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Effect of Short-Term and UV Irradiation Aging on the Behaviour of SBS-Modified Bitumen

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Abstract: To obtain road bitumen with improved temperature and fatigue resistance, polymers and/or rubbers could be added to it. A particularly suitable polymer for bitumen modification is styrene-butadiene-styrene (SBS) copolymer but limited information is available about the ageing behaviour of modified binders. In this work, two neat bitumens, with different penetration grades, and two SBS-modified bitumens, containing different SBS amounts, were selected, and their short-term and UV ageing behaviour were investigated considering dynamic shear rheometry and Attenuated Total Reflectance-Fourier Transformation InfraRed spectroscopy (ATR-FTIR). Short-time ageing behaviour was investigated performing the rolling thin film oven test (RTFOT), while artificial UV ageing was examined/investigated using UVB lamps. The structural changes in bitumen were monitored at different UV exposure times. All the results suggest that the bitumen having higher penetration grade is more stable than the one with a lower penetration grade in the RTFOT ageing condition, and SBS addition exerts a beneficial effect on thermal stability during processing. Further, SBS addition also has a beneficial effect on the UV ageing resistance of bitumen, reducing its oxidation tendency.

Keywords: SBS-modified bitumen; short-term ageing; UV irradiation; FTIR analysis

1. Introduction

Road bitumens, being organic compounds, are subject to degradation phenomena, which induce changes in their chemical structure, and subsequently, play a crucial role in worsening the mechanical properties [1,2]. Road pavements are overall subjected to short-term and long-term ageing during both processing/layering and in service. The chemical composition of bitumen plays a fundamental role in terms of the durability of the road pavement; effectively the ageing process is the result of various chemical oxidation reactions, in which the bitumen molecules are reorganized, the volatile components are lost, and carbonyl compounds and sulfoxides are formed. All this will influence road pavement performance in terms of durability and mechanical properties.

It should also be considered that once road pavements have been laid, they are exposed to atmospheric agents, such as rain, snow/ice and ultraviolet rays, which accelerate ageing and reduce their useful service life [1,3].

Several researchers have studied the impact that UV radiation has on ageing of road binders and how it accelerates ageing phenomena in terms of deterioration of mechanical performance and reduction of service life of the pavement [4–6]. Understanding the UV ageing mechanism of asphalt binders is a very important issue [7,8], although there are still complex phenomena not clearly understood, due to the presence of constituents with different chemical natures and range concentrations.

To increase the performance and durability of bitumen, pure bitumen is modified by the addition of polymer; several studies have reported on the beneficial effects of polymers added to bitumen, in terms of increasing physico-mechanical properties [9,10]. As is well
known, polymer-modified bitumen (PMB) is obtained by adding small amounts of polymer to bitumen by mixing at high temperatures, however, the final properties and performance of PMB depend on the nature of the bitumen, chemical nature and amount of polymer added and affinity/compatibility between bitumen and polymer [11,12].

Styrene-butadiene-styrene block copolymer (SBS) is the most highly regarded polymer as a bitumen modifier because of its ability to form cross-linked structures with the host bitumen [13], increase the elasticity of bitumen, ageing resistance and high-temperature performance [13,14].

Numerous studies in the scientific literature have reported the properties, performance and ageing behaviour of unmodified bitumen [7], while few studies deal with the ageing behaviour of PMBs [4,14,15]. Furthermore, all these studies agree that the presence of polymer-based modifiers could have a beneficial effect on the overall bitumen properties, and specifically, on the PMB ageing behaviour, showing improved resistance compared to unmodified bitumens. In addition, to ensure adequate ageing performance in the long term, the PMB must contain polymers having controlled size, dimensions, and composition [9,16].

Recently, many researchers have paid more attention to ageing processes involving unmodified bitumen and PMBs [17,18], focusing on performance changes before and after ageing. Various investigation techniques can be used to study the chemical/mechanical changes that ageing leads in bituminous asphalt, such as Fourier Transform Infrared Spectroscopy (FTIR) and Dynamic Shear Rheometer (DSR): FTIR is used to evaluate the chemical changes induced by ageing in terms of changes in carbonyl and sulfoxide [15,19,20] and DSR in terms of changes in viscoelastic behaviour at various temperatures [5,21].

The aim of this work was to investigate the behaviour of commercial bitumens of common use as road binders to artificial photooxidation ageing as well as to evaluate the effect of typical amounts of modifier SBS in bitumen in terms of both short- and long-term oxidative resistance. Two neat bitumens with different penetration grades and two styrene-butadiene-styrene (SBS) modified bitumens, containing different SBS amounts were considered. Their short-term and UVB ageing behaviour were investigated considering dynamic shear rheometry and Attenuated Total Reflectance-Fourier Transformation InfraRed spectroscopy (ATR-FTIR).

2. Materials and Methods

2.1. Materials

Two unmodified bitumens (named B1 and B2) for typical road applications with different penetration grades, i.e., 35–50 and 50–70 (measurements following EN 1426; see also Table 1 below), were considered. These two commercial bitumens were selected because of their large availability and common use in Italian engineering practice. Further, to obtain appropriate bitumen modification, commercial radial Styrene-Butadiene-Styrene (SBS) copolymer was added to B2 at two different concentrations (representative of the concentrations most commonly used in road construction). The composition being an industrial secret, the supplier only provided the following range concentration: low SBS concentration, ranging 2–4% wt/wt (named B2_LSBS) and high SBS concentration, ranging 6–8% wt/wt (named B2_HSBS).

In Tables 1 and 2, the main characteristics, conventional properties and chemical fraction components of all the bitumens considered are summarized; the results given in Table 1 are the arithmetic means of the valid repetitions performed for each test, as specified in the pertinent reference standards. A detailed chemical analysis was conducted using an analytical IATROSCAN MK-5 system (Iatron Laboratories Inc., Tokyo, Japan) TLC-FID, according to procedure IP 469/01 [22,23]. Based on the data in Table 2, the Gaestel Index (Ic), which represents the ratio between the flocculated and dispersed fractions, was determined as follows [24]:

\[
Ic = \frac{(\text{Saturates} + \text{Asphaltenes})}{(\text{Resins} + \text{Aromatics})}
\]
Table 1. Properties of all the bitumens used.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Standard</th>
<th>Unit</th>
<th>B1</th>
<th>B2</th>
<th>B2_LSBS</th>
<th>B2_HSBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration at 25 °C, pen</td>
<td>EN 1426</td>
<td>0.1 mm</td>
<td>36</td>
<td>52.25</td>
<td>50.5</td>
<td>51</td>
</tr>
<tr>
<td>Ring and ball softening point, TR&amp;B</td>
<td>EN 1427</td>
<td>°C</td>
<td>54.5</td>
<td>52.6</td>
<td>77.6</td>
<td>88.5</td>
</tr>
<tr>
<td>Penetration at 25 °C, pen (after short term ageing, according to EN 12607-1)</td>
<td>EN 1426</td>
<td>0.1 mm</td>
<td>-</td>
<td>39.3</td>
<td>36</td>
<td>40</td>
</tr>
<tr>
<td>Ring and ball softening point, TR&amp;B (after RTOFT according to EN12607-1)</td>
<td>EN 1427</td>
<td>°C</td>
<td>-</td>
<td>56</td>
<td>84</td>
<td>91.25</td>
</tr>
<tr>
<td>Viscosity at 100 °C</td>
<td>EN 13302</td>
<td>Pa s</td>
<td>5.25</td>
<td>2.20</td>
<td>11.46</td>
<td>19.83</td>
</tr>
<tr>
<td>Viscosity at 135 °C</td>
<td>EN 13302</td>
<td>Pa s</td>
<td>0.55</td>
<td>0.29</td>
<td>1.70</td>
<td>2.14</td>
</tr>
<tr>
<td>Viscosity at 150 °C</td>
<td>EN 13302</td>
<td>Pa s</td>
<td>0.27</td>
<td>0.15</td>
<td>1</td>
<td>1.25</td>
</tr>
<tr>
<td>Viscosity at 180 °C</td>
<td>EN 13302</td>
<td>Pa s</td>
<td>0.09</td>
<td>0.1</td>
<td>0.40</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 2. SARA fraction characteristics of neat bitumen (IATROSCAN-TLC/FID).

<table>
<thead>
<tr>
<th>Bitumen</th>
<th>Saturates %</th>
<th>Aromatics %</th>
<th>Resins %</th>
<th>Asphaltenes %</th>
<th>Gaestel Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>2.9</td>
<td>52.8</td>
<td>22.0</td>
<td>22.3</td>
<td>0.347</td>
</tr>
<tr>
<td>B2</td>
<td>3.2</td>
<td>58.9</td>
<td>21.4</td>
<td>16.6</td>
<td>0.25</td>
</tr>
</tbody>
</table>

According to the literature [25], bitumen can be classified as gel nature bitumen, if the Ic value is higher than 0.5, and as colloidally stable bitumen, if the Ic value is lower than 0.5. Based on this classification, both B1 and B2 can be considered as colloidally stable bitumens.

2.2. Methods

Empirical penetration and the softening point of unmodified bitumen and SBS-modified bitumen were examined according to EN 1426 and EN 1427, before and after short-time ageing.

The dynamic viscosity of all the samples was measured at different temperatures, i.e., at 100 °C, 135 °C, 150 °C and 180 °C, using a Brookfield viscometer (DV-III™ Ultra Rheometer, Middleboro, MA, USA), following the EN 13302 standardized procedure.

Dynamic mechanical analysis was carried out using a Dynamic Shear Rheometer (DSR) by Anton Paar Physica MCR 101. According to EN 14770, the dynamic viscosity of all samples was measured from −10 °C to 80 °C, considering two plate geometries, i.e., 8 mm and 25 mm, and for frequency sweep tests the maximum applied strain was 1%.

To simulate real-use conditions, the B1, B2, B2_HSBS and B2_LSBS samples were subjected to short-term ageing, and then to photo-oxidation exposure. Specifically, short-term ageing was carried out using the Thin Film Oven Lamination Test (RTFOT) at a constant temperature of 163 °C, according to standard procedure EN 12607-1. The unmodified (B1 and B2) and SBS-modified bitumen (B2_HSBS and B2_LSBS) samples were subjected to an airflow of 4000 mL/min and a rotation speed of 15 rpm for 75 min.

Then thin films of B1, B2, B2_HSBS and B2_LSBS were subjected to UV irradiation ageing using a Q-UV chamber (by Q-LAB, USA) equipped with UVB lamps (313 nm), at T = 70 °C, here called UVB irradiation. To prepare thin films, the bitumen was placed in an oven at 180 °C for 10 min and then, using a stainless-steel lab spatula, the thicknesses were reduced down to 1 mm.

The ageing behaviour, upon both RTFOT exposure and UVB irradiation, was monitored by Attenuated Total Reflectance-Fourier Transformation InfraRed spectroscopy (ATR-FTIR) in time, using a Perkin Elmer FTIR spectrometer (mod. Spectrum Two). ATR-FTIR spectra of all investigated samples were obtained performing 16 scans between 4000 and 500 cm⁻¹ on the aged samples at different exposure times. For each sample, at
different exposure times, triplicate measurements were carried out, in order to verify the reproducibility of the results.

The monitoring of UV irradiation ageing was performed by studying the changes in the obtained spectra, and specifically those affecting three characteristic bands: hydroxyl functions (at ca. 3600–3200 cm\(^{-1}\)), CH stretching vibrations (at ca. 2950–2800 cm\(^{-1}\)) and carbonyl functions (centred at ca. 1700 cm\(^{-1}\)). The increase of both C=O and hydroxyl bands provides monitoring of the oxidation of the whole bitumen, while the decrease of CH stretching bands permits monitoring of chain immobilization and/or crosslinking, also according to the literature [26]. Furthermore, the changes of butadiene double bonds C=C (centred at ca. 965 cm\(^{-1}\)) permits monitoring of the deterioration of the SBS copolymer as a result of modification of butadiene copolymer, usually by diminution of the double bond content.

According to the literature, the structural indices of unmodified and SBS-modified bitumen are calculated as follows [26]:

\[
I_{\text{C-O}} = \frac{\text{Area of the carbonyl band centred at ca. 1700 cm}^{-1}}{\text{Area of the CH2 centred at ca. 1455 cm}^{-1} + \text{Area of the CH3 band centred at ca. 1376 cm}^{-1}} \quad (2)
\]

\[
I_{\text{OH}} = \frac{\text{Area of the hydroxyl band centred between 3600–3200 cm}^{-1}}{\text{Area of the CH2 centred at ca. 1455 cm}^{-1} + \text{Area of the CH3 band centred at ca. 1376 cm}^{-1}} \quad (3)
\]

\[
I_{\text{SBS}} = \frac{\text{Area of the ethylene band centred at ca. 965 cm}^{-1}}{\text{Area of the CH2 centred at ca. 1455 cm}^{-1} + \text{Area of the CH3 band centred at ca. 1376 cm}^{-1}} \quad (4)
\]

3. Results and Discussion

3.1. Short-Term Ageing

To simulate bitumen production, neat (B1 and B2) and SBS-modified (B2_LSBS and B2_HSBS) bitumen were subjected to rolling thin film oven test (RTFOT) ageing treatment at a temperature of 163 °C for 75 min, and the rheological behaviour of all investigated samples before and after short-term ageing treatment was evaluated. Specifically, the complex modules of all investigated samples were measured, before and after ageing, as a function of frequency, and in Figure 1a–d the trends obtained are plotted.

It is worth noting that, as expected, the complex modulus values increase for both B1 and B2 bitumen upon RTFOT ageing, and this increase is more pronounced for the B1 sample than for the B2 one: See Figure 1a,b. This result suggests that B1 hardens much more when processed, and this can be understood considering that B1 is a low penetration grade sample, and apparently during RTFOT ageing, B1 experiences higher thermal degradation than B2. Interestingly, the complex modules of both B2_LSBS and B2_HSBS, before and after RTFOT ageing, remain almost unchanged (see Figure 1c,d), suggesting a beneficial effect due to the presence of SBS. In addition, it seems that, the positive effect of SBS is even more pronounced if it is added at a high amount, i.e., B2_HSBS before and after ageing shows the same complex moduli values in the whole investigated frequency range (see Figure 1d).
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To perform further characterization of bitumen before and after RTFOT ageing, all samples were investigated through ATR-FTIR analysis and the spectra obtained are shown in Figure 2a–d. In addition, also according to the literature [27], for a better understanding, the assignment of infrared spectra peaks of bitumen is reported.

The ATR-FTIR spectra of the unaged and short-term aged B1 are very similar (see Figure 2a), although there are slight differences, specifically, a shoulder at ca. 1700 cm\(^{-1}\) and a broad shoulder ranging 3600–3200 cm\(^{-1}\). This result suggests the formation of new chemical oxygen-containing groups, such as C=O, also according to the literature [25]. Although the detected differences are minimal and considering that the RTFOT ageing is conducted in the presence of reduced oxygen, the result obtained highlights the occurrence of some structural changes for B1, with these ageing conditions. As can be noticed in Figure 2b, the spectra before and after ageing of B2 are almost unchanged, suggesting that the B2 sample is more stable during processing than B1, also according to the rheological data, commented on above. In addition, no changes are noticeable in the ATR-FTIR spectra of either B2_LSBS or B2_HSBS, before and after short-term ageing (see Figure 2c,d), suggesting no occurrence of structural changes for either SBS-modified bitumen.

Figure 1. Viscosity trends of unaged (dark blue symbols) and short-term aged (light blue symbols) samples: (a) B1, (b) B2, (c) B2_LSBS and (d) B2_HSBS.
Therefore, the rheological and ATR-FTIR spectroscopy data obtained suggest that during processing, the bitumen with a higher penetration grade (B2) is more stable than the one with a lower penetration grade (B1), also considering that B2 contains slightly higher amounts of both saturates and aromatics, in comparison to B1. As can be noticed, the presence of a large amount of saturates and aromatics makes the bitumens more stable during the production processing. Furthermore, adding SBS to B2 has a very noticeable beneficial effect on thermal resistance during bitumen processing, especially, if SBS is added at a high amount. However, according to the literature, this result confirms that the use of radial SBS as a bitumen modifier can be considered a useful and industrially applicable method for the formulation of sustainable PMB. Additionally, here it is demonstrated that the B2_HSBS is more stable during the production process, i.e., in terms of rheological behaviour and short-term oxidative resistance, than the B2_LSBS one.

3.2. UV Irradiation Ageing

To simulate bitumen service life, neat (B1 and B2) and SBS-modified (B2_LSBS and B2_HSBS) bitumen were subjected to UV irradiation ageing, using UVB lamps that are suitable for investigation of organic material changes upon UVB irradiation. Although, the durability of organic compounds in real natural conditions cannot be precisely correlated with the results coming from artificially accelerated UVB ageing, this investigation method could be considered useful and credible to obtain a reliable and quick analysis, regarding the overall ageing behaviour of the organic compounds. Usually, the structural changes

![Figure 2. ATR-FTIR spectra of unaged (dark blue line) and short-term aged (light blue line) samples: (a) B1, (b) B2, (c) B2_LSBS and (d) B2_HSBS.](image-url)
of organic compounds upon UVB irradiations are monitored by spectroscopy techniques, which are able to identify the disappearance and/or appearance of new chemical groups. The formations of new chemical groups and/or changes in existing groups lead to the disappearance and/or appearance of bands in the spectra. Considering this issue and keeping in mind the appearance of bitumens that are in dark black colour, due to their petroleum-based nature, in this work, the choice was made to monitor the bitumen structural changes using surface Attenuated Total Reflectance-Fourier Transformation InfraRed spectroscopy (ATR-FTIR). In Figures 3–6, the ATR-FTIR spectra obtained for all the investigated bitumens at different exposure times (from 0 h to 76 h) are plotted. Specifically, in Figures 3a, 4a, 5a and 6a, the spectra in the whole investigated IR range (4000–500 cm\(^{-1}\)) are plotted, while for greater clarity, in Figures 3b, 4b, 5b and 6b, the hydroxyl range (3600–3200 cm\(^{-1}\)), in Figures 3c, 4c, 5c and 6c the CH stretching vibration range (3000–2800 cm\(^{-1}\)), and in Figures 3d, 4d, 5d and 6d the carbonyl range (1800–1650 cm\(^{-1}\)) are detailed. Regarding the ATR-FTIR analysis, it is considered here as a semi-quantitative study for comparison between the investigated samples, and it cannot be considered an absolute quantitative method for samples containing different SARA constituents.

**Figure 3.** ATR-FTIR spectra of B1 at different UV irradiation times: (a) whole spectra, (b) hydroxyl range, (c) CH stretching range and (d) carbonyl range.
However, all investigated samples show variations of some characteristic bands as a function of the UVB irradiation time; specifically, the changes are related to increases of hydroxyl and carbonyl functions, suggesting the occurrence of overall bitumen oxidation, which results from the formation of new oxygen-containing groups, and also to decreases of CH stretching vibrations, suggesting the occurrence of chain immobilization and/or crosslinking. Overall, the simultaneous changes in hydroxyl, CH stretching vibration and carbonyl ranges suggest the occurrence of chains immobilization, probably, through formation of crosslinking structures, and occurrence of oxidation, but considering the presence of different SARA constituents, it is not easy to identify the exact chemical nature of new oxygen-containing groups. It is worth noting that the ATR-FTIR analysis of ageing behaviour of bitumens is representative for overall oxygen resistance, but is not exhaustive for identification of oxidation products, from the chemical point of view, of different SARA constituents and/or bitumen modifiers.

Some more general considerations regarding ATR-FTIR analysis of B1, B2, B2_LSBS and B2_HSBS bitumens as a function of UVB irradiation:

(i) the gradual increases of broad peaks in the hydroxyl range, i.e., ca. 3600–3200 cm\(^{-1}\), as a function of UVB irradiation for all investigated bitumens, see Figures 3b, 4b, 5b and 6b, can be related to the appearance of further free hydroxyl and/or carboxyl groups, which are typical degradation products upon UVB exposure.

(ii) the gradual decreases of peaks at ca. 2925, 2850 and 2830 cm\(^{-1}\), which are attributed to asymmetric and symmetrical stretching vibration of C-H in methylene groups and...
to stretching vibration of aldehyde groups (see peaks assignments in Table 3), as a function of UVB irradiation time, can be related to the formations of crosslinked structures of chains containing unsaturation and/or butadiene units. These effects are noticeable for all investigated bitumens, i.e., B1, B2, B2_LSBS and B2_HSBS (see Figures 3c, 4c, 5c and 6c).

(iii) the gradual increases of peaks in the carbonyl range, mainly related on the building-up of new peak at ca. 1750 cm\(^{-1}\) and the increase in intensity of small peaks at ca. 1700 cm\(^{-1}\), can be related to the formation of esters and lactones, and the formation of further carboxyl contents, respectively (see Figures 3d, 4d, 5d and 6d).

Figure 5. ATR-FTIR spectra of B2_LSBS at different UV irradiation times: (a) whole spectra, (b) hydroxyl range, (c) CH stretching range and (d) carbonyl range.

To perform a quantitative surface analysis of UV irradiation, Equations (1)–(3) reported in the experimental section were considered, and in Figure 7 the trends obtained are plotted. According to the literature, the increase of I\(\text{C=O}\) and I\(\text{OH}\), which can be related to the formation of new oxygen-containing groups, such as carbonyls, carboxylase, esters, lactones and other oxygen-containing groups, suggests the occurrence of oxidative degradation upon UV irradiation. In Figure 7a,b, the I\(\text{C=O}\) and I\(\text{OH}\) trends increase as a function of the UV irradiation time for all investigated samples, as expected, and these increases are more pronounced for B1 than for B2, again suggesting that higher penetration grade bitumen is less likely to oxidize. Furthermore, further improved oxidative stability can be noticed for both SBS-modified bitumens, and it seems that B2_HSBS shows better oxidative resistance than B2_LSBS, upon UV irradiation ageing. Further confirmation of this comes from the