

# **Influence of Branching on the Rheology, Filmability and Mechanical and Optical Properties of a Biodegradable and Compostable Co-Polyester**

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## **Abstract**

Over the last years, bio-based and biodegradable alternatives have gained considerable attention both of academic and of packaging industrial communities, driven by recent legislation and increasing awareness concerning environmental issues related to traditional plastic. However, it is often observed that packaging products made from bioplastics do not exhibit comparable performance to those produced using common non-biodegradable ones. The presence of long chain branching improves the processing behavior under elongational flow and, then, the filmability of low viscosity polymers such as polyesters. In this work it has been demonstrated that the presence of long chain branching in a bio-co-polyester, induced by the use of pentaerythritol in the synthesis of poly(butylene adipate-co-butylene terephthalate), is able to dramatically change the rheological behavior of the linear chain polyester improving its filmability. The addition of branching lead to an increase of the elastic modulus and the tensile strength in branched polyester films if compared to the linear ones, while the elongation at break decreased. This is due to the answer of the branched polyester to the non-isothermal elongational flow that allows a better orientation of the macromolecules of the branched polyester. The film obtained with the branched polyester showed a

decrease in clarity and a slight increase in haze if compared to linear one due to differences in the morphology of the two samples.

**Keywords:** bio-co-polyesters, branching, non-isothermal elongational viscosity, filmability, biopolymers, packaging.

## 1. Introduction

Driven by recent European legislation and increasing awareness concerning environmental issue related to traditional fossil-based plastic materials, bio-based and biodegradable alternatives have gained considerable attention both of the academia and of industrial communities over the last years [1]. Many efforts have been made to produce greener plastic materials that can replace traditional ones equaling them in term of processability and performances of the final product, especially for plastic films [2–9]. Poly(butylene adipate-co-terephthalate) (PBAT) is one of the most promising biopolyester for the production of green flexible packaging among these biodegradable alternatives. PBAT is an aliphatic-aromatic co-polyester that can be easily biodegraded due to its aliphatic unit (adipic acid) and, at the same time, is characterized by good macroscopic properties imparted by the aromatic unit (terephthalic acid) [10]. Thanks to its flexibility, resilience, easy processability, nontoxicity and gas permeability, PBAT has been recognized as the most suitable alternative to low-density polyethylene (LDPE) for the production of films for packing industry [10–12]. Most films for packaging applications are fabricated using the film blowing process [13–17]. In this process, the polymer melt is extruded at a constant rate through a circular die, forming a continuous tube that is simultaneously pulled upwards by a system of rollers and expanded transversely by air blown into the tube, forming a bubble. The bubble is typically cooled from the outside by a stream of air from an outer ring placed above the die (air cooling ring) [18].

The film blowing process requires the use of polymeric materials with suitable rheological characteristics, both in shear and in elongational flow, and peculiar macroscopic properties, such as good deformability, tear resistance and sufficient rigidity [18]. Particularly important is the response of the melt in non-isothermal elongational flow, the flow involved during the formation of the bubble. The filmability in film blowing is defined by two important rheological properties:

- i. melt strength, i.e. the force at which the melt is broken during drawing;
- ii. breaking stretching ratio, i.e. the maximum drawability of the melt.

However, biopolymers are often challenging to process through film blowing due to their typical low melt strength and reduced elongation compared to standard polyolefins, resulting in unstable and wrinkled bubbles that tend to collapse during the fabricating process.

Usually, the addition of branches to the macromolecules gives rise to many changes in the rheological and mechanical properties and in the processability of linear polymers. The rheology of polymers, in fact, is strongly modified by the presence of long and short branching. Long chain branching induces a more pronounced non-Newtonian behavior and an increase of the Newtonian viscosity. Short branching, on the contrary, does not cause appreciable modification of the rheological behavior, but the non-Newtonian behavior is really less-pronounced [19]. The non-Newtonian behavior is a very important parameter in the processability. A pronounced non-Newtonian behavior in fact improves melt processability in extrusion and injection molding [20]. Long chain branching is not only responsible of non-Newtonian behavior but it also induces a remarkable increase of melt strength that, conversely, dramatically improves the filmability in film blowing. As regards the mechanical properties, the presence of long branches decreases the crystallinity of the polymers and, as a consequence, a reduction of the rigidity (decrease of the elastic modulus) and an increase of the deformability (increase of the elongation at break) [19–21]. The use of chain extenders in the reactive extrusion of polyesters has been extensively reported, in the scientific literature, as an effective strategy to obtain long-chain-branched (LCB) structures,

leading to an increase in melt strength and to improved processability [22–29]. Recently, the same strategy has been applied also to biodegradable polymers with excellent results. For example, Tiwary et al. [30] added chain extenders agents (peroxide initiators), in reactive extrusion, to thermoplastic biopolyesters, such as poly(lactide) (PLA) and various poly(hydroxyalkanoates) (PHAs), including poly(hydroxybutyrate) (PHB), aiming to improve the processability and the properties of the polymers. Similarly, Zhao et al. [31] and Tuna et al. [32] used a commercial multi-epoxide chain extender (Joncryl®) to improve PLA melt strength, obtaining strain-hardening behavior comparable with film grade LDPE. Moreover, Yousfi et al. [33] exploited glycerol as a chain extender to synthesize a poly(butylene succinate-co-terephthalate) (PBST) with an LCB structure in one-step by reactive extrusion. The biopolymer obtained by reactive extrusion revealed remarkable melt strength and appropriate rheological behaviors for the film blowing process. Lu et al. [34] obtained similar results using pentaerythritol as a branching agent for PBST. Zhao et al. [35] investigated the microstructural evolution of poly(butylene adipate-co-butylene terephthalate) (PBAT) modified by a chain extender during film blowing. The addition of the chain extender was found to significantly improve bubble stability and macroscopic performances of the biodegradable polymeric products.

Furthermore, Li et al. [36] prepared biodegradable blends of PLA/PBAT in the presence of a chain extender (Joncryl®). Rheological characterizations of the blends showed enhanced viscoelastic behavior, which proved to be beneficial for film production during the film blowing process.

In this work, the effect of the branching on the rheological and mechanical and optical properties and on the processability in film blowing of a biodegradable polyester (PBAT) is investigated. This biodegradable polyester was obtained by performing the polycondensation in the presence of pentaerythritol.

All the rheological tests, and in particular the tests in non-isothermal elongational viscosity, demonstrate that the presence of long chain branching allows obtaining good filmability – better than that shown by the same linear sample – and mechanical properties of the films better than

those shown by the linear one. The slight higher crystallinity of the branched sample gives rise to a less clear film.

## **2. Experimental**

### **2.1 Materials and Methods**

#### *2.1.1 Materials*

Two different biodegradable co-polyesters were used. Specifically, these biodegradable and compostable co-polyesters were obtained by polycondensation of a diol, 1,4-butanediol (butane-1,4-diol), and two diacids such as adipic acid and terephthalic acid (PBAT). The first sample, MB-L, is a linear polyester, while, the second sample, MB-LCB, is a branched polyester; the latter contains a small amount of branches. This last branched biodegradable polyester was obtained by performing the polycondensation in the presence of pentaerythritol.

#### *2.1.2 Synthesis and molecular characterization of the bioco-polyesters*

The process used for the synthesis of bioco-polyesters from diacids and diols consists in two main stages. In the first stage, commonly called esterification, the monomers and an esterification catalyst are loaded in the stirred reactor, with or without branching agent. In the second stage, called polymerization, the reaction leads to a molecular growth, supported by a polycondensation catalyst, until the desired molecular weight has been achieved. At the end of this second stage the polymer is discharged and pelletized.

In detail, concerning the synthesis of MB-L (linear PBAT), a steel reactor was charged with a mixture comprising 18.0 mol of adipic acid (hexanedioic acid), 16.0 mol of terephthalic acid (benzene-1,4-dicarboxylic acid), 47.5 mol of 1,4-butanediol (butane-1,4-diol) and 0.017 mol of glycerol (propane-1,2,3-triol). Subsequently, 5.7 g of monobutyl tin oxide (monobutyl stannane oxide) were added as a catalyst. The temperature of the mass was gradually raised to 230 °C in

approximately 60 min and maintained at 230-235 °C until more than 90% of the theoretical amount of water had been distilled off. The pressure was gradually reduced to less than 2 mbar over 60 minutes, and the melt temperature was then increased to 240 °C. The reaction was allowed to proceed for approximately 3.40 hours. On the other hand, for MB-LCB (branched PBAT), a steel reactor was charged with a mixture comprising 18.0 mol of adipic acid (hexanedioic acid), 16.0 mol terephthalic acid (benzene-1,4-dicarboxylic acid), 47.5 mol of 1,4-butanediol and 0.1 mol of pentaerythritol. Then 5.7 g of monobutyl tin oxide (monobutyl stannane oxide) were added as a catalyst. The temperature of the mass was gradually raised to 230 °C in approximately 60 min and kept at 230-235 °C until more than 90% of the theoretical amount of water had been distilled off. The pressure was gradually reduced to less than 2 mbar over a period of 60 minutes and the melt temperature was raised to 240 °C. The reaction was allowed to proceed for approximately 3.00 hours.

### *2.1.3 Processing and Preparation of the samples*

Compression-molded samples were obtained using a Carver laboratory press at 180 °C and 180 bar for 2 min. The sample were cut into specimens of appropriate geometry for further characterizations.

Film blowing was carried out in a single screw extruder (D = 19 mm, L/D = 25) Brabender (Duisburg, Germany) equipped with a film blowing head, with a temperature profile of 150–160–160 °C, die temperature 180 °C and screw speed set at 80 rpm. The draw ratio was about 5.5 and the blow-up ratio was about 8 for both polymers. The thickness of the films was about 60 µm.

## **2.2 Characterizations**

### *2.2.1 Molecular characterization*

Inherent viscosity was determined by using an Ubbelohde viscometer for solutions in  $\text{CHCl}_3$  at a concentration of 0.2 g/dl at 25°C.

Molecular weight distribution was measured by a Malvern GPC Omnisec instrument. The determination was conducted with the chromatographic system held at 40 °C using a set of two columns in series (particle diameters of 5  $\mu\text{m}$  and 3  $\mu\text{m}$  with mixed porosity), a refractive index detector, chloroform as eluent (flow rate 0.5 ml/min) and polystyrene as the reference standard).

### *2.2.2 Rheological characterization*

Rheological characterization was performed under shear and non-isothermal elongational flow.

Rheological properties under shear flow were analyzed by using a rotational rheometer (ARES- G2) equipped with a 25 mm parallel-plate geometry, 1mm gap, in Frequency Time Frequency mode (in the range 1-100 rad/s) and a CEAST (Italy) Rheologic 1000 capillary viscometer.

The same capillary viscometer equipped with a tensile drawing unit tool was used to determine the rheological behavior of the biopolymers in non-isothermal elongational flow. More in detail, the force at break applied to the molten filament, i.e., the melt strength (MS), as well as the drawing speed at breaking and the extrusion rate ratio, i.e., the breaking–stretching ratio (BSR), were evaluated. All the rheological tests were performed at 180 °C.

### *2.2.3 Mechanical characterization*

The mechanical behaviour of the samples was investigated by tensile tests, carried out with a laboratory dynamometer (Instron model 3365, UK) equipped with a 1 kN load cell. The tests were performed on rectangular shaped specimens (10 × 60 mm). The measurements were performed by using a double crosshead speed: 1 mm min<sup>-1</sup> for 2 min and 50 mm min<sup>-1</sup> until fracture occurred. The grip distance was 30 mm whereas the sample thickness was measured before each test. Eight

specimens were tested for each sample and the outcomes of elastic modulus (E), tensile strength (TS), and elongation at break (EB), have been reported as average values.

#### *2.2.4 Optical characterization*

Optical properties were measured according to ASTM D1003 by using a Haze Meter BYK-Gardner Haze-Gard Plus 4725.

#### *2.2.5 Thermal Properties*

The calorimetric analyses were carried out with a Perkin-Elmer DSC Pyris Diamond under the conditions given below:

- a. 60 s isotherm at -20°C
- b. 1st scan from -20°C to 200°C at 20°C/min
- c. 60 s isotherm at 200°C
- d. 2nd scan from 200°C to -20°C at 10°C/min
- e. 60 s isotherm at -20°C
- f. 3rd scan -20°C to 200°C at 20°C/min

Melting enthalpy ( $\Delta H_m$ ) is measured as the area of the endothermic peak found in the third scan using the Pyris<sup>TM</sup> software from Perkin Elmer, specially designed to process DSC diagrams. The melting point ( $T_m$ ) is the maximum of the endothermic peak found in the third scan.

### **3. Results and discussion**

Sample code and main molecular characteristics of the above materials are reported in Table 1.



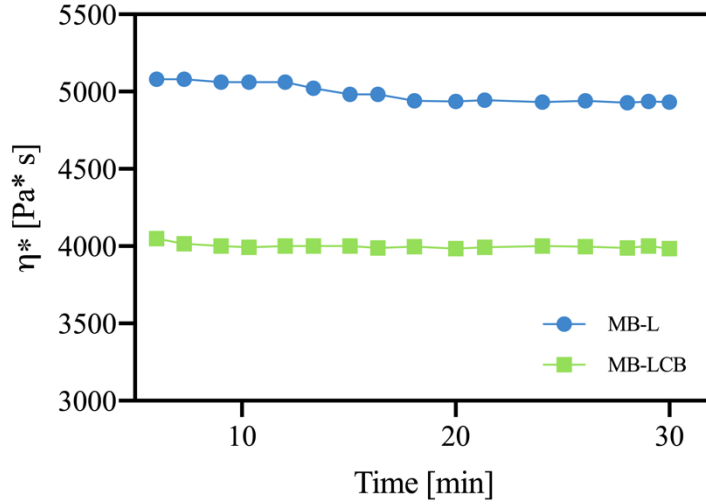
**Table 1.** Sample code, and the main molecular characteristics of the two co-polyesters

Sample Code	Type of polyester	Inherent viscosity [g/l]	Mn [g/mol]	Mw [g/mol]
MB-L	linear PBAT	1.18	86273	144830
MB-LCB	branched PBAT	1.00	53416	152170

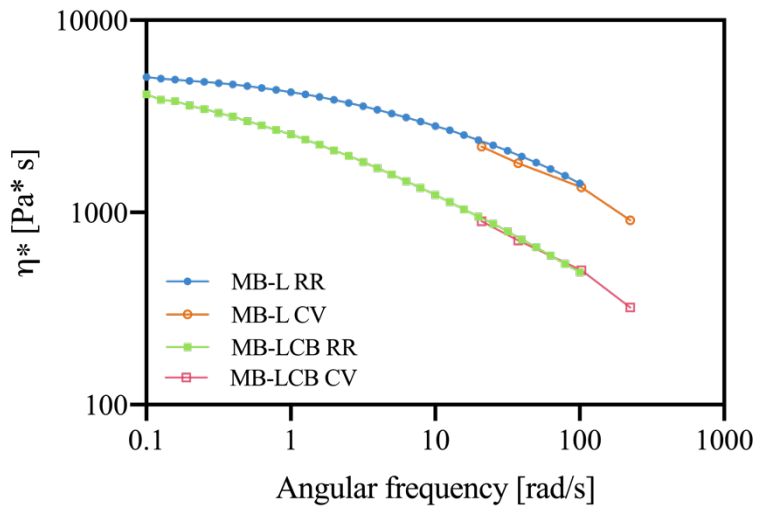
The average weight molecular weight is almost the same for both samples, while the average number molecular weight was different as the Mn value is lower for the branched sample. The polydispersity index is about 1.7 for the linear sample and about 2.8 for the branched one. The inherent viscosity of the branched polymer is lower than that of the linear polymer because, being very similar the length of the macromolecules, their dimensions are lower because of the presence of the branches. The lower inherent viscosity is a direct test of the presence of long chain branches in the macromolecules. Indeed, the viscosity depends on the dimensions of the macromolecules and, being the same the molecular weight, the dimensions of the macromolecules decrease only in presence of long chain branching.

The viscosity-time curves of both polymers, shown in Figure 1, were carried out with the rotational rheometer in time-sweep mode, at the temperature of 180 °C, 10% of strain and at a frequency of 1 rad/s. Both bioco-polyesters are characterized by excellent thermal stability, and indeed, the complex viscosity remains almost constant over the investigated time of about 30 min. The branched sample shows a slightly better thermal stability.

Figure 2 reports the flow curves of the two samples, measured using both rotational rheometer (RR) and capillary viscometer (CV). The complex viscosity measured with the rotational rheometer as a function of the frequency superimposes to the viscosity curve measured as a function of the shear rate in the capillary viscometer. This indicates that the two polyesters follow the Cox-Merz rule [38,39].



**Figure 1.** Complex viscosity as a function of the time for MB-L and MB-LCB samples.

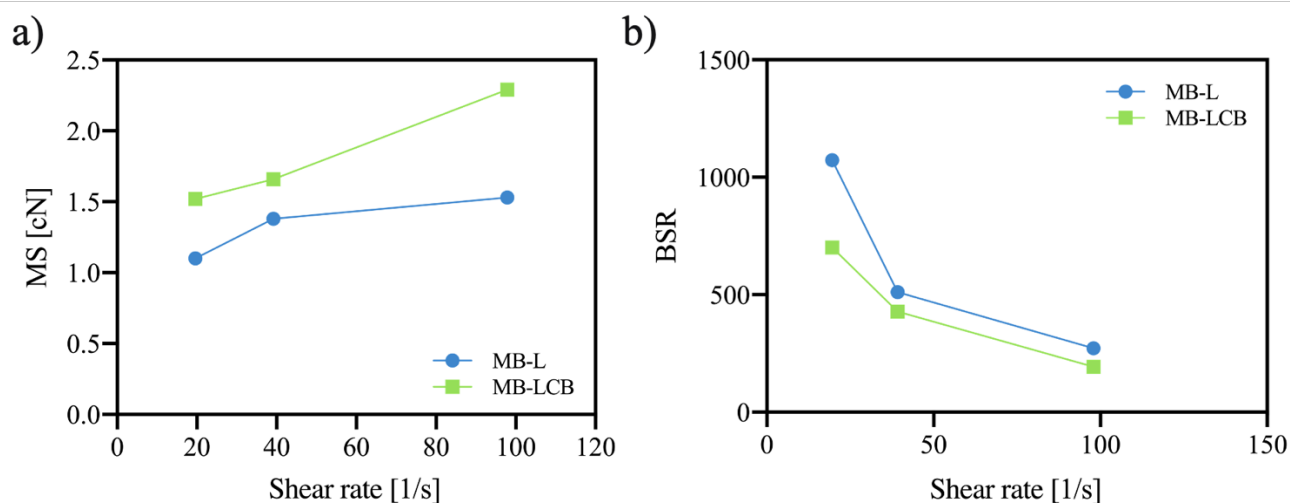


**Figure 2.** Flow curves of MB-L and MB-LCB measured using both rotational rheometer (RR) and capillary viscometer (CV).

In Figure 2 it is also possible to notice that the MB-L sample seems to show, at low frequency values, a Newtonian plateau, while, the branched sample shows a curve still increasing. This means that for MB-LCB the Newtonian plateau occurs at lower frequency and with a higher viscosity. Moreover, the flow curve of the branched polymer shows a more pronounced non-Newtonian behavior. These last two features are typical of branched polymers if compared to the linear ones,

being very similar the weight average molecular weight values. In particular, this behavior can be observed in the presence of long chain branching as short branches do not impart this rheological behavior to linear polymers [40].

Figure 3a and 3b reports MS and BSR values as a function of the shear rate in the capillary viscometer of the two bioco-polyesters respectively. The presence of chain branching resulted in an increase in MS values, while BSR show the opposite behavior.



**Figure 3.** MS (a) and BSR (b) values as a function of the shear rate in the capillary.

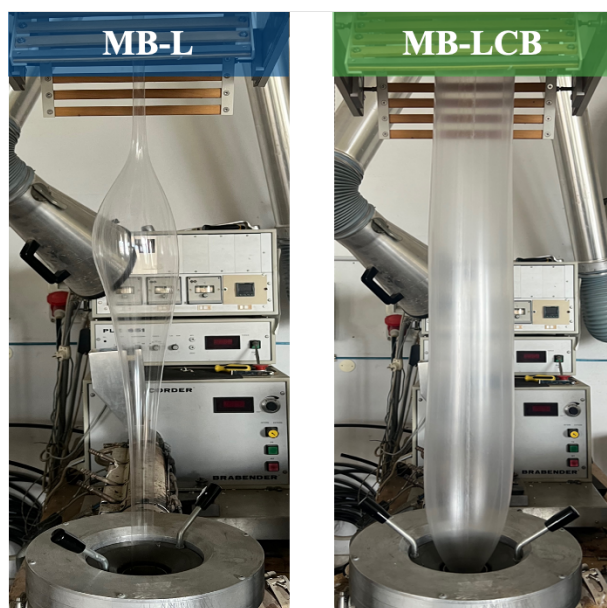
This behavior was expected since the presence of long chain branches increases the elongational viscosity and decreases the deformability of the melt [37–39].

The tensile properties of the two polymers are reported in Table 2. The compression molded samples do not show break in the operational range of the instrument. Both elastic modulus and tensile strength of the two polymers however are very similar.

**Table 2.** Elastic modulus, E, tensile strength, TS, elongation at break, EB of the investigated polymers, 1mm thick samples.

Sample	E (MPa)	TS (MPa)	EB (%)
MB-L	$81 \pm 1.3$	>15	>1500
MB-LCB	$79 \pm 0.9$	>17	>1500

The photos reported in Figure 4 refer to the film blowing operation with the two polymers. It is well evident that the branched polymer forms a bubble certainly more uniform and stable than that formed by the linear polymer. As well known the higher MS of the branched polymer is likely responsible for this better filmability [44,45].



**Figure 4.** Film blowing operation with MB-L and with MB-LCB.

In Table 3 the tensile strength in machine direction of the films of the two polymers are reported.

**Table 3.** Elastic modulus, E, tensile strength, TS, elongation at break, EB of the obtained films in machine direction.

<b>Sample</b>	<b>E (MPa)</b>	<b>TS (MPa)</b>	<b>EB (%)</b>
MB-L	91 ± 1.4	33 ± 0.3	689 ± 7.4
MB-LCB	150 ± 2.8	35 ± 0.2	295 ± 5.3

It seems quite unexpected that the values of E and TS are higher and the elongation at break is lower for the branched polymer. It is reasonable, however, to interpret these results considering the best filmability of the MB-LCB sample. This means that the macromolecules are better and more uniformly oriented in the machine direction giving rise to a more rigid and less deformable film in this direction.

The optical properties, clarity and haze, of the two films are reported in Table 4.

**Table 4.** Clarity and haze of the films of the two samples.

<b>Sample</b>	<b>Clarity [%]</b>	<b>Haze [%]</b>
MB-L	97	13
MB-LCB	75	23

In order to obtain information about the optical properties of the films, clarity and haze were measured. These two properties describe the transparency and scattering of light of the material respectively [46,47]. Clarity and haze are significantly different for the two samples. Indeed, as also evident in the photos of the film blowing operation, the MB-L film is certainly much clearer than the MB-LCB film. In particular, the clarity is larger and the haze much lower. A possible interpretation of this behavior can be correlated with the different morphology of the two samples. In Table 5 the crystallization and melting temperatures and the melting enthalpies of the bioco-polyesters are reported. DSC curves of the two samples are reported in Figure S1.

**Table 5.** Crystallization and melting temperatures and melting enthalpies of the two samples.

Sample	T <sub>c</sub> [°C]	T <sub>m</sub> [°C]	ΔH <sub>m</sub> [J/g]
MB-L	55	110.1	11.45
MB-LCB	75	118.7	14.42

Both samples show low amount of crystalline phase, but, the branched sample shows a slightly higher value of crystallinity. This is quite unexpected as, usually, the presence of long chain branching in polyesters gives rise to a lower amount of crystallinity. However, the effect of the branching on the crystallinity behaviors of the biodegradable polyesters seems to be less clear [21]. The ordered branches could be responsible for this slightly more crystallinity. This morphology is certainly responsible for the optical properties. Indeed, increasing the crystallinity, the clarity decreases and the haze increases.

## Conclusions

In this work, the effect of the branching on the rheological, mechanical, optical properties and on the processability in film blowing of a biodegradable polyester (PBAT) was investigated. By rheological characterization it has been demonstrated that the use of pentaerythritol in the synthesis a of poly(butylene adipate-co-butylene terephthalate) allowed to obtain long-chain-branched (LCB) structures. MB-LCB sample allows an optimum film blowing processing compared to its linear counterpart (MB-L sample), being suitable for use in the manufacture of extensible film for industrial and food packaging. The mechanical properties of the films are better for the long branched polymer because of the better filmability that allows a better orientation of the macromolecules. Finally, the optical properties of the film obtained with the branched sample are less clear because of the slightly higher crystallinity degree of this polyester.

In conclusion, the incorporation of branching structures has proven to significantly enhance the macroscopic properties of the film, thereby making it highly promising for packaging applications.

Moreover, the use of biodegradable polymer in the production of this film offers notable environmental advantages. The ability of the film to undergo biodegradation ensures a reduced environmental impact compared to traditional plastic counterparts, as it contributes to the mitigation of plastic waste accumulation. By adopting such biodegradable materials in packaging applications, we can take a significant step towards sustainable and eco-friendly practices.

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**Data Availability Statement:** The data presented in this study are available on request from the corresponding authors.

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