged from approximately 0.5 percent to over 100 percent, depending upon the temperature.

For the reasons, all the frequency sweeps within this research have been conducted at 0,5% strain for all binders. Only at the highest testing temperature (80°C) binders were subjected to frequency sweeps with at level of 2 and 12%, in order to check high temperature linearity (§ 3.3.1).

Gap setting study:

An additional complication to the measurement of TR-MBs properties is the presence of the rubber particles. As a result, it was necessary to determine an acceptable gap width for the parallel plate geometry. This gap width was found to be strictly a function of the rubber particle size and rubber content. The gap width for a given rubber size and content was determined by measuring the rheological properties of a given tyre rubber-bitumen blend at multiple gap settings. To ensure the elimination of the 'gap effect', the gap width was chosen such that the rheological properties taken at as wide or wider gap widths, were independent of the gap width and also such as at high temperature sample geometry was maintained. As a results, 1 mm has been found suitable for neat bitumen, while the range 1-1.5mm and 1.5 – 2mm have been find suitable for the commercial used SBS-modifed binders and the produced TR-MBs.

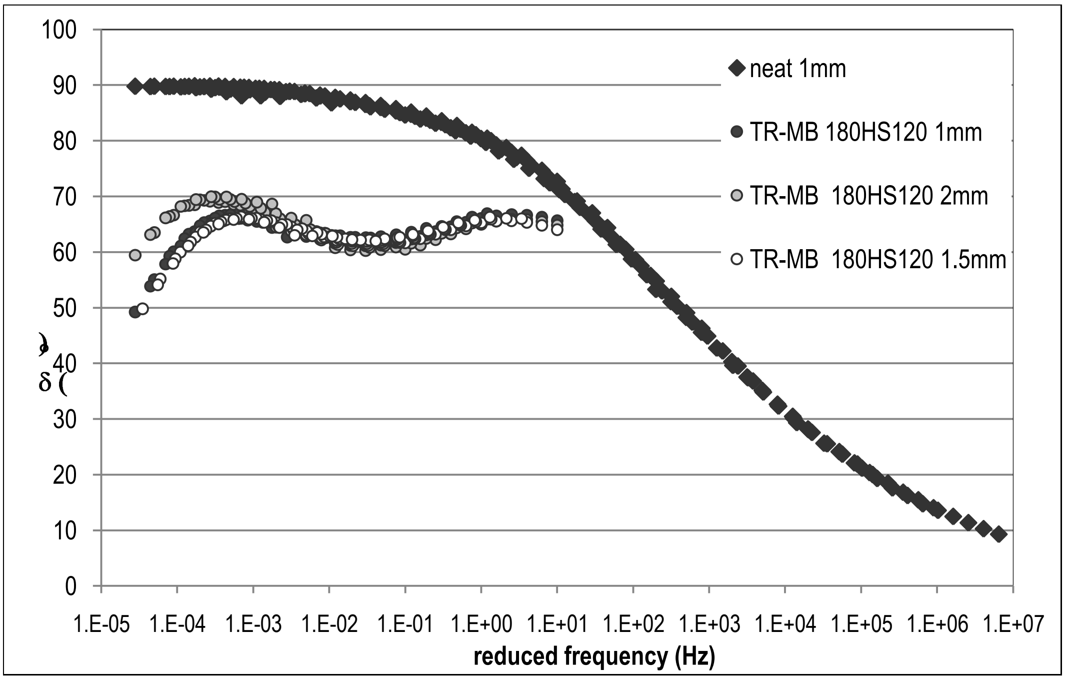
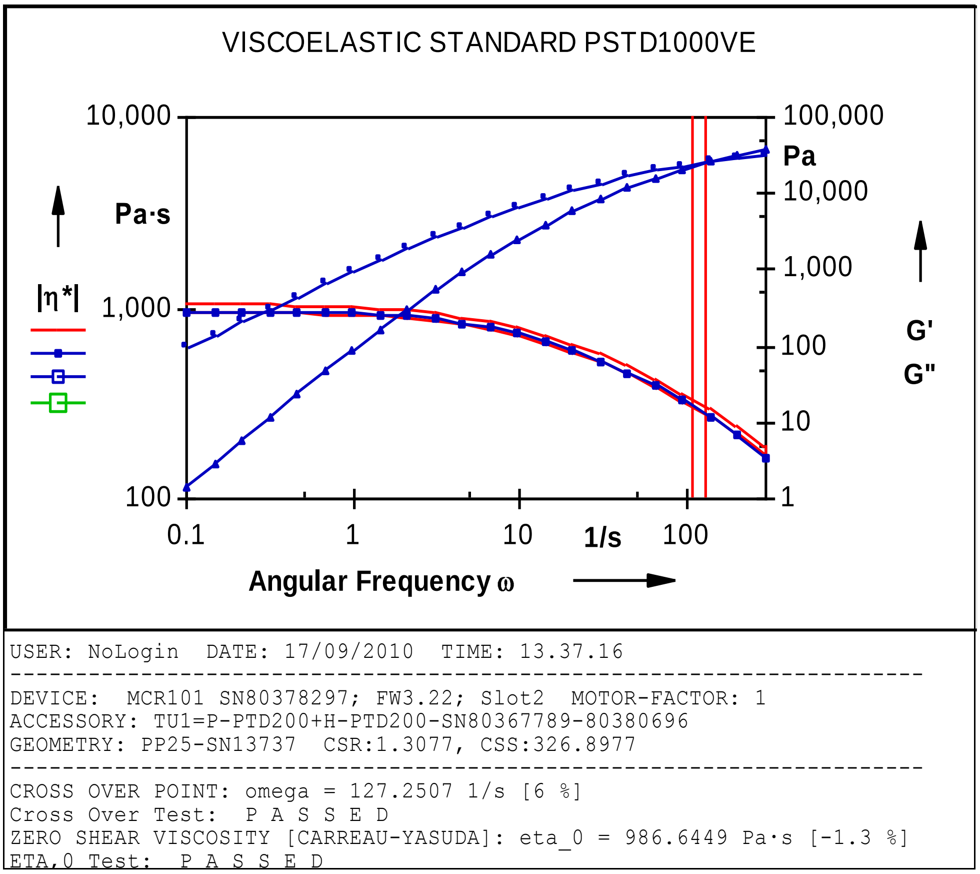


Figure C.2. Gap setting effect on the measurment of the elastic properties of TR-MBs

DSR calibration and mainteinance

Dynamical Shear Rheometer is a very powerfull but also sensible equipment. A periodical calibration and maintenance ensure the instrument's long life and optimal performance. For this reason, every three months the reliability of the results provided by the DSR, have been checked by performing rheological test (amplitude sweep) with a using a standard viscosity material provided by the DRS manufacturer. In 2 years of testing, the equipment never showed lack of accuracy and ensured very good repeatibility. An example of the calibration procedure for the Antoon Paar Physica MCR 101 is shown in Figure C.1.



```
USER: NoLogin  DATE: 17/09/2010  TIME: 13.37.16
-----------------------------------------------------------------------
DEVICE:  MCR101 SN80378297; FW3.22; Slot2  MOTOR-FACTOR: 1
ACCESSORY: TU1=P-PTD200+H-PTD200-SN80367789-80380696
GEOMETRY: PP25-SN13737  CSR:1.3077, CSS:326.8977
-----------------------------------------------------------------------
CROSS OVER POINT: omega = 127.2507 1/s  [6 %]
Cross Over Test:  P A S S E D
ZERO SHEAR VISCOSITY [CARREAU-YASUDA]: eta_0 = 986.6449 Pa·s [-1.3 %]
ETA,0 Test:  P A S S E D
```

Figure C.3. Results of the Antoon Paar DSR periodical calibration

APPENDIX D - DSR data analysis

Analysis of the raw data obtained from rheological analysis and the procedures to obtain the master curves

D.1 Analysis of raw data

The principal viscoelastic parameters that are obtained from rheometrical measurements, mainly with the DSR, are the complex shear modulus, G*, and the phase angle, δ. G* is defined as the ratio of maximum (shear) stress to maximum strain and provides a measure of the total resistance to deformation when the bitumen is subjected to shear loading. It contains elastic and viscous components which are designated as the storage modulus, G', and loss modulus, G'',respectively. These two components are related to the complex (shear) modulus and to each other through the phase (or loss) angle δ which is the phase, or time, lag between the applied shear stress and shear strain responses during a test.

In order to obtain the indicated parameters, Dynamic mechanical analyses (DMA) have been performed on bituminous binders by making frequency sweeps tests over a wide range of temperatures with an Antoon Paar Physica MCR 101 dynamic shear rheometer (DSR). The first step consisted in establishing the strain level to set in order to remain within the LVE range at any temperature (usually 0.5%). The frequency sweep have been performed usually under the following conditions:

• Loading Mode:	controlled-strain
• Temperatures:	0ºC to 80 ºC at 5 or 10 ºC intervals
• Frequencies:	0.10, 0.16, 0.25, 0.40, 0.63, 1, 1.6, 2.5, 4, 6.3 and 10 Hz
• Plate geometries:	8 mm ϕ and 2 mm gap (0-45ºC) 25 mm ϕ and 1 or 1.5 mm gap (25-80ºC) in order to have an overlap of data between 25-45 ºC
• Strain amplitude:	0.5% with 8 mm plates (within LVE response dependent on *G**)

For every sample 2 or 3 repetitions have been done and the average results were taken as final data. Particular attention was paid on the reliability of the data: whenever the torque reached the machine’s limits (maximum at low temperatures and minimum at high temperatures) the data was discarded (Tab D.1).

In order to know at which temperature was convenient to take data as most reliable within the overlap range (25-45 ºC), the raw data, obtained by testing sample with 25mm plates and 8mm plates, were compared. The swap between the data series was done at the temperature which provided the minimum differences between the values of G* and δ obtained from the 8mm test and 25mm test.

Only by properly selecting the raw data, it was possible to have a rheological fingerprinting of the binders by plotting the following diagrams:

- Black Diagram (Fig. D.1)
- Cole Cole Diagram (Fig. D.2) (only for neat bitumen)
- Isochronal plots of G* and δ (Figs. D3 and D.4)
- Isothermal plots of G* and δ (Figs. D.5 and D.6)

Table D.1. Results of a frequency sweep at 25ºC

DSR Raw data

Name:	[FS 25 °C] 25mm 1
Time Setting:	11 Meas. Pts.
Measuring Profile:	Amplitude gamma = 0.5 %
	Frequency f = 0.1 ... 10 Hz log

Meas. Pts.	Temperature	Frequency	Storage Modulus	Loss Modulus	Complex Modulus	Phase Angle	Torque	Deflection Angle	Time	Status
	[°C]	[Hz]	[Pa]	[Pa]	[Pa]	[°]	[µNm]	[mrad]	[min]	[]
1	25	0.1	1.67E+04	1.26E+05	1.27E+05	82.44	3.84E+03	0.79	1.1	
2	25	0.158	2.86E+04	1.92E+05	1.94E+05	81.51	5.88E+03	0.79	1.9	
3	25	0.251	4.84E+04	2.91E+05	2.95E+05	80.54	9.01E+03	0.8	2.2	
4	25	0.398	8.17E+04	4.38E+05	4.45E+05	79.43	1.36E+04	0.8	2.3	
5	25	0.631	1.37E+05	6.54E+05	6.69E+05	78.19	2.05E+04	0.8	2.5	
6	25	1	2.28E+05	9.71E+05	9.97E+05	76.81	3.04E+04	0.8	2.5	
7	25	1.58	3.75E+05	1.43E+06	1.47E+06	75.26	4.52E+04	0.8	2.7	
8	25	2.51	6.11E+05	2.07E+06	2.16E+06	73.53	6.60E+04	0.8	2.7	
9	25	3.98	9.85E+05	2.95E+06	3.11E+06	71.54	9.52E+04	0.8	2.8	
10	25	6.31	1.57E+06	4.16E+06	4.44E+06	69.34	1.25E+05	0.74	2.9	WE+,WMa
11	25	10	2.43E+06	5.83E+06	6.31E+06	67.41	1.25E+05	0.52	2.9	WE+,WMa

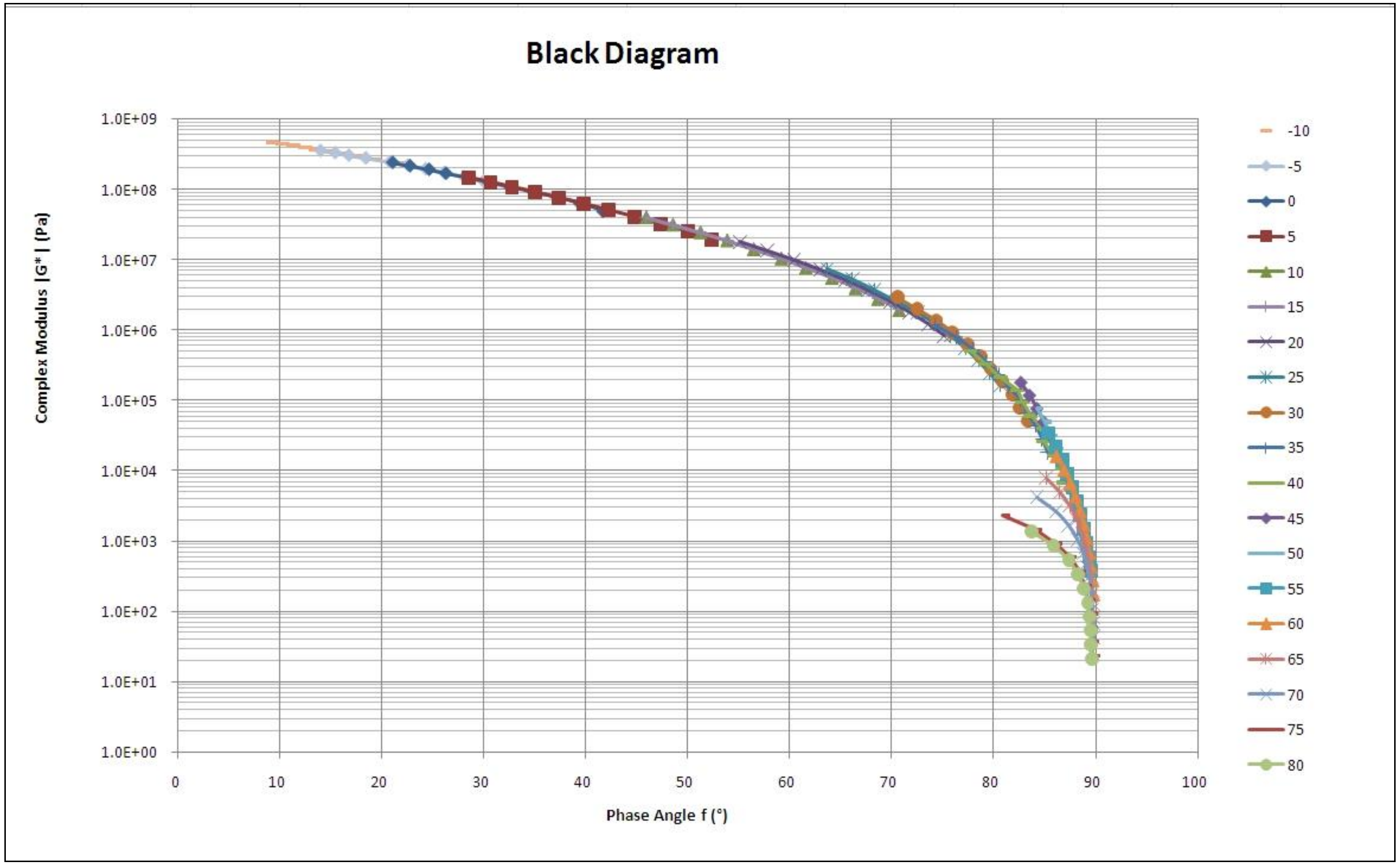


Figure D.1. Black Diagram of bitumen UB01 obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

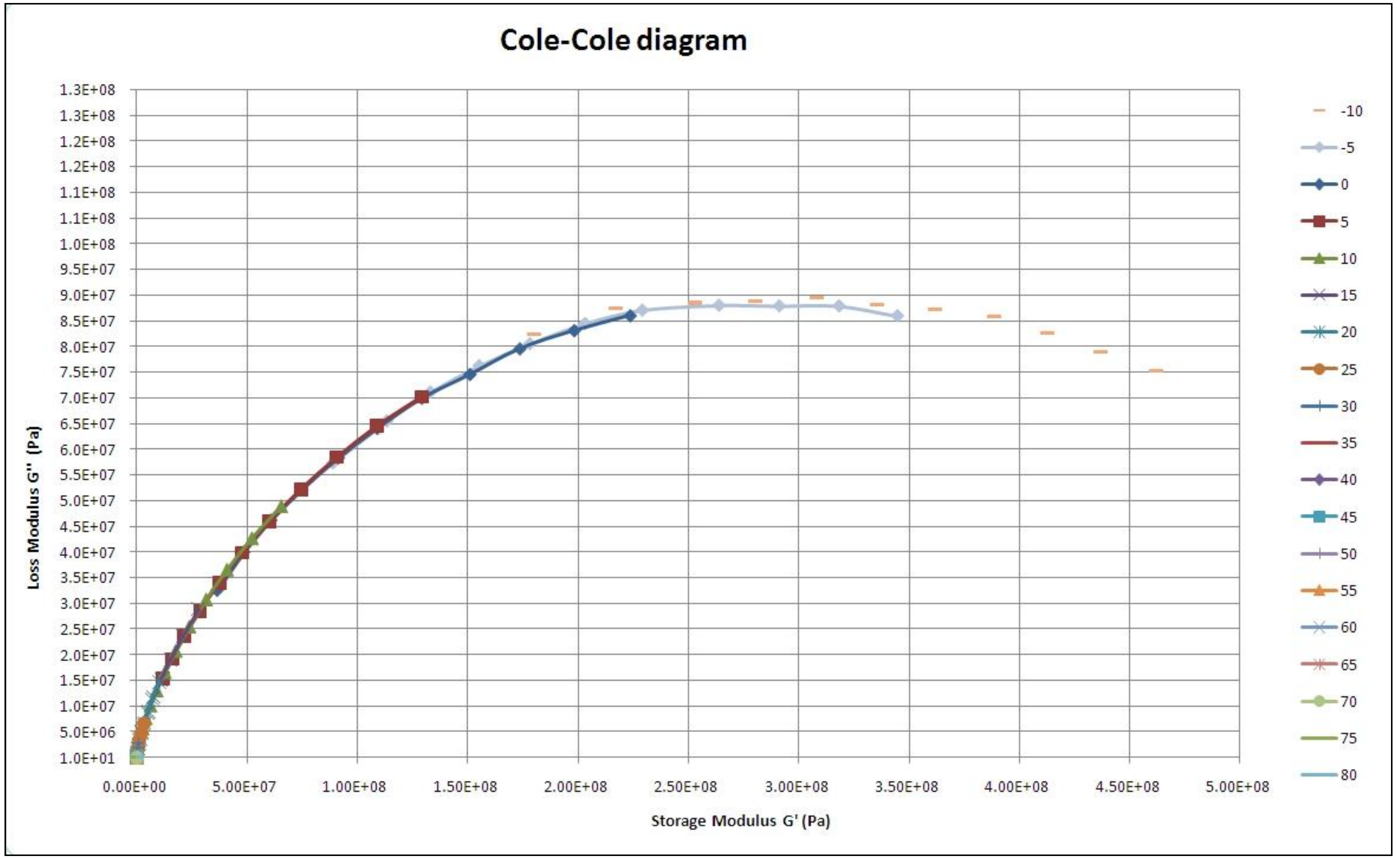


Figure D.2. Cole-Cole Diagram of bitumen UB01 obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

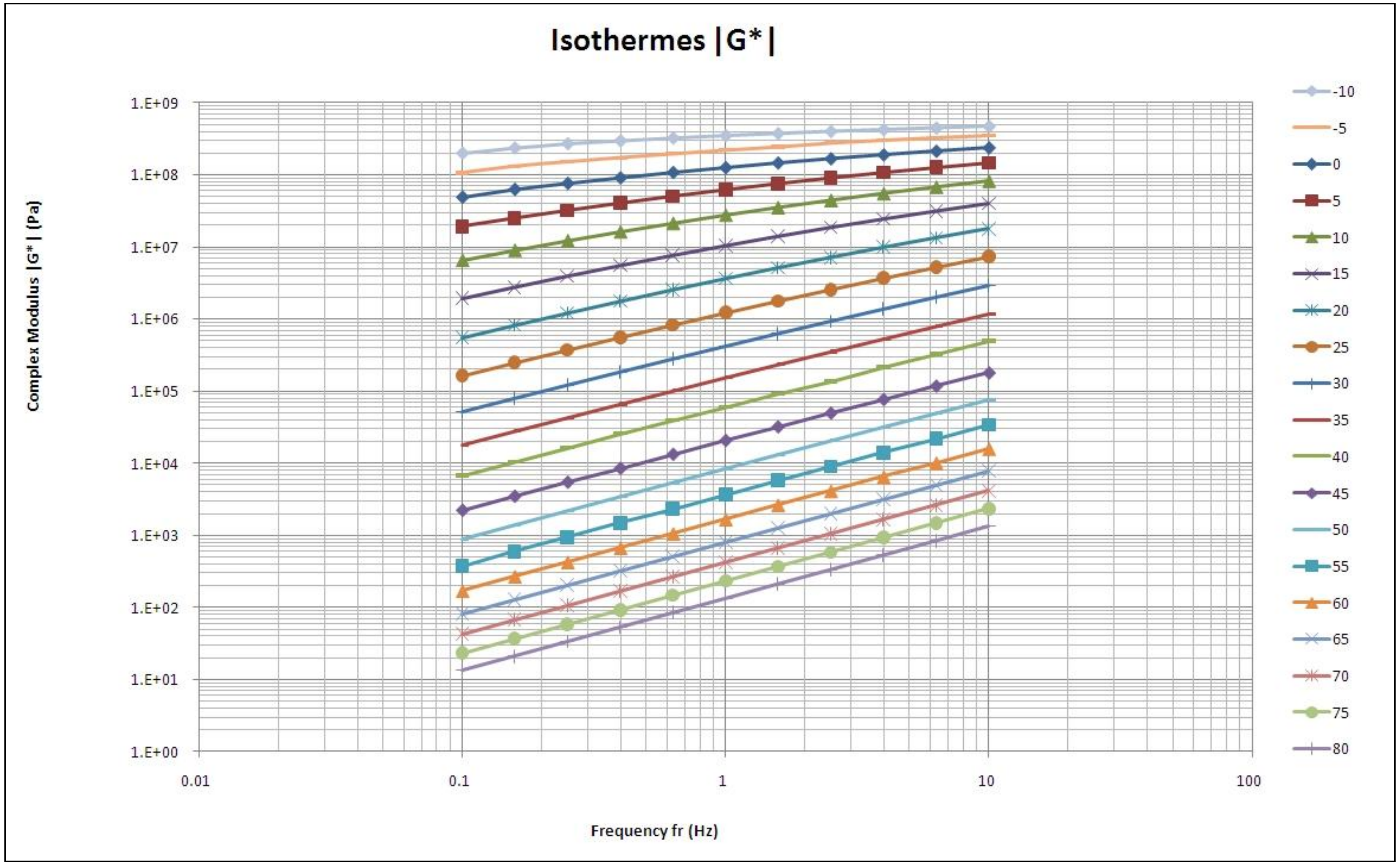


Figure D.3. Isothermes |G*| of bitumen UB01 obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

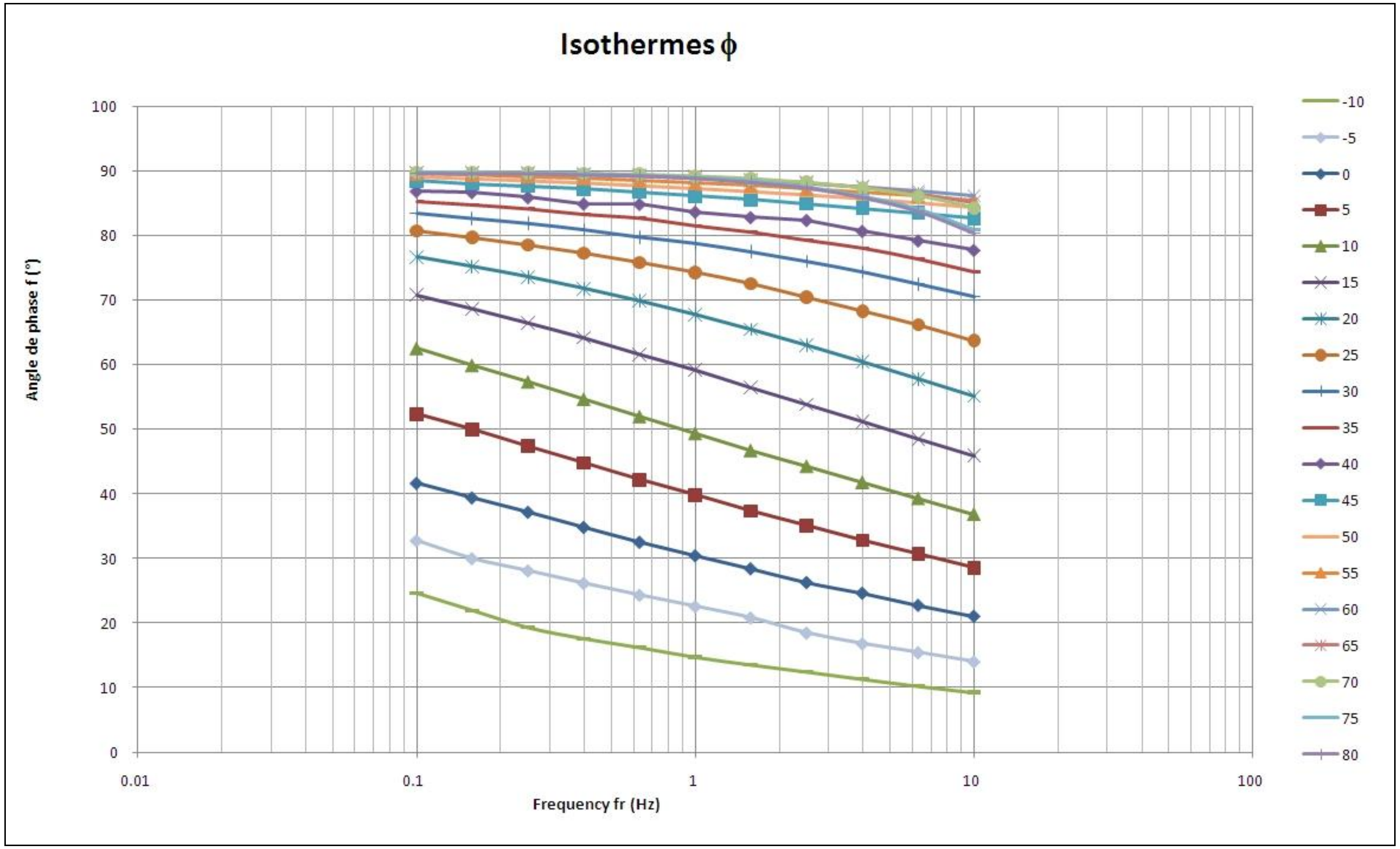


Figure D.4. Isothermes δ of bitumen UB01 obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

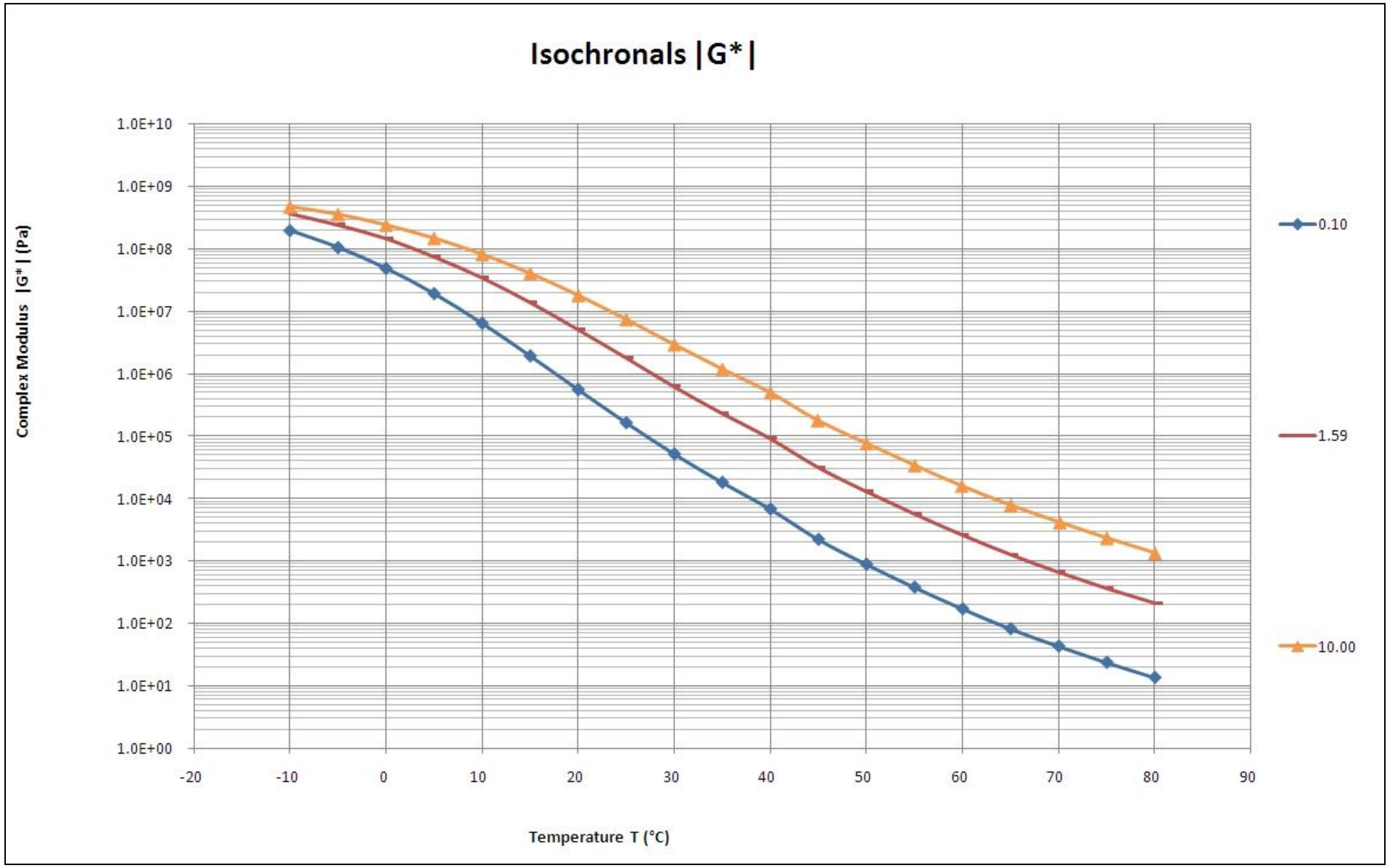


Figure D.5. Isochronals |G*| of bitumen UB01 obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

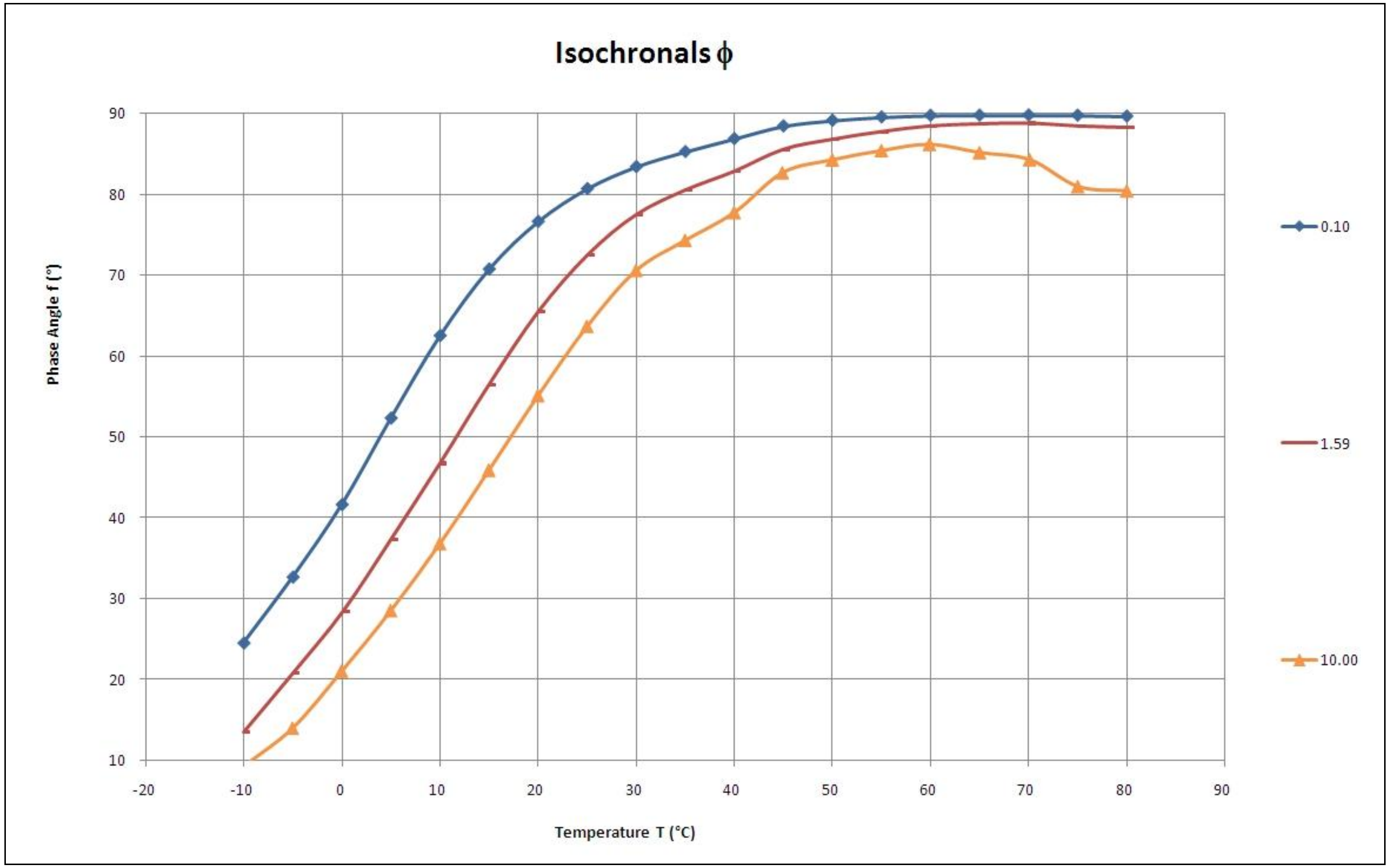


Figure D.5. Isochronals δ of bitumen UB01 obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

D.2 Master curves and WLF fitting

In order to perform a complete rheological characterisation of the tested materials, it is necessary to firstly collect the rheological parameters with oscillatory tests with variable frequency and constant small strain level within the Linear Visco-Elastic response (LVE) over a range of temperatures (DMA), and then elaborate the results through analytical techniques. One of the primary analytical techniques used in analysing dynamic/cyclic mechanical data involves the construction of master curves, which represents the viscoelastic behaviour of a bituminous binder at a given temperature for a large range of frequencies. The principle that is used to relate the equivalency between time and temperature and thereby produce the master curve is the Time Temperature Superposition Principle (§ 3.7.4). In order to obtain the the master curves (Figs D.8 and D.9)a manual shifting of the isothermes obtained from the DSR, was performed at the reference temperature (T_R : 25 or 30°C), followed by a subsequent fitting with the William Landel and Ferry equation (WLC) (Tab D.2 and Fig. D.7). The WLF constants C_1 and C_2 were obtained by minimizing the sum of the “$\mathbf{\Delta a_T/a_T}$“

Table D.2. Application of the WLF equation to the shift factors used to build the master curve of a bituminous binder by manually shifting the isothermes at 30ºC

T	**T_R**	**$T-T_R$**	**$a_{T\_calculated}$**	**a_{T_manual}**	**$\Delta a_T/a_T$**
-10.00	30	-40	5.37E+05	500000.00000	7.4388E-02
-5.00	30	-35	6.00E+04	60000.00000	1.6099E-08
0.00	30	-30	8.16E+03	9200.00000	1.1310E-01
5.00	30	-25	1.32E+03	1500.00000	1.2189E-01
10.00	30	-20	2.47E+02	280.00000	1.1747E-01
15.00	30	-15	5.29E+01	60.00000	1.1794E-01
20.00	30	-10	1.27E+01	14.00000	8.9603E-02
25.00	30	-5	3.41E+00	3.50000	2.6479E-02
30.00	30	0	1.00E+00	1.00000	0.0000E+00
35.00	30	5	3.19E-01	0.32000	2.7248E-03
40.00	30	10	1.10E-01	0.12000	8.4788E-02
45.00	30	15	4.05E-02	0.03800	6.4844E-02
50.00	30	20	1.59E-02	0.01500	5.7352E-02
55.00	30	25	6.58E-03	0.00600	9.6105E-02
60.00	30	30	2.87E-03	0.00280	2.5295E-02
65.00	30	35	1.31E-03	0.00135	2.7052E-02
70.00	30	40	6.27E-04	0.00070	1.0367E-01
75.00	30	45	3.12E-04	0.00038	1.7938E-01
80.00	30	50	1.61E-04	0.00022	2.6932E-01
				SUM	*1.5714E+00*

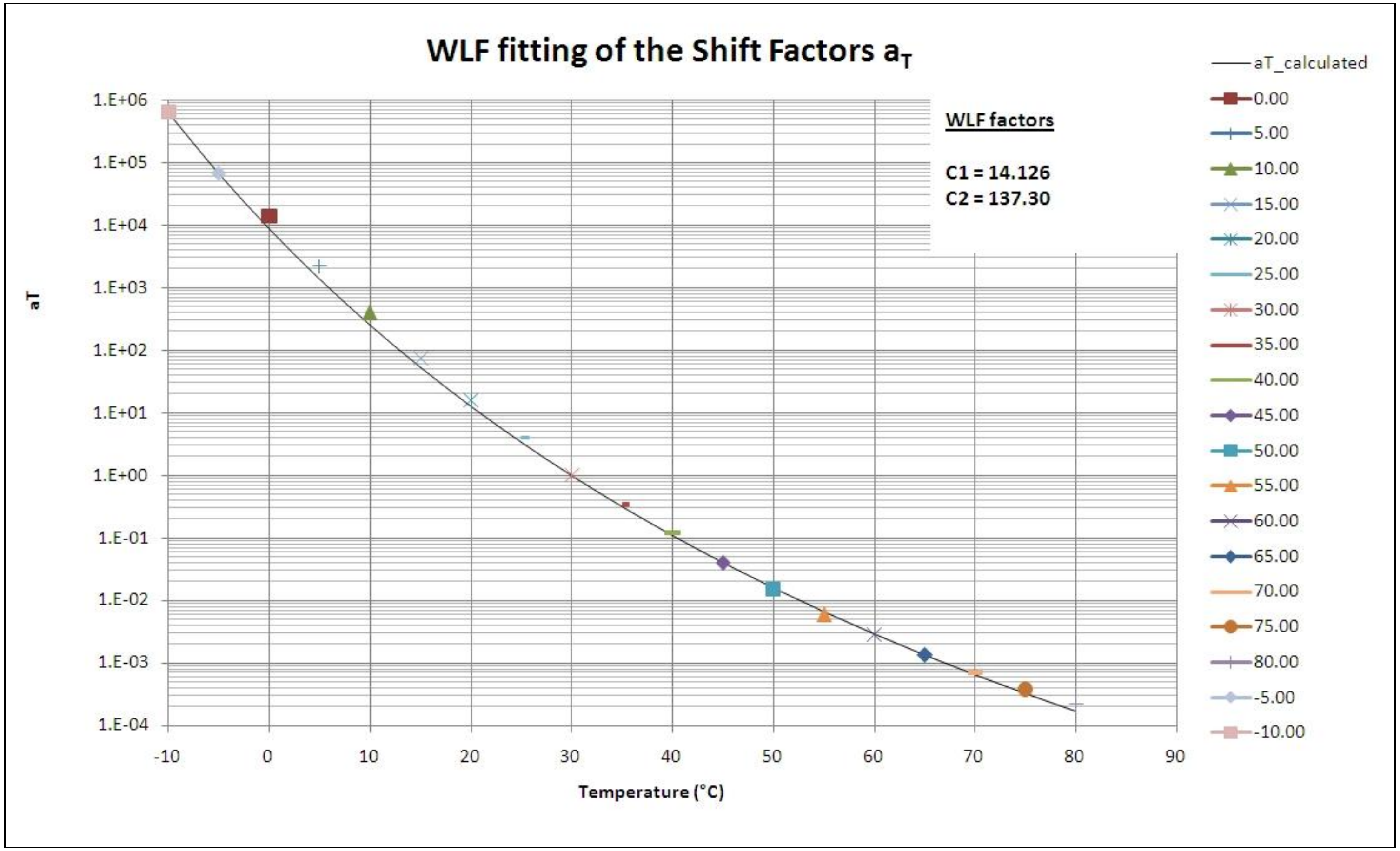


Figure D.7. _Shift factors curve of UB01:_ obtained by a fitting with the WLF equation

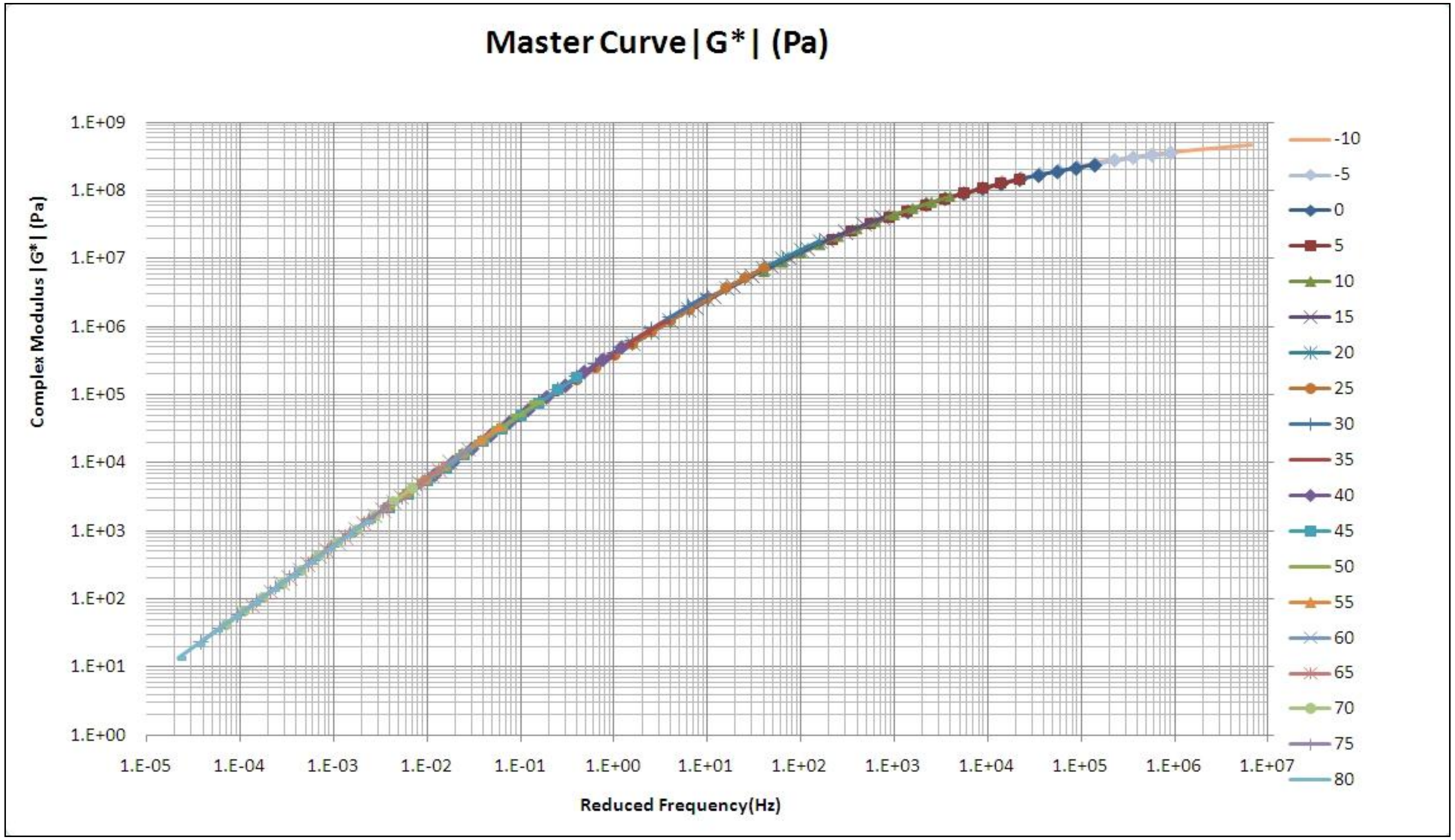


Figure D.8. Master curve |G*| of bitumen UB01 @ 30 ºC

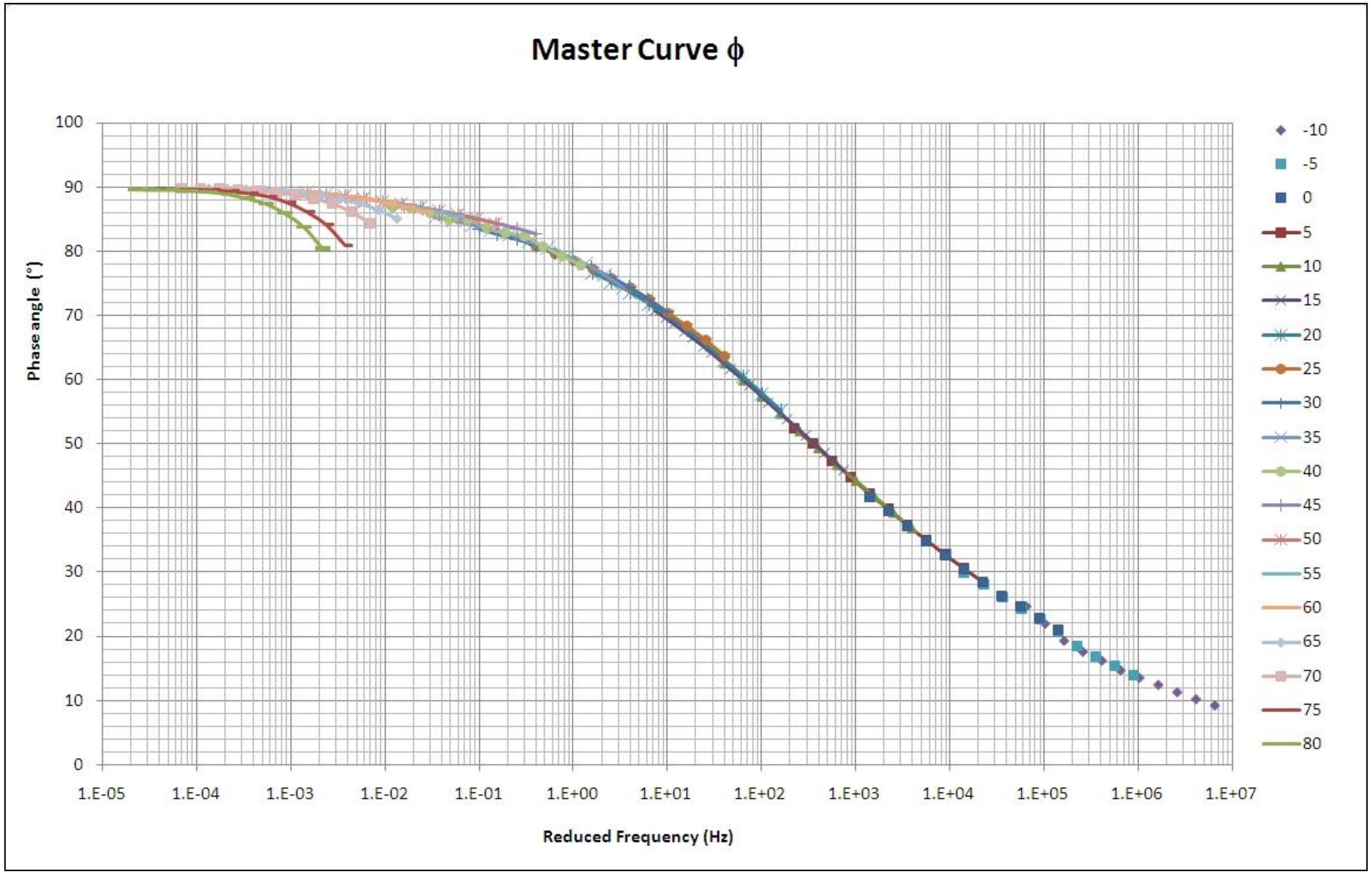


Figure D.9. Master curve δ of bitumen UB01 @ 30 ºC

APPENDIX E - Results

Rheological diagrams and WLF fitting of several binders tested during the whole project

TR-MBs – All Tyre Rubber Modified Bitumens, processed at 180ºC and 210 ºC in Low shear and High shear mode

T	T_R	$T-T_R$	a_{T_calc}	a_{T_manual}	Da_T/a_T
-10.00	30	-40	6.28E+05	460000.00000	3.6615E-01
-5.00	30	-35	6.20E+04	62000.00000	1.3171E-12
0.00	30	-30	7.80E+03	9500.00000	1.7888E-01
5.00	30	-25	1.21E+03	1500.00000	1.9540E-01
10.00	30	-20	2.23E+02	300.00000	2.5682E-01
15.00	30	-15	4.80E+01	64.00000	2.4991E-01
20.00	30	-10	1.18E+01	14.00000	1.5646E-01
25.00	30	-5	3.26E+00	3.75000	1.2945E-01
30.00	30	0	1.00E+00	1.00000	0.0000E+00
35.00	30	5	3.36E-01	0.34000	1.3084E-02
40.00	30	10	1.22E-01	0.13000	6.1010E-02
45.00	30	15	4.77E-02	0.05000	4.5424E-02
50.00	30	20	1.99E-02	0.02000	4.5480E-03
55.00	30	25	8.80E-03	0.00850	3.5592E-02
60.00	30	30	4.10E-03	0.00410	5.1573E-04
65.00	30	35	2.00E-03	0.00200	2.4934E-03
70.00	30	40	1.02E-03	0.00110	6.9651E-02
75.00	30	45	5.43E-04	0.00060	9.4313E-02
80.00	30	50	2.99E-04	0.00035	1.4523E-01
				SUM	*2.0085E+00*

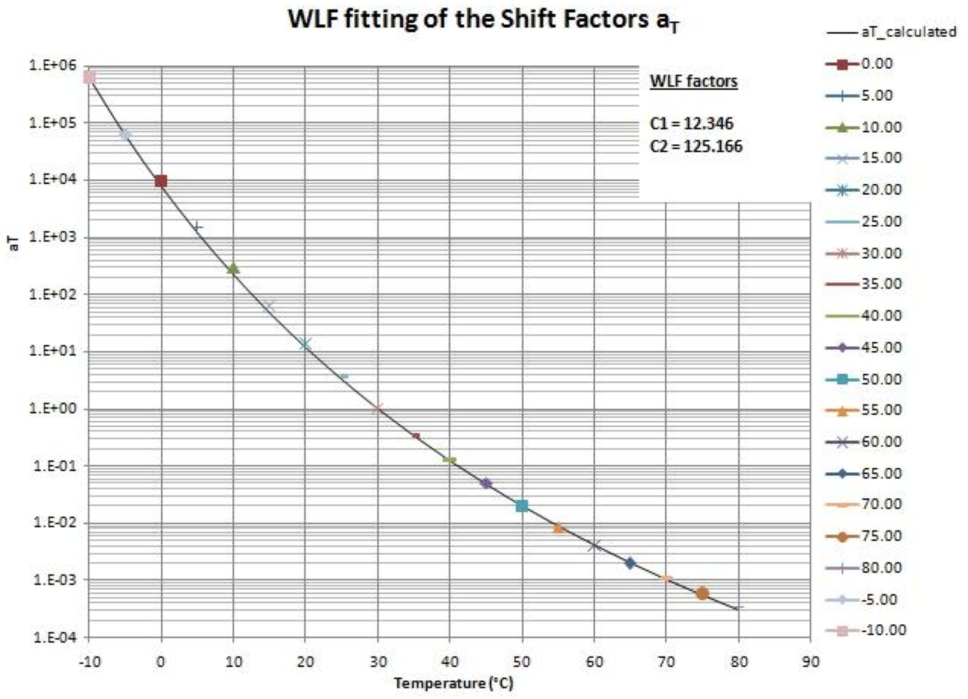


Figure E.1. *Shift factors curve of TR-MBs@30º* obtained by fitting with WLF equat.

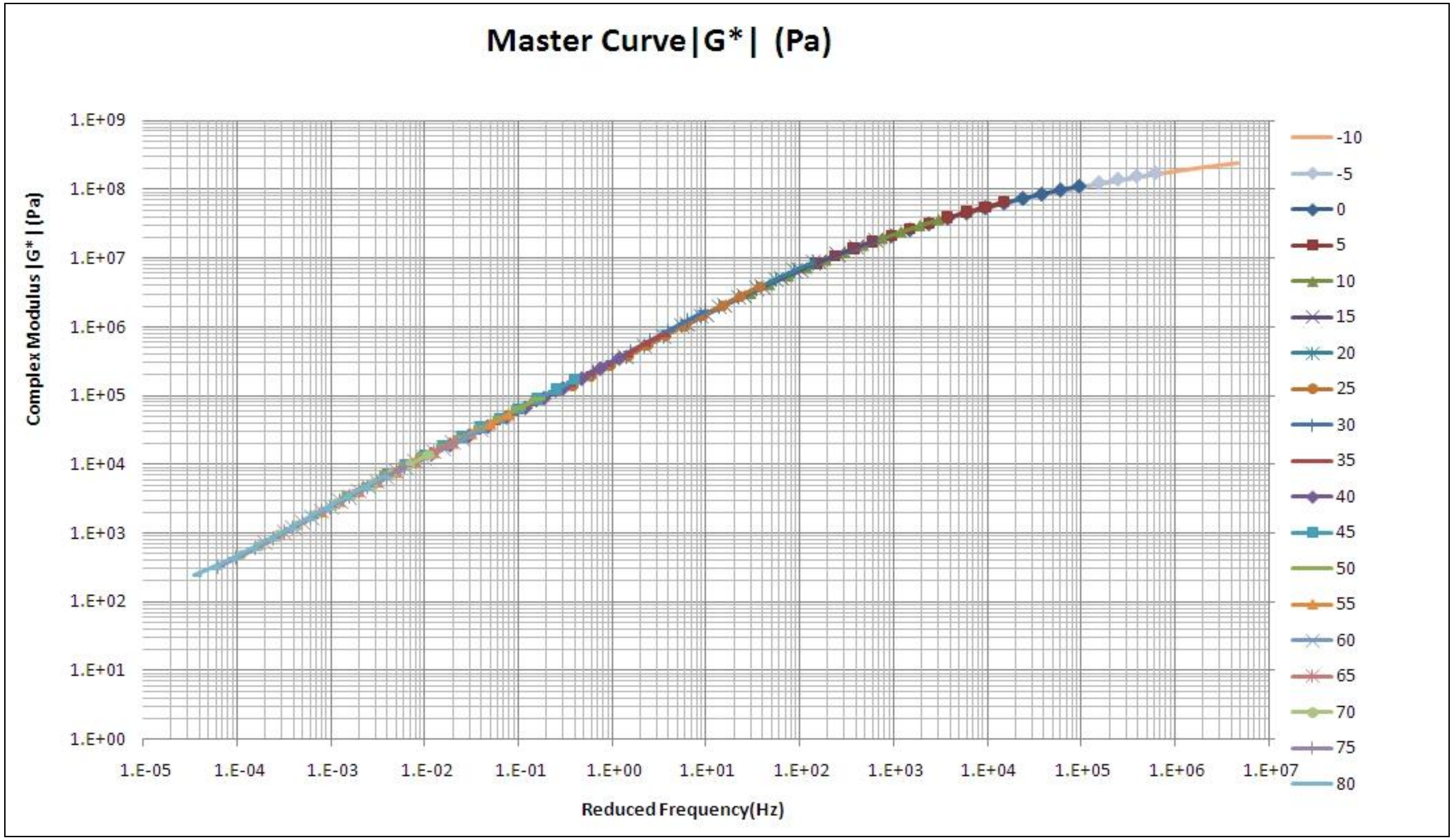


Figure E.2. Master curve |G∗| of TR-MB HS 180 @ 30 ºC – (processed at 180C in High Shear)

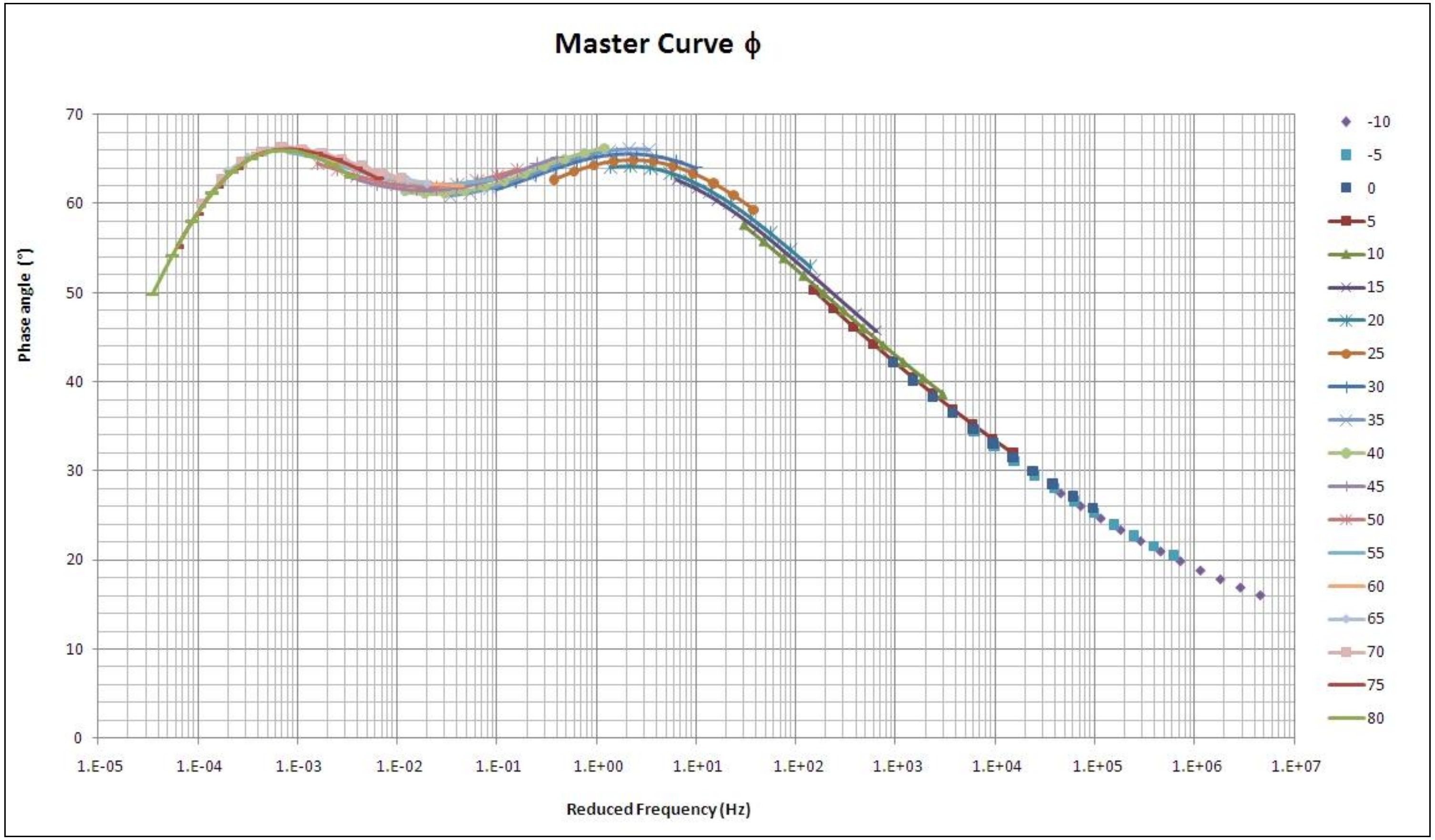


Figure E.3. Master curve δ of TR-MB HS 180 @ 30 ºC – (processed at 180C in High Shear)

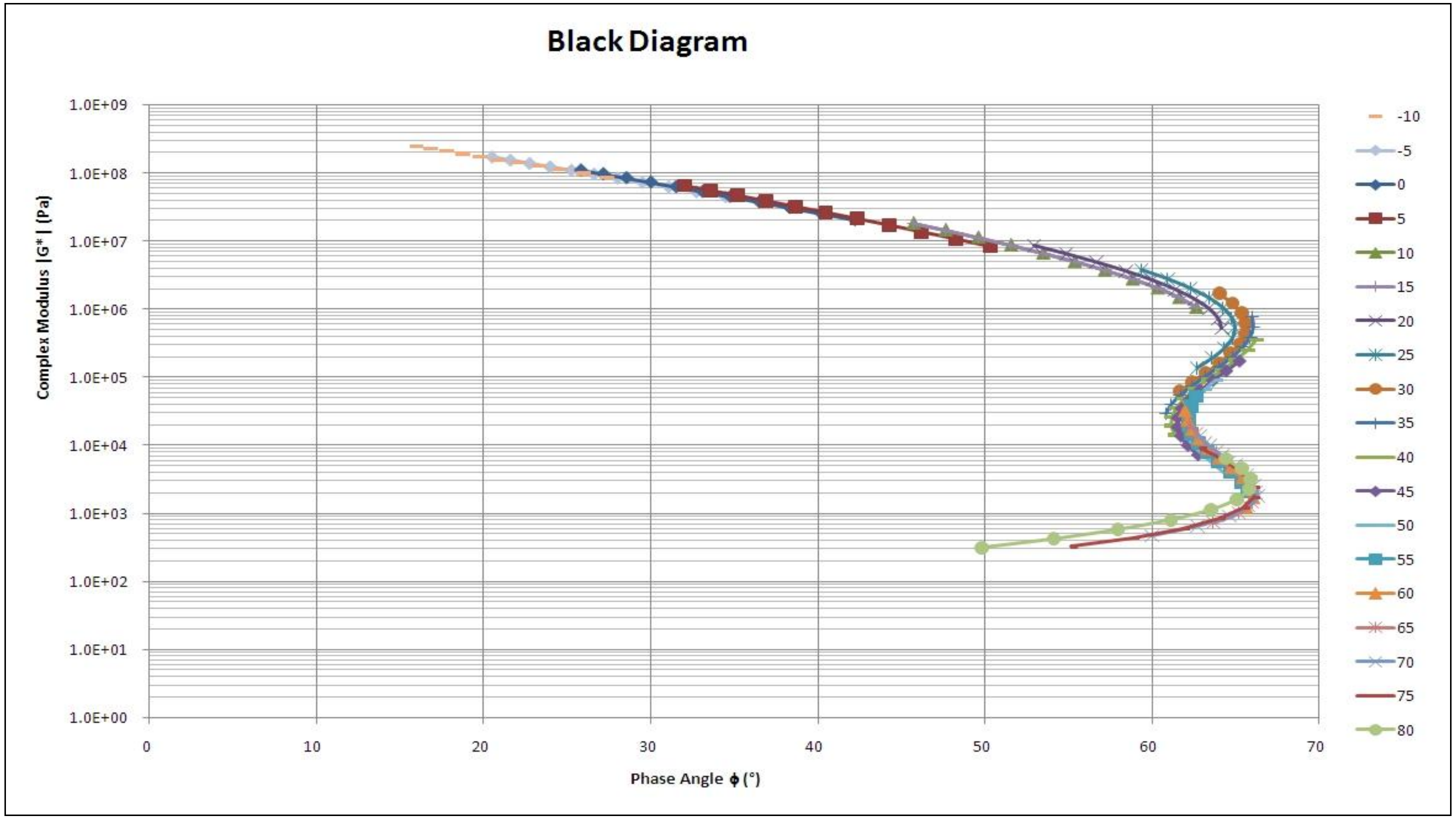


Figure E.4. Black Diagram of TR-MB HS180 obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

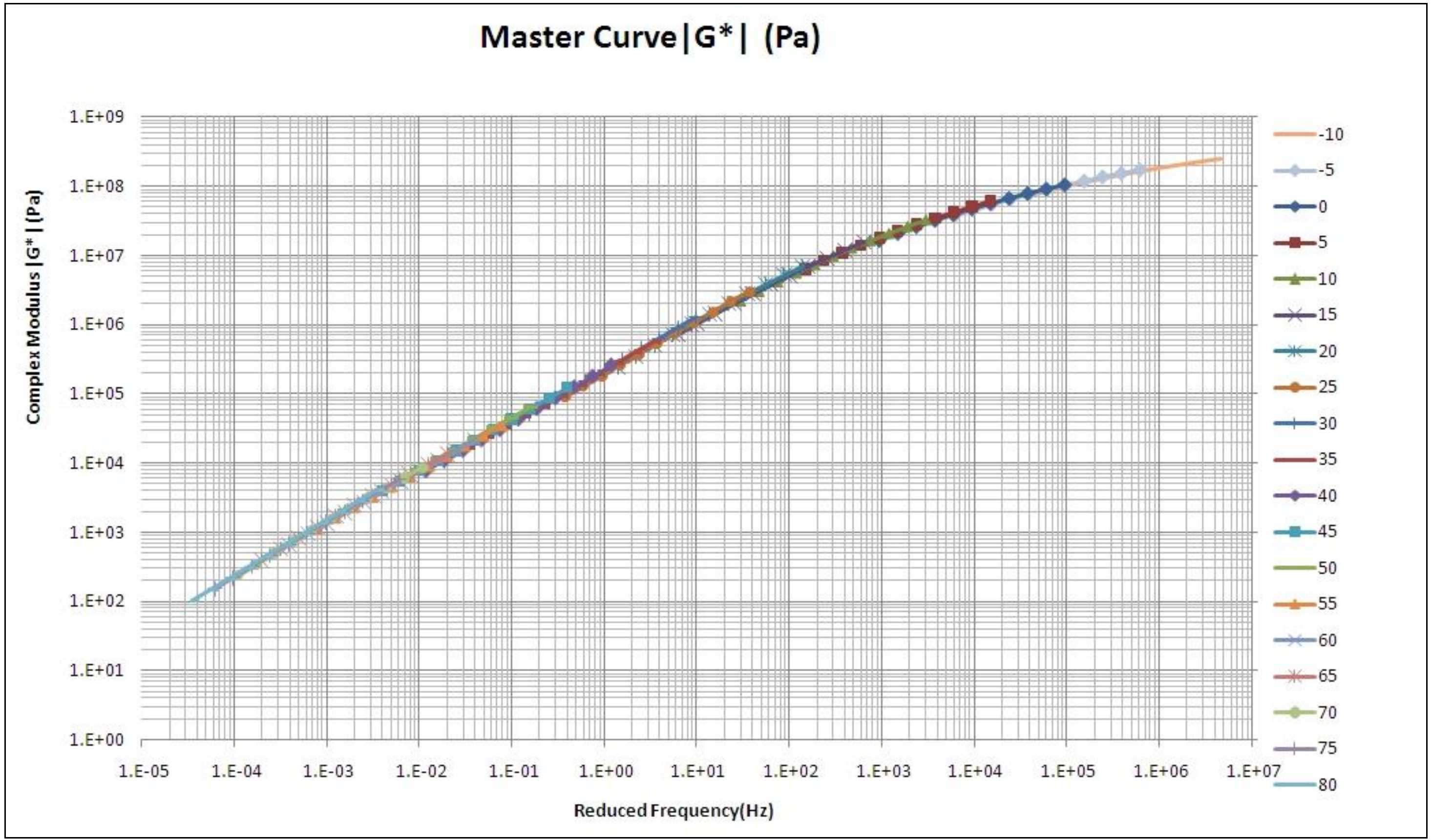


Figure E.5. Master curve |G∗| of TR-MB HS 210 @ 30 ºC – (processed at 180C in High Shear)

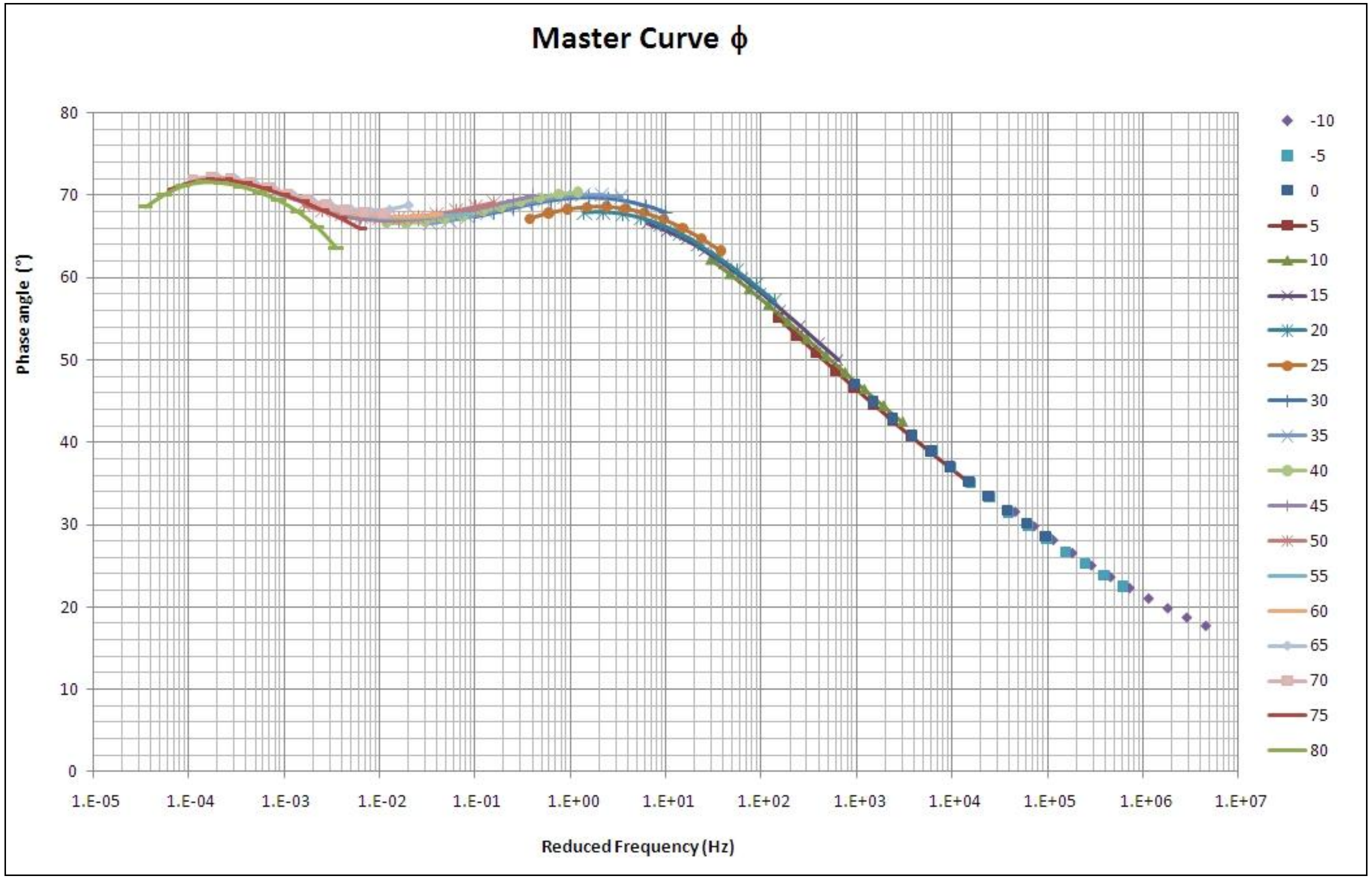


Figure E.6. Master curve δ of TR-MB HS 210 @ 30 ºC – (processed at 180C in High Shear)

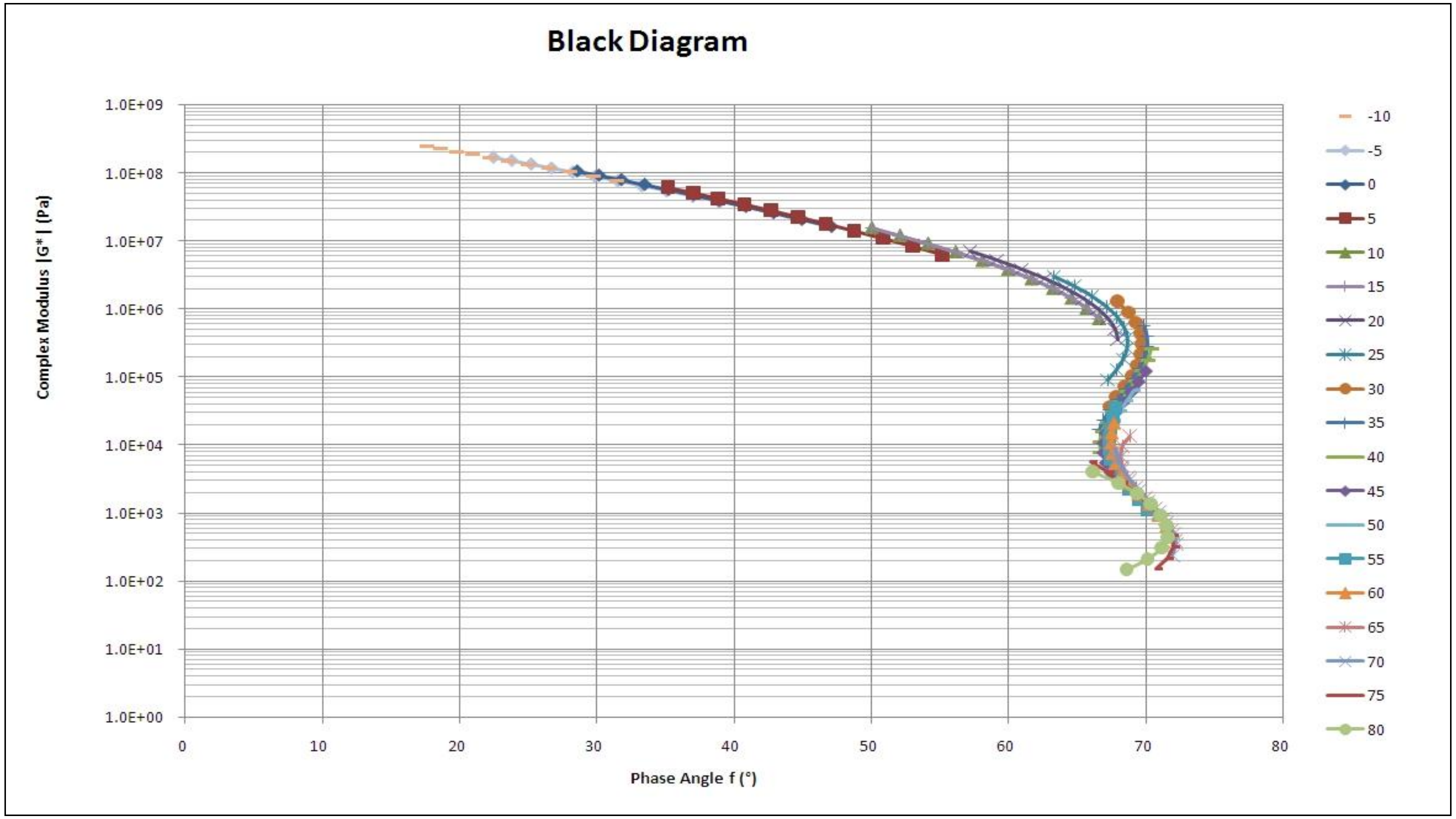


Figure E.7. Black Diagram of TR-MB HS210 obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

PMB Medium – Polymer Modified Bitumen MEDIUM

T	T_R	$T-T_R$	a_{T_calc}	a_{T_manual}	Da_T/a_T
-10.00	30	-40	4.54E+05	300000.00000	5.1413E-01
-5.00	30	-35	5.00E+04	50000.00000	3.5084E-07
0.00	30	-30	6.81E+03	8000.00000	1.4864E-01
5.00	30	-25	1.11E+03	1200.00000	7.1000E-02
10.00	30	-20	2.14E+02	280.00000	2.3572E-01
15.00	30	-15	4.72E+01	80.00000	4.0980E-01
20.00	30	-10	1.18E+01	14.00000	1.5906E-01
25.00	30	-5	3.27E+00	3.70000	1.1607E-01
30.00	30	0	1.00E+00	1.00000	0.0000E+00
35.00	30	5	3.33E-01	0.30000	1.1020E-01
40.00	30	10	1.20E-01	0.11000	8.8722E-02
45.00	30	15	4.61E-02	0.04200	9.8374E-02
50.00	30	20	1.89E-02	0.01800	5.0508E-02
55.00	30	25	8.20E-03	0.00700	1.7132E-01
60.00	30	30	3.74E-03	0.00350	6.9048E-02
65.00	30	35	1.79E-03	0.00180	6.2017E-03
70.00	30	40	8.92E-04	0.00095	6.0666E-02
75.00	30	45	4.63E-04	0.00055	1.5847E-01
80.00	30	50	2.49E-04	0.00030	1.7066E-01
				SUM	*2.6386E+00*

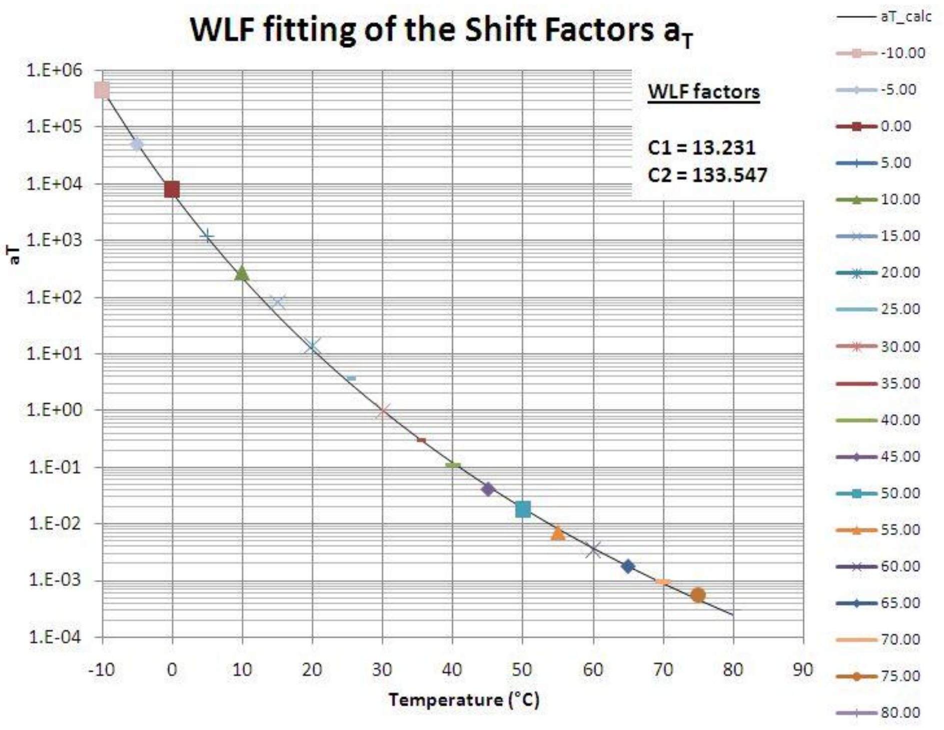


Figure E.8. *Shift factors curve of PMB M edium@30º* obtained by fitting with WLF

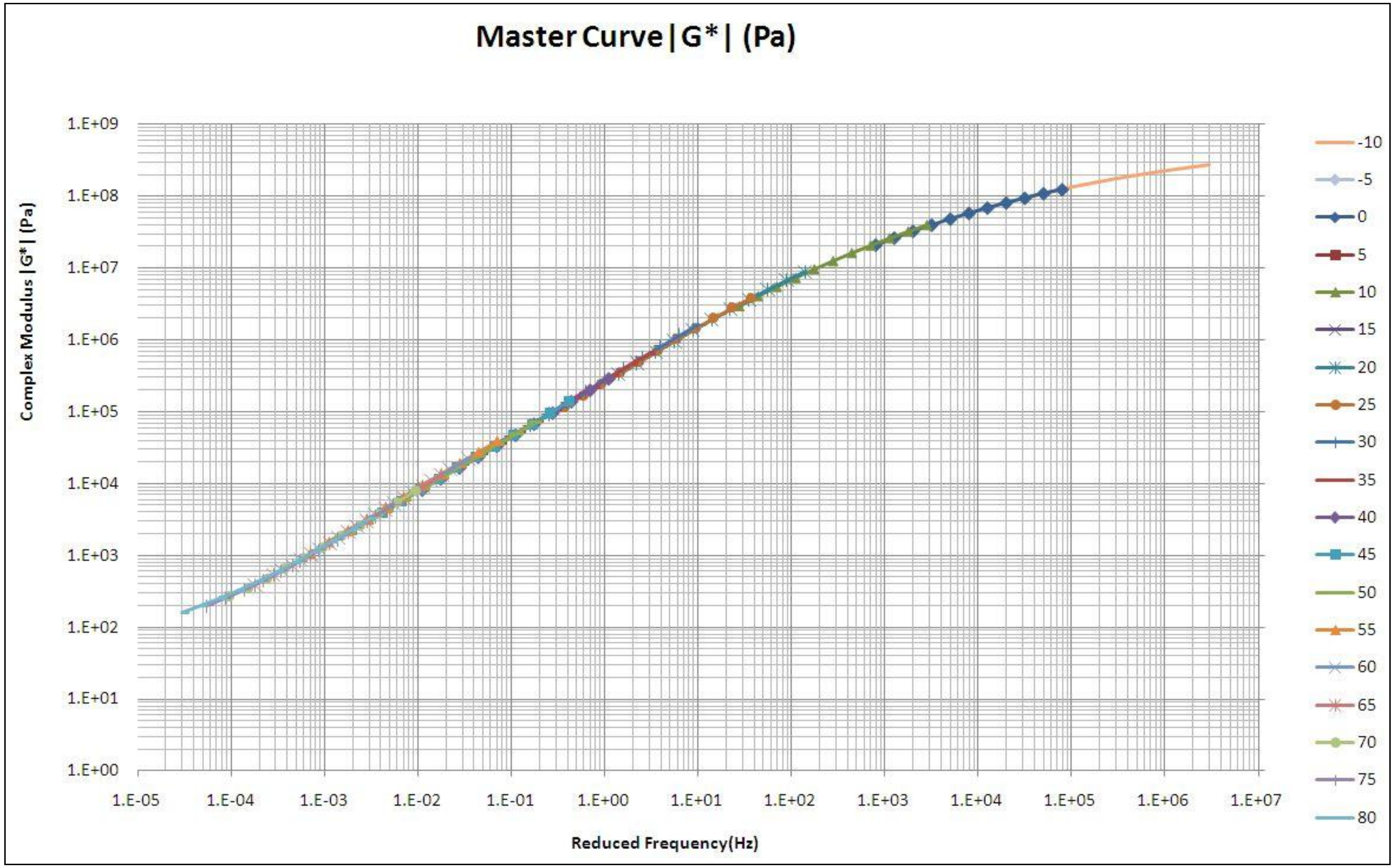


Figure E.9. Master curve δ of PMB MEDIUM at 30 ºC

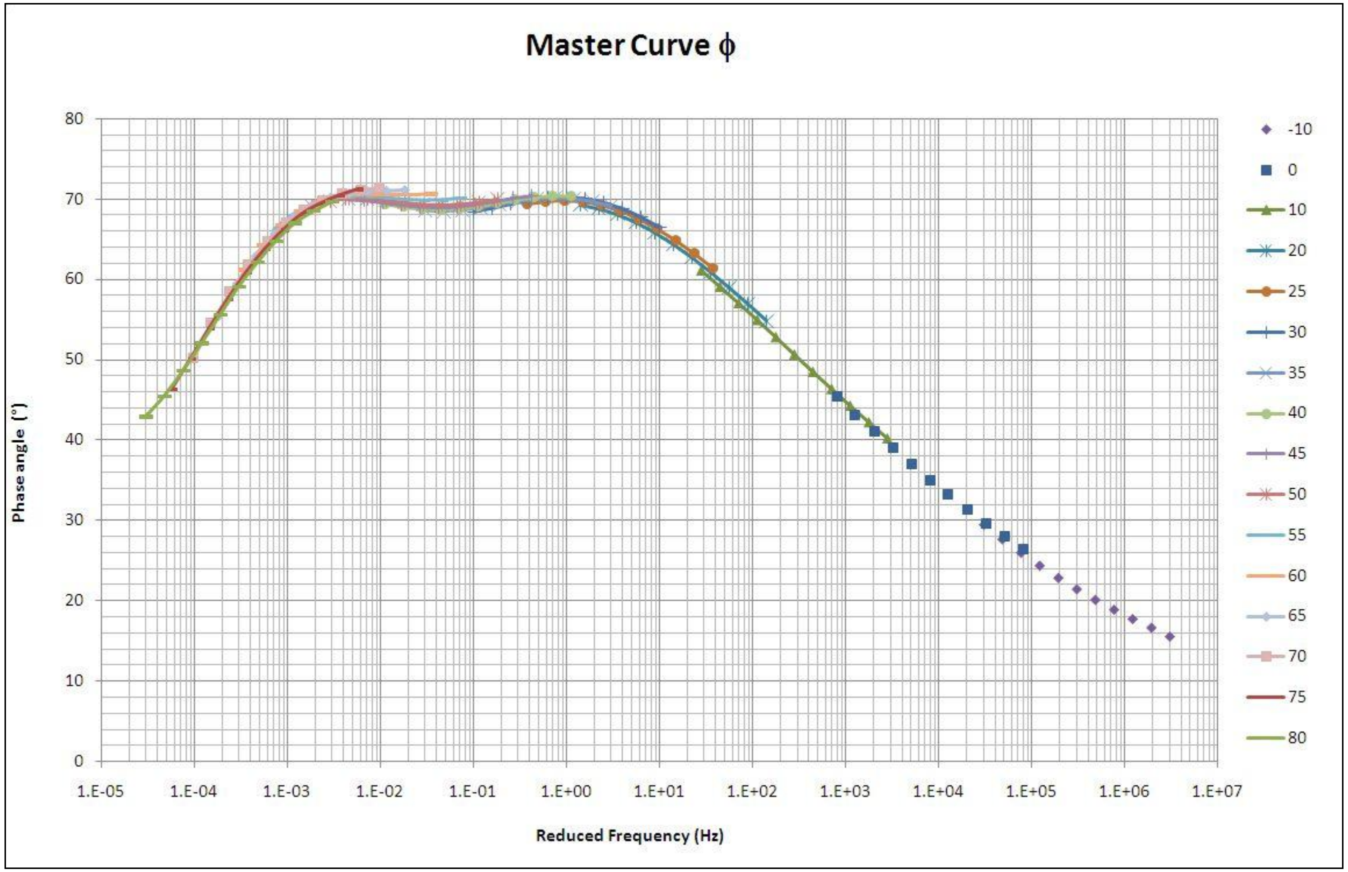


Figure E.10. Master curve δ of PMB MEDIUM at 30 ºC

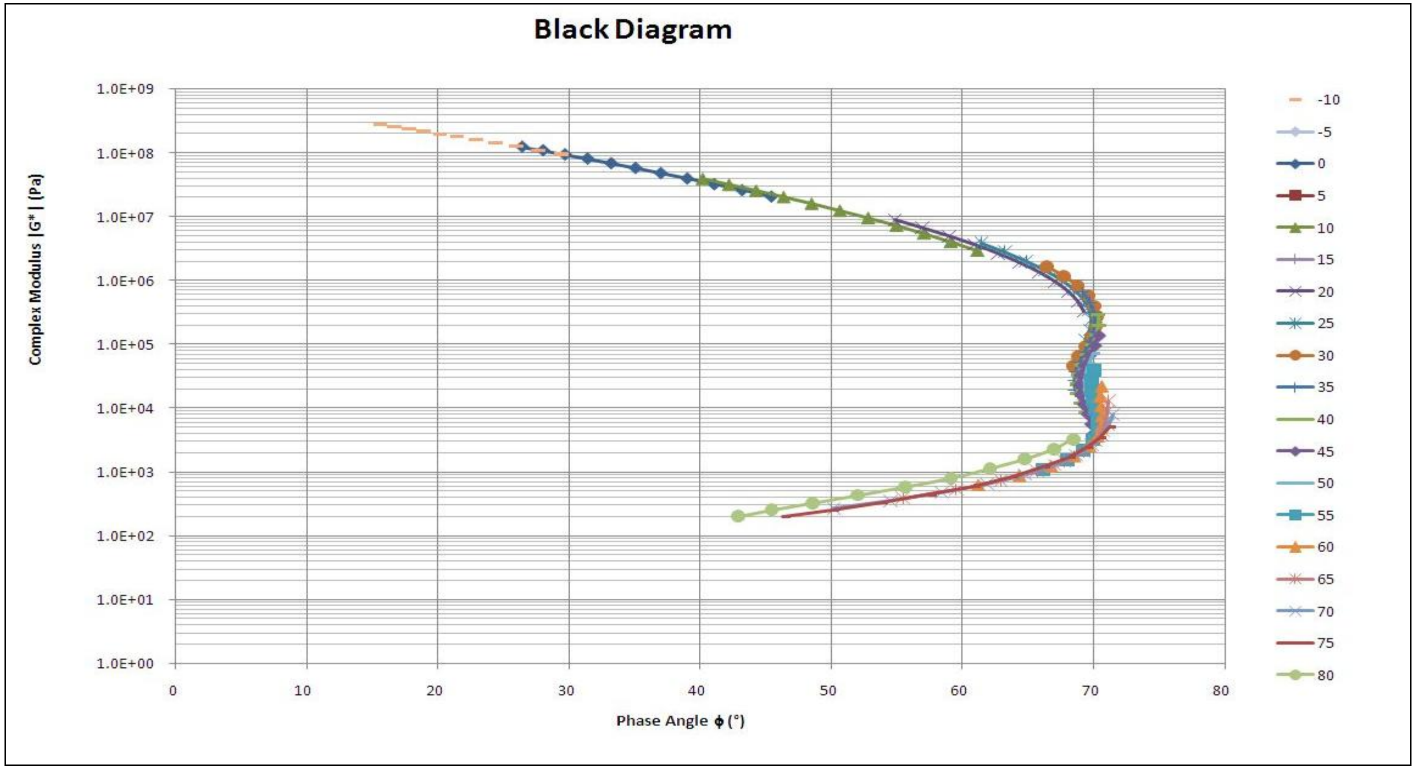


Figure E.11. Black Diagram of PMB MEDIUM obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)

PMB Hard – Polymer Modified Bitumen HARD

T	**T_R**	**$T-T_R$**	**a_{T_calc}**	**a_{T_manual}**	**Da_T/a_T**
-10.00	30	-40	4.48E+05	225000.00000	9.9283E-01
-5.00	30	-35	4.95E+04	50000.00000	1.0696E-02
0.00	30	-30	6.75E+03	8000.00000	1.5606E-01
5.00	30	-25	1.11E+03	1500.00000	2.6195E-01
10.00	30	-20	2.13E+02	280.00000	2.3977E-01
15.00	30	-15	4.70E+01	90.00000	4.7737E-01
20.00	30	-10	1.17E+01	13.50000	1.3004E-01
25.00	30	-5	3.27E+00	4.50000	2.7406E-01
30.00	30	0	1.00E+00	1.00000	0.0000E+00
35.00	30	5	3.33E-01	0.34000	1.9346E-02
40.00	30	10	1.20E-01	0.12000	8.5622E-05
45.00	30	15	4.63E-02	0.03500	3.2205E-01
50.00	30	20	1.90E-02	0.01500	2.6555E-01
55.00	30	25	8.24E-03	0.00700	1.7687E-01
60.00	30	30	3.76E-03	0.00350	7.4942E-02
65.00	30	35	1.80E-03	0.00180	1.5291E-09
70.00	30	40	8.99E-04	0.00095	5.4161E-02
75.00	30	45	4.66E-04	0.00050	6.7308E-02
80.00	30	50	2.51E-04	0.00030	1.6387E-01
				SUM	*3.6870E+00*

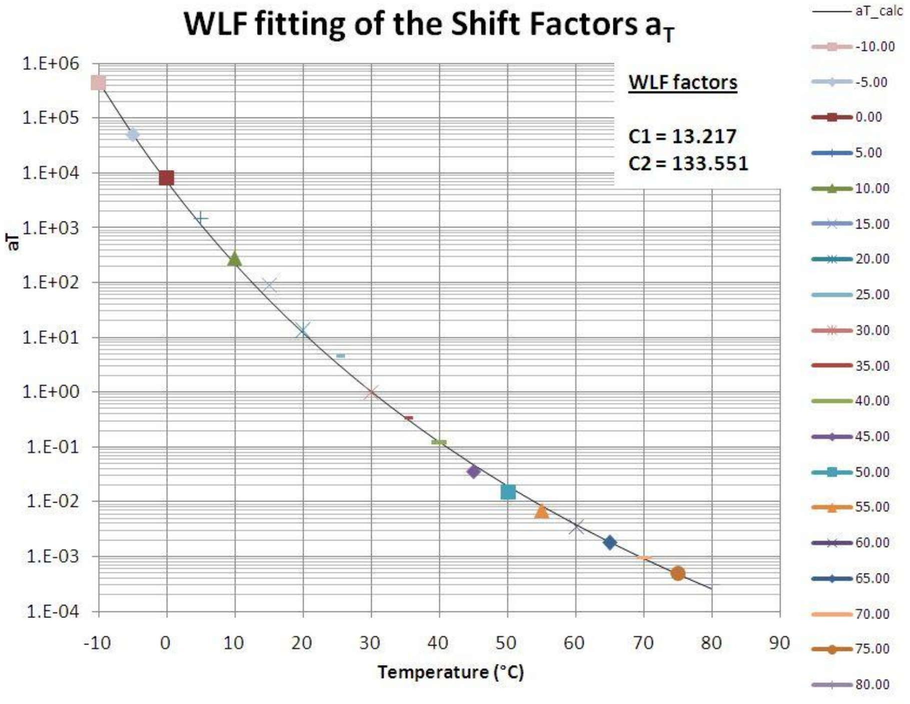


Figure E.12. *<u>Shift factors curve of PMB Hard @30º:</u>* obtained by fitting with WLF

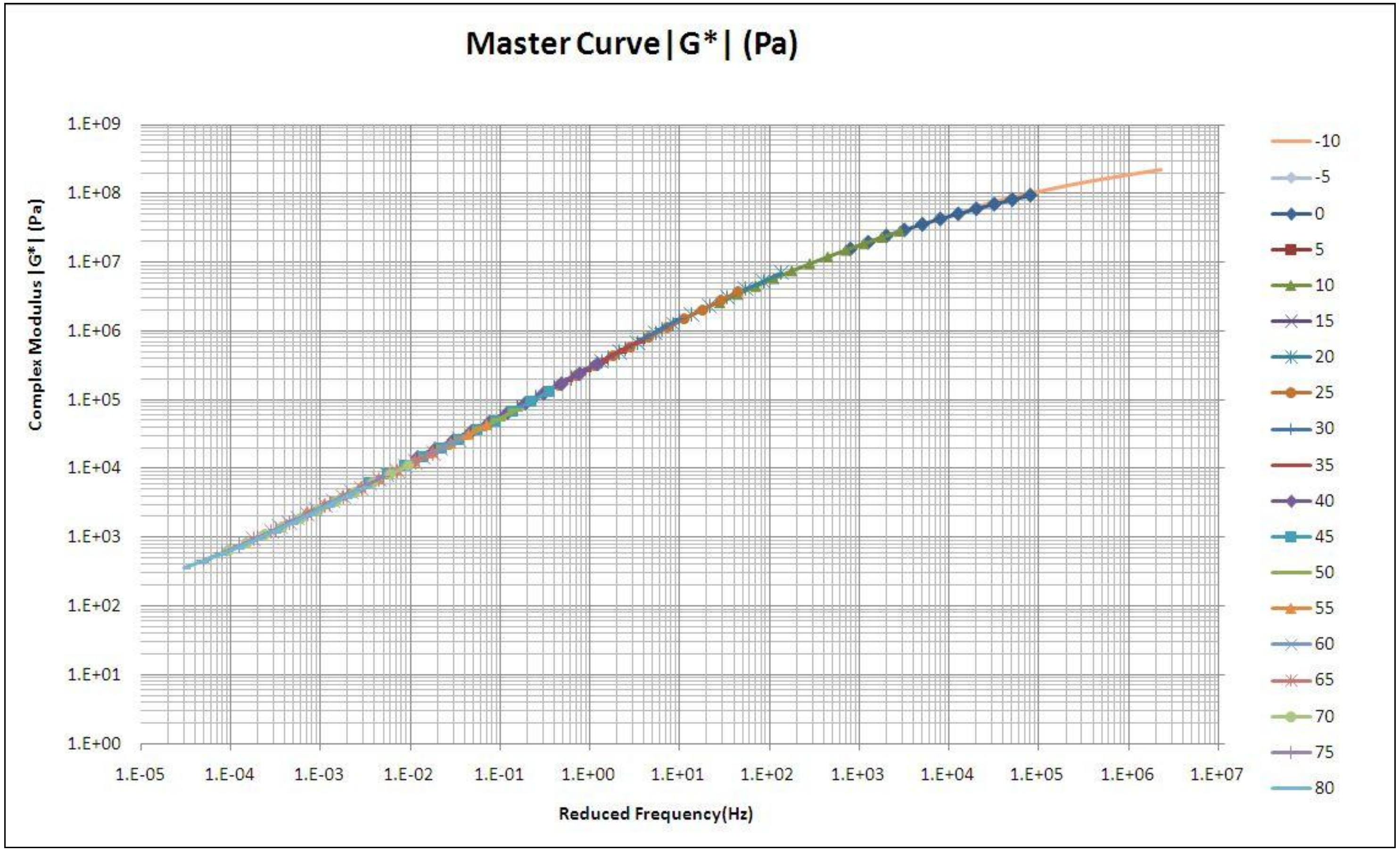


Figure E.13. Master curve δ of bitumen PMB at 30 ºC

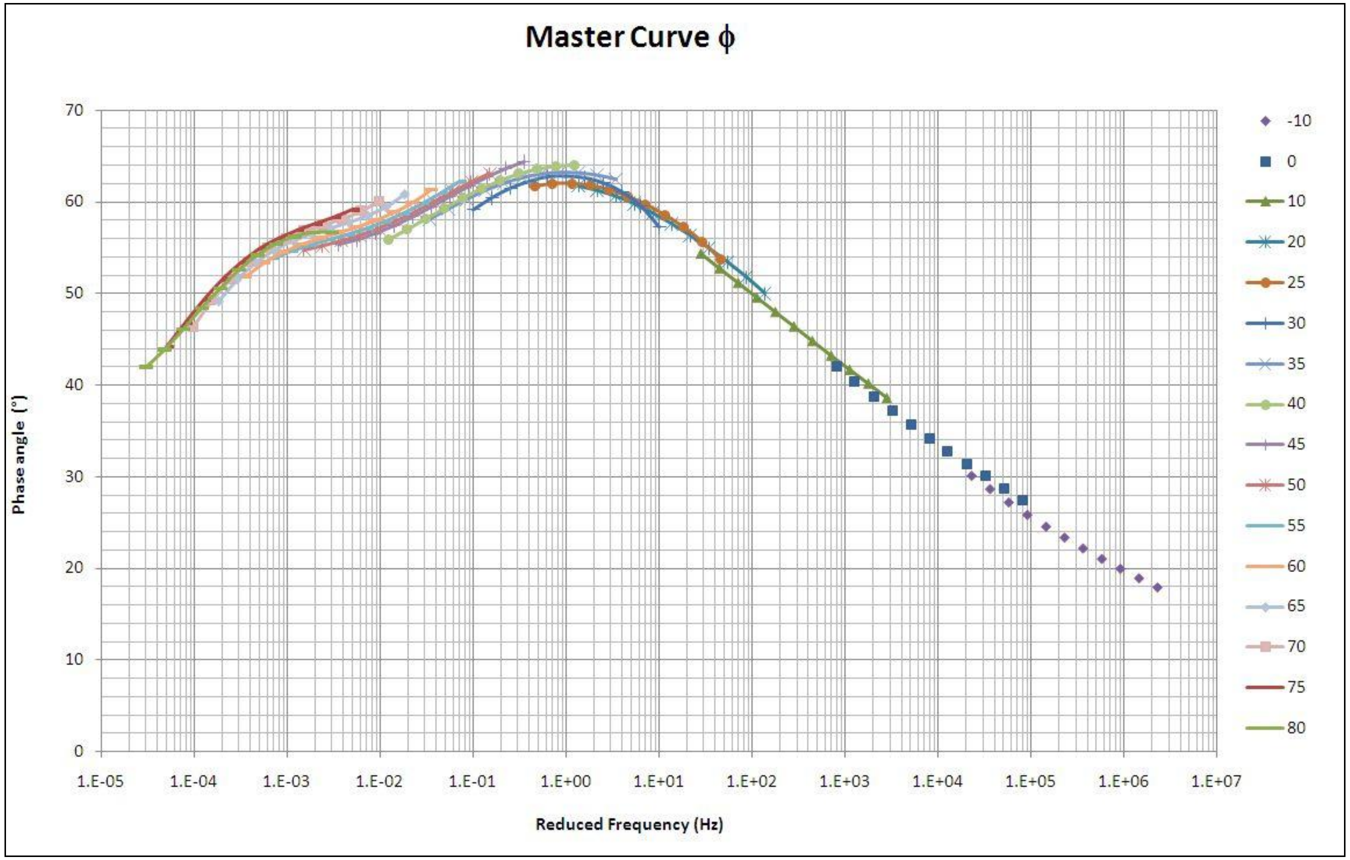


Figure E.14. Master curve δ of bitumen PMB HARD at 30 ºC

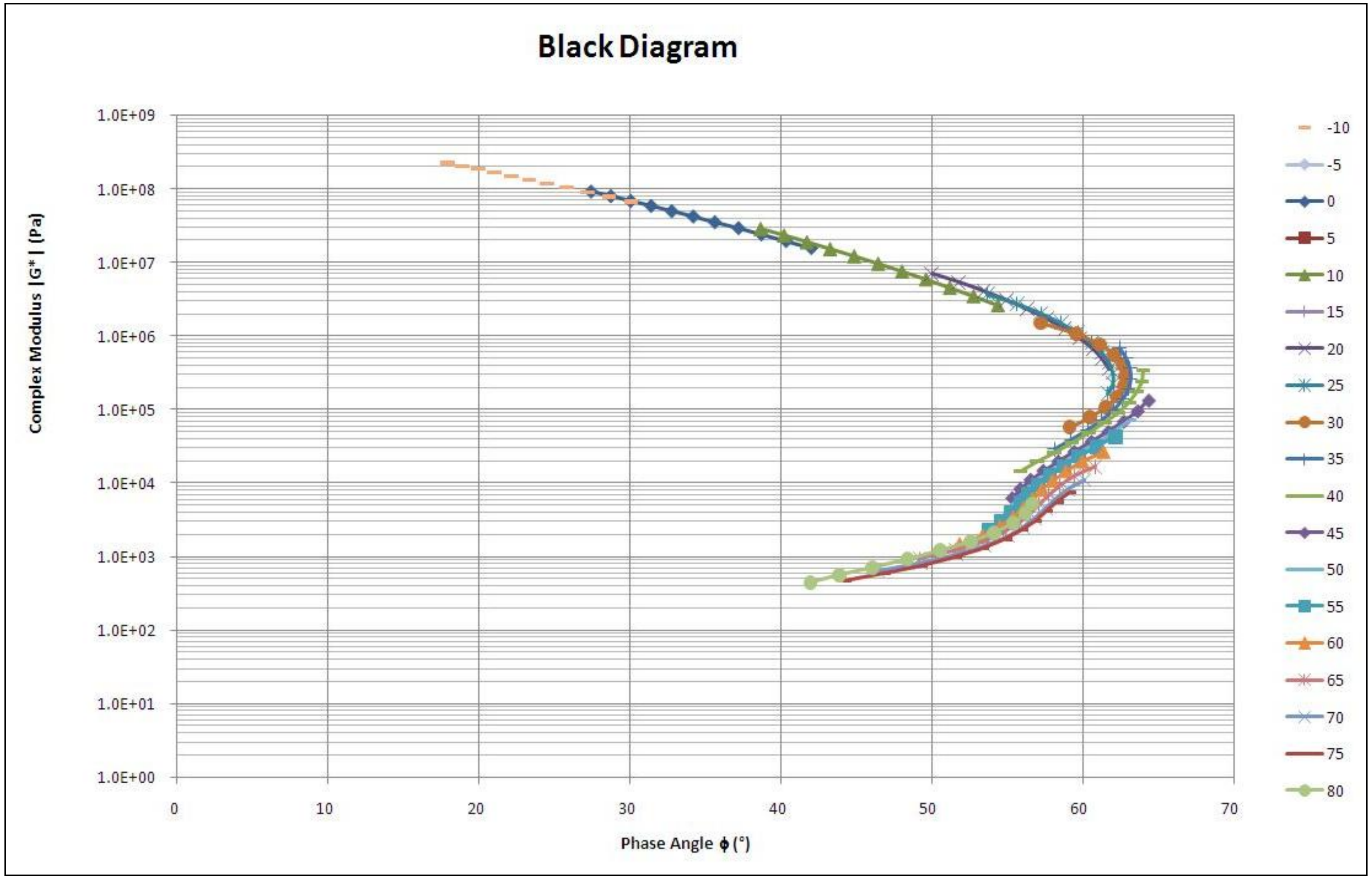


Figure E.15. Black Diagram of PMB Hard obtained with a frequency sweep (0.1-10Hz from -10ºC to 80ºC)