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FINAL PROJECT

Effect of different compatibilizers on the final properties of the PLA/PBSA biopolymers-based blend prepared by reactive extrusion

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Abstract

It is well known that the research for biopolymers-based materials is crucial in these times where the environmental issues resulting from the plastic industry keep increasing. Poly Lactic Acid (PLA), a biodegradable and bio-based polymer with comparable strength and stiffness to petroleum-based polymers, holds promise as a bio-based material. However, PLA-based materials suffer from limitations, particularly poor toughness characterized by low ductility and impact resistance.

To address this challenge, the blending of PLA with PBSA, a polymer known for its high ductility and impact resistance, is explored. However, the resulting blend exhibits immiscibility and low compatibility, leading to poor mechanical properties. Reactive compatibilization is employed as an effective approach to tackle this problem. This process involves mixing the polymers in an extruder while incorporating a reactive agent to improve interactions between PLA and PBSA.

In this study, four different compatibilization techniques are evaluated. The first one involves direct compatibilization by simultaneously feeding the polymers with Dicumyl peroxide (DCP), as the reactive agent, into the extruder. The second one follows the same method, but Maleic anhydride (MA) is used as the reactive agent, and the reaction is initiated by DCP. The last two approaches involve preparing maleated polyesters using MA initiated by DCP in a preliminary extrusion process. In one approach, the resulting PLA-g-MA is then utilized as a compatibilizer in the blend during a second extrusion process, replacing a portion of PLA in the blend. In the other approach to compatibilize, PBSA is replaced by PBSA-g-MA in the blend. The effect of the reactive agent's proportion is also investigated in all the attempts.

Injection molding is used to produce specimens for testing. Comprehensive characterization, including thermal, mechanical, and microstructure analysis, is conducted to evaluate the properties of the blends.

1. Introduction

Biopolymers, derived from renewable resources and/or possessing biodegradability offer an alternative to non-biodegradable petroleum-based polymers and bring numerous environmental benefits. Notably, they have the potential to lower greenhouse gas emissions. Bio-based polymers are manufactured from biomass sources such as starch, cellulose, vegetable oils, or other bio-based substances, promoting sustainability and decreasing reliance on fossil fuels. Also, the ability to naturally decompose in the environment gives biodegradable biopolymers the advantage of reducing waste buildup and addressing issues associated with plastic pollution.

In this context, Poly Lactic Acid (PLA), a biodegradable and bio-based polymer has gained significant attention. It is derived from lactic acid monomers through bacterial fermentation of renewable resources like corn starch or sugars. With comparable strength and stiffness to petroleum-based polymers, PLA is considered a promising candidate among bio-based materials. As a result, it demonstrates suitability across various industrial sectors, including automotive, electronics, medical devices, from commodity polymers to engineering polymers. Researchers and industries are actively exploring PLA as an alternative to petroleum-based plastics, particularly in the packaging industry, which accounted for 44 % of global plastic production in 2021. However, PLA-based materials face limitations, such as brittleness, low impact resistance, and low glass transition temperature (T_g). Additionally, the crystallinity of PLA significantly affects its final properties, hindering widespread utilization.

To address these challenges associated with PLA, various strategies can be employed. One of them consists of blending PLA with other components. Blending process allows for the combination of the advantageous characteristics of each component, resulting in a material with enhanced properties. Effectively, to overcome the inherent toughness limitations of PLA, blends with other polymers are commonly employed. These blends combine PLA with polyesters or natural rubber, known for their favorable toughness properties. Reactive extrusion, a technique that utilizes reactive agents during the extrusion process, enhances compatibility among the blend components. This method improves dispersion, dispersed phase size, and interfacial bonding which results in reduced phase

separation. As a result, the blend components are effectively compatibilized, leading to an overall improvement in the final material's properties.

In this study, reactive extrusion will be employed to produce blends of PLA and Poly (butylene succinate-co-adipate) (PBSA). This last one is a biodegradable aliphatic polyester that can be produced from renewable resources. It shows high elongation at break and impact resistance and when mixed in low proportion with a brittle polymer can enhance its toughness. The process of reactive extrusion aims to enhance compatibility between the components and improve the adhesion between the polymeric matrix and the dispersed phase. Various reactive agents will be employed during reactive extrusion to facilitate these improvements. Comprehensive characterization, including thermal, mechanical, and microstructure analysis, will be conducted to evaluate the resulting blends.

In the present work, we will first outline the objectives of the study and subsequently provide a comprehensive background on the reactive extrusion of PLA-based blends. The experimental characteristics will be detailed, followed by the presentation and discussion of the results. Finally, conclusions will be drawn based on the findings.

2. Objectives

The objective of this study is to improve the microstructure and thermal and mechanical properties of a PLA-based materials, specifically its toughness.

With this aim, PLA will be blended with PBSA, a polymer which has a high toughness. The mixture will result in an immiscible blend consisting of a minority phase (PBSA) dispersed in a matrix (PLA). To obtain a blend with optimum properties, it is necessary to optimize the blend morphology. This involves reducing the particle size of the dispersed phase, improving its dispersion within the matrix, and stabilizing the blend morphology. In other words, a good interfacial adhesion with reduced surface tension is desired. To achieve this, reactive extrusion will be employed to prepare blends with improved compatibility between the two phases using a twin-screw extruder.

Once the optimal uncompatibilized PLA/PBSA weight ratio is established, the selected blend composition will be modified using four different compatibilization techniques. These techniques will involve blending PLA and PBSA with different reactive agents. The effect of the reactive agents' proportion will be tested as well.

In a first attempt, a direct compatibilization by feeding the polymers and reactive agents all together in the extruder will be studied. Two different reactive agents were selected with this method, that is a peroxide, Dicumyl peroxide (DCP) and Maleic anhydride (MA).

Secondly, maleated polyesters using Maleic Anhydride will be prepared and the resulting product is used in a second step as a compatibilizer. In both steps, the mixing is done in the extruder. We will denote that method as indirect compatibilization and both maleated PLA and maleated PBSA will be studied independently as reactive compatibilizers.

3. State of art

3.1. Biopolymers

3.1.1. General overview

Biopolymers encompass a category of polymers that are either derived from renewable resources, biodegradable, or both. [1] The growing need for the development of biopolymers arises from the environmental concerns associated with the production and consumption of conventional plastics. Addressing global warming, reducing CO_2 emissions, and mitigating the depletion of finite fossil resources serve as primary motivations for researchers and industries to explore biopolymers as a viable solution. According to a literature review conducted by Spierling *et al*. [2], the global warming potential (GWP) of biobased plastics was found to be within the range of -0.3 to 11.9 kg CO_2-eq/kg. In comparison, Plastics Europe [3] reported a GWP range of 1.6 to 6.4 kg CO_2-eq/kg for fossil-based plastics. Whether in the case of bio-sourced or biodegradable polymers, there is an inherent improvement in at least one aspect of their life cycle: the reduction of toxic or harmful substances used in their production or their degradation in the environment.

The so-called bio-based polymers are the ones which are obtained from renewable resources. Bio-based polymers can be categorized into three main groups based on their origin and production methods (Figure 1): those directly obtained from biomass, called natural biopolymers, those derived from bio-based monomers through synthesis, and those produced by microorganisms. [4]
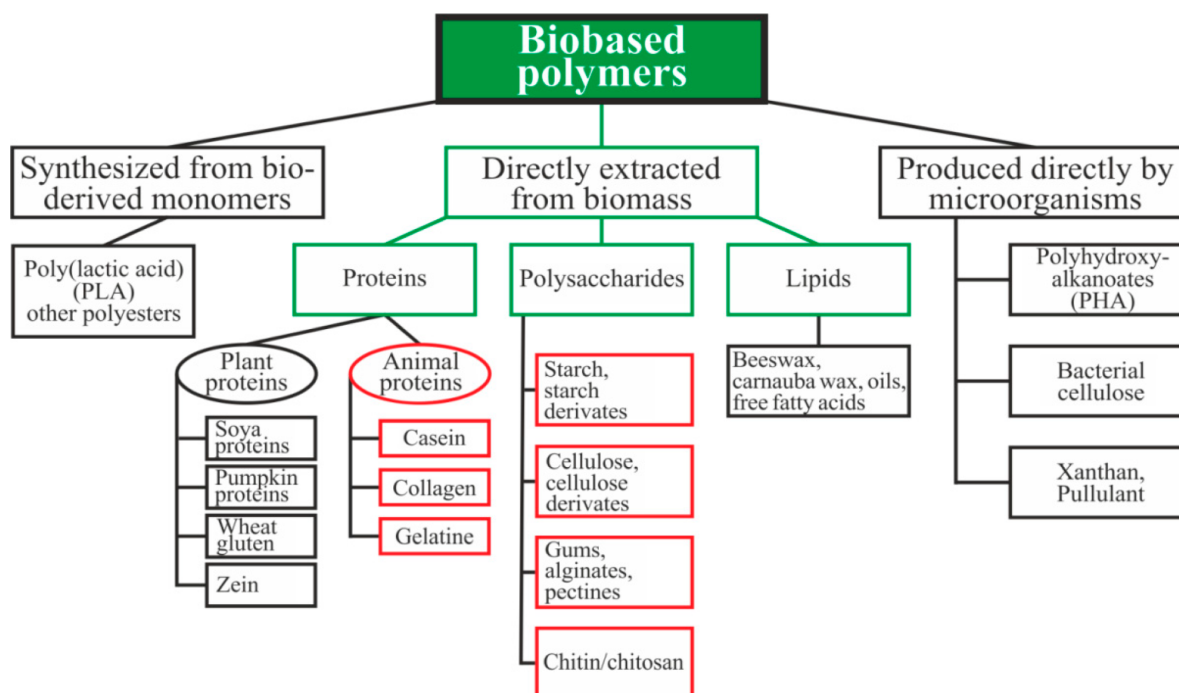
Figure 1: Classification of bio-based polymers

The natural bio-based polymers are the ones occurring naturally in nature such as starch, cellulose, chitin and other polysaccharides, and lipids and proteins found in plants and animals. They are recovered by extraction and then chemical modifications allow to obtain materials with improved properties.

Starch, as an example, is a plentiful carbohydrate found in plants, consisting of glucose unit polymers known as amylose and amylopectin. It can be extracted from sources like wheat, rice, corn, and potato through a process involving grinding and purification. Starch possesses unique semi-crystalline granules with the ability to form gels and thicken solutions when heated with water, making it valuable in food and packaging applications. [5]

Cellulose is another natural polymer found in plant walls and is the most abundant organic compound on Earth. It is widely used as a biopolymer. One of its key advantages is that it can be sourced from agricultural waste, reducing competition with food sources. [6]

Additionally, chitin is a bio-based polysaccharide composed of N-acetylglucosamine units, derived from glucose, and is commonly found in fungi cell walls and arthropod exoskeletons. It is being investigated for various applications, including its use as a food packaging coating, offering microbial and antioxidant protection. [7]

Another type of bio-based polymers are the ones produced directly by microorganisms. The process begins by providing the microorganisms with a suitable growth medium that contains the necessary nutrients and conditions for their growth and polymer production. The microorganisms consume the nutrients and, as part of their metabolic process, synthesize and store the polymers within their cells. Many advantages make them suitable as bio-based materials: microorganisms can be genetically engineered to produce polymers with specific properties and functionalities, the yield and efficiency can be tailored, and finally microorganisms used for polymer production can often utilize a wide range of feedstocks, including waste materials or by-products from various industries. As an example, Polyhydroxyalkanoates (PHAs) are extensively studied bio-based polymers produced through microbial fermentation. These polyesters are characterized by their hydrophobic nature, thermal stability, rigid crystalline structure, and remarkable tensile strength. Moreover, PHAs possess significant elasticity. The properties of PHAs can be modulated based on the number of carbon monomers present in their side chain constituents, resulting in a range of materials with diverse characteristics.

Finally, the last class of bio-based materials are the ones synthesized from bio-based monomers. These monomers are derived from the biomass and subsequently polymerized. The presence of greater functionality groups in bio-based polymers presents an exciting opportunity to obtain bio-based monomers with specific functionalities. [8] The subsequent polymerization and modification processes enable the customization of the final polymer properties to meet specific requirements. Nevertheless, it is crucial to emphasize that the polymerization routes must prioritize sustainability to the greatest extent. [9] Bio-based polyesters, particularly Poly lactic acid (PLA), constitute a significant portion of polymers derived from renewable monomers. However, the development of other bio-polyesters from renewable monomers is still under research, as these monomers can also be sourced from fossil-based resources, which creates economic competition. For instance, Polybutylene succinate (PBS), which is produced through the direct esterification of succinic acid (SA) with 1,4-butanediol (BDO), relies on fossil-based monomers and entails high energy costs, resulting in elevated greenhouse gas emissions. However, bio-SA acid and bio-BDO can be derived from renewable resources. The main challenge lies in the economic feasibility, as the

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bio-refinery processes present significant production costs. If these economic barriers are overcome, bio-PBS would offer a substantial impact in reducing greenhouse gas emissions. As PBS is already a biodegradable polymer, the combination of bio-based resources and biodegradability in bio-PBS could further contribute to environmental sustainability. [10]

3.1.2. PLA

Poly lactic acid (PLA) is a linear thermoplastic bio-based polyester firstly discovered by Carothers (at DuPont) in 1932. Herein, this polymer is classified as a bio-based polymer obtained from renewable lactic acid monomer and is biodegradable. [11, 12] As presented before, these advantages compete with petroleum-based polymers for reducing environmental impacts caused by world plastic production.

PLA-based materials offer desirable mechanical properties compared to other bio-based materials. PLA is known for its attractive appearance, high mechanical strength, low toxicity, and excellent barrier properties. Figure 2 presents a comparison of PLA's tensile modulus, impact strength, flexural modulus, and elongation at break with conventional polymers. PLA exhibits a tensile modulus of 556 kpsi ($\sim$ 3833 MPa), largely higher to High Density Polyethylene (HDPE) and Polypropylene (PP), two widely produced fossil-based plastics. However, PLA has lower toughness, as indicated by its significantly lower Notched Izod Impact resistance and reduced elongation at break compared to HDPE and PP. On the other hand, PLA and Polystyrene (PS) demonstrate similar mechanical properties.
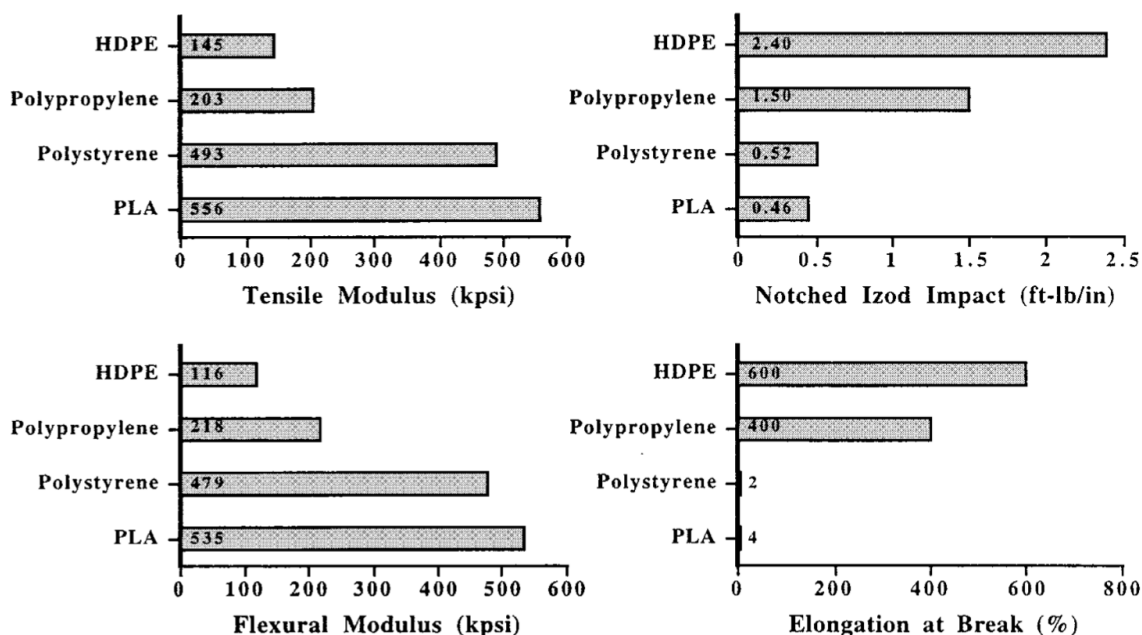
Figure 2: Mechanical properties of PLA and petroleum-based polymers [12]

Additionally, PLA experiences thermal instability, leading to a decline in molecular weight and the subsequent impact on the mechanical properties of the final material. The degradation mechanism primarily involves main chain scission. Research conducted by Taubner *et al.* [13] has highlighted that extrusion parameters, such as processing temperature, residence time, rotation speed, and moisture content, greatly influence PLA degradation. The resulting reduction in molecular contributes to decreased strength and strain at the break, attributed to shorter-length chains with fewer chain entanglements required to maintain molecular integrity. Södergård *et al.* [14] demonstrated that the tensile modulus of PLA undergoes an increase of factor two when the molecular weight is elevated from 50 to 100 kDa.

PLA can exist in two different states in its solid form: amorphous and semicrystalline, which are determined by its stereochemistry and thermal history. Semicrystalline PLA has regular repeating units that allow the chains to fold into dense regions called crystallites. These crystallites act as crosslinks, providing the polymer with higher tensile strength and stiffness compared to its amorphous counterpart. In amorphous form, PLA has a glass transition temperature (T_g) ranging between 45 and 60 °C which makes it brittle at room temperature. Moreover, the T_g is crucial for determining the upper temperature use. For semicrystalline PLAs, both T_g and the melting temperature (T_m) ranging from 130 to 230 °C play significant roles in defining suitable applications temperatures. The overall optical

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composition, thermal history, and molecular weight (M_w) strongly influence the T_g and T_m transitions of PLA. Additionally, these thermal transition temperatures are crucial parameters in determining the processing conditions of a material.

Regarding barrier properties, PLA shows CO_2 and O_2 permeability coefficients similar to those of Polyethylene Terephthalate (PET). [15]

PLA offers a wide array of functions and finds applications across diverse industries. In the packaging industry, PLA's barrier properties against oxygen and carbon dioxide make it ideal for food packaging. [16] The textile industry benefits from PLA fibers. [17] Biomedical applications profit from PLA's biocompatibility, low toxicity, and biodegradability. Surgical sutures, drug delivery systems, tissue engineering scaffolds, and biodegradable implants all are good examples of PLA applications in that domain. [18] Agricultural applications employ PLA-based mulch films to enhance crop yields through weed control and soil moisture conservation. Biodegradability eliminates the need for film removal, reducing plastic waste in fields. [19] In 3D printing, PLA's ease of processing, good printability, and wide availability make it a popular choice for rapid prototyping. [20]

The unique combination of PLA's physical and mechanical properties, coupled with its biodegradability and low environmental cost, positions it as a versatile and sustainable alternative in numerous industries.

However, despite the favorable properties demonstrated by PLA, certain shortcomings still need to be addressed for its applications. These limitations include its low ductility and poor impact resistance, being the most limiting ones, as well as its limited heat resistance, slow crystallization rate, and high sensitivity to moisture.

3.1.3. PBSA

Poly (butylene succinate-co-adipate) (PBSA) is an aliphatic copolyester produced from the co-condensation of succinic acid, and adipic acid with 1,4-butanediol. Usually, the monomers are fossil-based, even though the equivalent renewable ones are available from renewable resources. The higher cost for the production of bio-based monomers renders the market poor of bio-PBSA. Yet, *Mitsubishi Chemical*, producers of bio-based PBS and PBSA,

show a biobased content of 54 wt.% in the polymers while using bio-based succinic acid. [21] Consequently, the obtained product is considered as a partial bio-based polymer.

PBSA is a biodegradable polymer, with higher degradability in comparison with PBS, caused by its lower crystallinity. Trademarked BIONOLLE polyesters such as PBS, PBSA and polyethylene succinate were compared regarding their behavior to degrade in different environments. Fujimaki *et al.* [22] found that bottles of PBSA showed the fastest degradation in hot compost, moist soil and in the sea.

PBSA is known for its toughness and exhibits a significant elongation at break, higher than 400 % and an important impact resistance under notched impact test (higher than 25 kJ/m^2). The high elongation and good impact strength are attributed to chain mobility at room temperature, facilitated by PBSA's low glass transition temperature (T_g) of -40 °C. Consequently, the material is flexible at room temperature. However, the strength of PBSA based materials remains low with a tensile strength lower to 19 MPa and an Elastic Modulus lower to 200 MPa. [23]

Biodegradable PBSA is an attractive material which finds applications in the packaging industry. It is employed as bag liners, mulch film, and agricultural films. [24] However, the relatively higher cost of PBSA compared to petroleum-derived plastics and other bioplastics like poly-lactic acid (PLA) slows its adoption for short-term applications. For these reasons, PBSA is blended with other materials to reduce its cost and/or to improve its mechanical strength. [25]

3.2. Reactive extrusion of polymer blends

3.2.1. Polymer blends

Homopolymers frequently lack all the desired characteristics, and the development and synthesis of an entirely new polymer can be a time-consuming and expensive process.

With this in mind, blending polymers answers the growing need for polymers that exhibit improved performance at a lower cost. A polymer blend corresponds to a mixture of at least two macromolecular substances, polymers or copolymers, in which the minor

ingredient content is above 2 wt.%. Additionally, these blended polymers must maintain processability comparable to or even enhanced compared to single-phase polymers. [26]

Therefore, on one hand, blending different components allows the production of materials with a full set of new properties or with enhanced specific properties. For instance, this involves toughening brittle polymers to eliminate the need for additives, blending polymers with higher rigidity to enhance mechanical strength, or incorporating semi-crystalline polymers into amorphous ones to adjust thermal resistance. Like this, toughened Polypropylene (PP) has been obtained by preparing PP/natural rubber blends. The elastomeric dispersed phase acts as a stress contractor upon stress, absorbing the energy and reducing the brittleness of PP. [27]

On the other end, the blending may be intended to decrease the cost of an already performant polymer. In particular, incorporating less expensive polymers into engineering resins helps lower the overall cost and enables the wider utilization of these materials with exceptional properties. Herein, starch has been used to reduce the cost of some engineering polymers. [28]

In addition to all of that, blending polymers not only facilitates the recycling of industrial and/or municipal plastics waste but also enables the restoration of high molecular weights for partially degraded polymers. As a result, it becomes feasible to produce high-performance polymers utilizing the recycled plastics waste. Therefore, reactive extrusion demonstrates an intriguing potential as a method for recycling plastic waste derived from post-consumer sources.

Blends are prepared by various methods which are the melt blending, the solution blending, fine powder mixing, and by preparation of interpenetrating polymer networks (IPN). [29]

Melt mixing, the most commonly employed method, is a mechanical blending. In this process, the blend components are mixed together in a molten state using extruders or batch mixers. As for solution blending, it involves dissolving the blend components in a co-solvent, followed by film casting, freeze drying, or spray drying techniques. This method offers advantages such as rapid mixing without significant energy consumption and the ability to prevent unfavorable chemical reactions. Latex blending is mainly used for blending elastomers and corresponds to the mixing of different latex. Fine powder mixing, as the name suggests, involves blending powdered polymers. An IPN is formed by blending two or more polymers in a network structure, with the unique characteristic that at least one of the

polymers is synthesized and/or cross-linked immediately when mixed with the other component.

The polymer blends' performance depends on the properties of the ingredients, their proportion, and the morphology of the overall blend. The majority of polymeric blends exhibit immiscibility (see Figure 3), resulting in the formation of distinct phases when the components are mixed. The compatibility between these phases plays a crucial role in achieving enhanced properties in the blend. In particular, the impact strength, maximum deformation at break, and the yield strength are highly dependent on the blend morphology. Compatibility is defined by a reduced surface tension, characterized by an effective dispersion and size of the minor phase within the major phase of the system and by a strong interfacial adhesion between phases in the solid state. Additionally, morphology of the blend must be stable. That is, the blend structure developed during the compounding step, which is a dynamic process, should remain with time upon removal of stress.
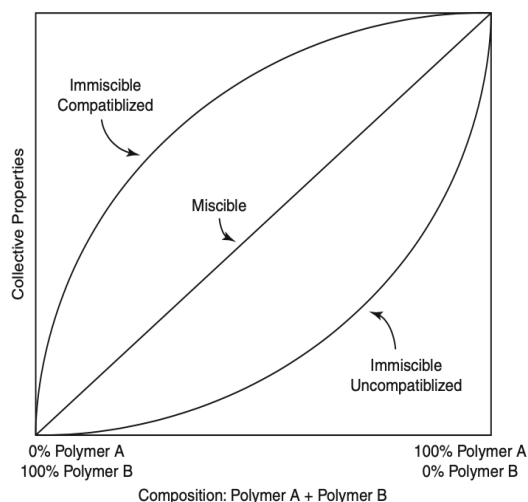

Figure 3: Principle of miscibility and compatibility in polymer blends

While a few immiscible polymer blends without compatibilization exist in the commercial market, the majority of commercially available immiscible polymer blends have undergone a compatibilization process.

Compatibilization is carried out by the addition of compatibilizers and/or by the reactive processing or blending.

3.2.2. Reactive compatibilization

Reactive compatibilization involves the formation of a copolymer through the establishment of covalent or ionic bonds between the constituents of the distinct phases within a blend, during an extrusion process. This is carried out in an extrusion process. The formation of bonds takes place at the interface between the molten phases, leading to a heterogeneous reaction. [30]

Reactive extrusion (REX) process employs single or twin-screw extruders, traditionally used to melt, homogenize, and pump polymers through certain dies, as continuous flow reactors to effectively blend polymers. In a typical REX process, the reactants are introduced into the extruder, typically through a feed hopper. The reactive mixture is then conveyed through the extruder, where the reaction progresses to the desired extent. Once achieved, the molten polymeric product is pumped through a die, followed by solidification, and pelletization. As a result, production and processing can be harmoniously integrated into a single step, which results in a cost-effective method.

The use of extruders as reactors has gained interest in the polymerization and modification of polymers as it is free from solvent leading to an environmentally friendly method. Practically speaking, it allows the tailoring of the energy and mixing conditions of the materials resulting in efficient mass and heat transfer. Furthermore, the use of extruders enables the process of viscous polymers.

In reactive compatibilization, a compatibilizing copolymer is formed at the interface between the immiscible polymers. This formation occurs precisely where it is needed to stabilize the blend morphology.

Compatibilization techniques include graft copolymer or block copolymer formation, covalently cross-linked copolymer formation or ionic interaction to form copolymer at the interface.

In most cases, an additional reactive species may be introduced to promote copolymer formation through various mechanisms. In many cases, the reactive species added has the ability to react with each polymer independently. These reactive agents are added in low proportions compared to the other components.

Alternatively, catalysts can be used to support the copolymer formation.

Huang *et al.* [31] demonstrated the effective compatibilization of polyamide-6,6 (PA66) and poly(butylene terephthalate) (PBT) using an epoxy resin. The low molecular weight epoxy resin's epoxide terminal groups can react with the carboxyl (PBT) and amine (PA) end groups in the melt state, resulting in an epoxy-co-PBT-co-PA6 copolymer that places itself at the interface. These mixed copolymers are believed to be the major contributor in improving the compatibility of incompatible PA66/PBT blends. Additionally, they used the processability versatility available in reactive extrusion process to monitor the die swelling effect and melt fracture of the extrudate. This study shows the advantages of using reactive compatibilization. That is enhancing compatibility and monitoring the process, at the same time, allowing to obtain a material with improved properties and good final shape.

Singh *et al.* [32] investigated the role of a catalyst for compatibilizing Polycarbonate (PC) / Poly methyl methacrylate (PMMA) blends by a reactive extrusion process. Reaction between the carbonate and ester groups of PC and PMMA supported by the catalyst led to PC-g-PMMA graft copolymer formation. The obtained blend shows a significant improvement in microstructure and mechanical properties confirming the enhancement of compatibility by the graft copolymer.

3.3. Reactive extrusion of biopolymers-based blends

3.3.1. General overview

As stated before, polymer blends offer the possibility to produce cost-reduced materials with innovative properties from already existing polymers. On the other hand, the growing polymer production concurrently generating environmental issues has pushed the research to explore more into biopolymers. However, biopolymers are newly investigated, and their applications remain limited due to unenhanced properties.

With this in mind, blending of biopolymers appears to be a good solution for the production of eco-friendly polymers with desirable properties.

As such example, Gutiérrez *et al.* [33] explored the production of films using a blend of plantain flour and Polycaprolactone (PCL). Starch-rich flours are favored as raw materials for biodegradable film production due to their cost-effectiveness and superior performance compared to pure starch. However, these materials are hydrophilic and prone to water sensitivity. To address this, blends of plantain flour and PCL are prepared via reactive extrusion, and films are formed through compression molding. PCL, is a biodegradable and semi-crystalline thermoplastic polymer. Also, it possesses good water resistance and hydrophobic properties. The blend was effectively compatibilized by the use of a catalyst to induce cross-linking between the constituents. Microstructure analysis revealed that the blend exhibited a good interfacial adhesion between plantain flour and PCL leading to films with improved properties. These findings demonstrate the potential for obtaining eco-friendly films with enhanced properties under reactive extrusion conditions.

Feijoo *et al.* [34] investigated poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV)/ poly(butylene succinate-co-butylene adipate) (PBSA) blend. PHBV is a biopolymer from the polyhydroxyalkanoates' family (PHA). Because of its highly crystalline structure, it exhibits a fragile behavior which restricts its applications in the packaging industry for instance, where flexibility is an important parameter. Therefore, it has been blended with PBSA which demonstrates high ductility. An epoxy-functionalized chain extender (JON) was used to enhance interaction between both immiscible biopolyesters. In 70/30 PHBV/PBSA with 0.5 phr of JON, the particles' size of the dispersed phase decreased and made the material more homogeneous showing an increased interaction between both polymers. Enhanced interaction improved the elongation at break by 45 % and turned the material into a non-breakable one under flexural stress. However, it did not succeed in creating good adhesion under high-strain rates, the impact resistance remaining unchanged. This shows that the morphology was not stable. This example effectively highlights the challenge of enhancing biopolymers' properties and underscores the significance of blends compatibilization.

3.3.2. PLA-based blends prepared by reactive extrusion

Although PLA possesses favorable properties, some limitations exist restricting its applications. Low ductility and impact resistance being the main issues to overcome are

driving the exploration of PLA based blends. To develop PLA-based blends with satisfactory thermo-mechanical properties, it is crucial to generate a dispersed phase with good dispersion and limited size and that has a strong interfacial adhesion with the matrix. Reactive processes such as reactive extrusion (REX) have proven to be an efficient method.

Reactive blending of PLA with ductile biopolymers is widely used to improve the ductility of the PLA. One of the most investigated is the PLA/PCL blend where the poly(ε-caprolactone) (PCL) is a ductile biodegradable polyester blended with PLA. However, the two polymers are incompatible and form a two-phase system with a poor interfacial adhesion. To overcome this issue, different compatibilization techniques are investigated.

In this study [35], PLA and PCL underwent reactive processing using a twin-screw extruder with the addition of lysine triisocyanate (LTI) as the reactive agent. The introduction of LTI significantly improved the mechanical properties of the sample specimens compared to the uncompatibilized blend. Remarkably, the impact strength exhibited a significant increase, particularly at 20 wt.% of PCL content along with 0.15 – 0.3 phr of LTI. Additionally, the presence of LTI led to an important 270 % increase in ultimate strain compared to the blends in the absence of LTI. However, it was observed that this enhancement in certain properties came at the cost of a reduction in mechanical strength, including tensile strength and tensile modulus. The inclusion of LTI resulted in an increase in the Torque value, providing evidence of cross-linking between the two phases. The morphology analysis confirmed the successful compatibilization achieved in the study. The PLA/PCL blends in the presence of LTI demonstrated a sea-island structure, where PLA formed a continuous phase while PCL existed as a dispersed phase. The presumed compatibilization reaction occurred between the isocyanate groups of LTI and the hydroxyl or carboxyl groups at the ends of the polyesters.

Similar observations were described again by Harada *et al.* [36], using in that case PLA/PBS blend.

Semba *et al.* [37] used Dicumyl peroxide (DCP) in the PLA/PCL blend through reactive extrusion to enhance interfacial adhesion and ultimately improve the toughness of PLA. In the processing conditions, this highly reactive peroxide decomposes into radicals that extract hydrogen from both PLA and PCL, leading to the formation of free radicals. This

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facilitates the formation of co-crosslinks between the primary alkyl radicals from PCL scission and the tertiary radicals of PLA. The results revealed that the ultimate tensile strain reached its highest point with a low concentration of Dicumyl peroxide (DCP). Additionally, the impact strength of the PLA/PCL blend (70 wt.% /30 wt.%) with 0.3 phr of DCP was significantly superior, being 2.5 times higher than that of neat PLA. Notably, the blend displayed ductile behavior, including plastic deformation, as observed on its fracture surface.

In another study, Gardella *et al.* [38] suggested to replace a part of PLA by the Maleic anhydride (MA) grafted PLA (PLA-g-MA). Prior to the blending, the grafted PLA was prepared in the extruder through a free-radical process initiated by 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane radical. Then, the MA grafted to PLA reacts with the hydroxyl end groups of PCL, enhancing the interfacial adhesion. This was confirmed by a reduction of the PCL dispersed phase in the PLA matrix, observed by microstructure analysis. The improvement of the elongation at break clearly confirmed the positive effect of the compatibilization.

PLA/PBSA blends have been previously investigated to improve PLA toughness. However, due to the immiscibility of the blend, compatibilization is necessary to improve interfacial tension and adhesion, ultimately achieving a blend that exhibits the optimal combination of properties from both polymers.

Lascano *et al.* [23] investigated the impact of incorporating poly(butylene succinate-co-adipate) (PBSA) on the mechanical properties of poly(lactic acid) (PLA) specimens. Since the addition of PBSA alone does not significantly improve the mechanical properties, an epoxy styrene-acrylic oligomer (ESAO) is utilized as a compatibilizer to enhance the interaction between PLA and PBSA. The PLA/PBSA blends with ESAO exhibit improved elongation at break. Microstructure analysis reveals increased shear on the surface fracture, indicating enhanced PLA-PBSA interaction facilitated by the compatibilizer. Differential scanning calorimetry (DSC) confirms the limited miscibility between PLA and PBSA, even with the presence of the compatibilizer. Overall, the study suggested that incorporating PBSA with effective compatibilization can enhance the ductility while the toughness remains low due to relatively poor miscibility.

In another study, Aliotta *et al.* [39] explored PLA/PBSA binary blends with varying compositions of PBSA and the effect of an epoxy oligomer (EO) as a compatibilizer. The results showed that EO improved compatibility between the dispersed PBSA phase and PLA matrix. The microstructure was enhanced by the addition of EO. Thermal properties were minimally affected by EO addition. The mechanical analysis demonstrated higher ductility. Finally, EO showed promise as an effective compatibilizer of this blend.

To our knowledge, no paper has been published on the reactive compatibilization of PLA/PBSA blends with the use of DCP, MA or maleated polyesters as reactive compatibilizers.

4. Experimental part

4.1 Materials

4.1.1. PLA

Poly lactic acid (PLA) is a linear thermoplastic bio-based polyester whose structure is depicted below.
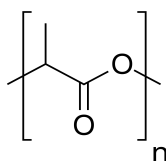

Image 1: Chemical structure of PLA

PLA (Polylactic acid) Ingeo3052D (L-lactic acid/D-lactic acid: 96/4), provided by NATUREWORKS, was used in this work. The polymer is received in the form of pellets. Its main physical and mechanical properties, extracted from the datasheet, are depicted in Table 1. [40]

Table 1: Physical and mechanical properties of PLA Ingeo3052D [40]

Physical properties	Value	ASTM Method
Density (g/cm3)	1,24	
MFR, g/10 min (210°C, 2,16 kg)	14	D1238
Relative Viscosity	3,3	
Crystalline Melt Temperature (°C)	145-160	D3418
Glass Transition Temperature (°C)	55-60	D3418
Clarity	Transparent	

Mechanical properties	Value	ASTM Method
Tensile Yield Strength (Mpa)	62	D638
Tensile Elongation (%)	3,5	D638
Notched Izod Impact (J/m)	16	D256
Flexural Srength (Mpa)	108	D790
Flexural Modulus (Mpa)	3600	D790
Heat Distorsion Temperature (°C)	55	E2092

4.1.2. PBSA

Poly(butylene succinate-co-adipate) (PBSA) is an aliphatic copolyester synthesized by co-condensing succinic acid, adipic acid, and 1,4-butanediol.
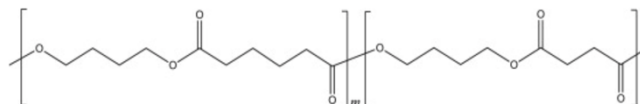

Image 2: Chemical structure of PBSA

Poly (butylene succinate-co-adipate) (PBSA), commercially known as PBE001 Natureplast (France), presents an MFI (190 °C/2,16 Kg) of 4-5 g/10 min. The polymer is received in the form of pellets.

4.1.3. Dicumyl Peroxide (DCP)

Dicumyl peroxide (DCP) is an organic peroxide whose structure is depicted below. It can be utilized as a polymerization initiator, or as a cross-linking agent.

Image 3: Chemical structure of DCP

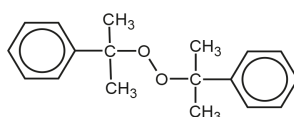In polymer blend systems, DCP can react with functional groups present on the polymer chains. During the reactive extrusion process, the formation of DCP free-radicals, able to react with the polymer backbone and/or other components, leads to the formation of covalent bonds between the different components of the blend. This promotes intermolecular interactions and reduces phase separation. [41]

DCP (CAS No. 80-43-3, Sigma-Aldrich) shows a molecular weight of 270.37 g/mol and a density of 1.56 g/cm3 at 25 °C. DCP is received in the form of powder and is stored in a refrigerator.

4.1.4. Maleic Anhydride (MA)

Maleic Anhydride (MA) is an organic compound whose structure is depicted below. It is also commonly used as a compatibilizer in polymer blends. Maleic anhydride is obtained through the oxidation of butane in the presence of a catalyst. The MA molecule possesses a double bond and two dehydrated carbonyl groups, rendering it highly reactive.
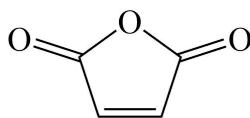
Image 4: Chemical structure of MA

When maleic anhydride is grafted onto a polymer chain, it introduces reactive functional groups, such as carboxylic acid or anhydride groups, onto the polymer's backbone. These functional groups can react with other polymers, allowing for chemical bonding or intermolecular interactions. [42]

MA (MA, 95%) furnished by Sigma-Aldrich (CAS No. 108-31-6) has a molecular weight of 98.06 g/mol, a density of 1.48 g/cm3 at 20 °C, and a melting point ranging between 51 - 56 °C. The product is received in the form of powder.

4.2. Processing

4.2.1. Blends composition

We separated the work into two different techniques. One approach is to do the compatibilization by directly mixing the polymers with the reactive agents in the extruder, which we will call direct compatibilization. The other approach is to prepare in the first place

the compatibilizer using extrusion and in the second step to compatibilize the polymers using the previously prepared compatibilizer with reactive extrusion. This method will be called indirect compatibilization.

Direct compatibilization

Two different compatibilizers will be employed which are DCP and MA. It is worth saying that DCP is also used in the blends compatibilized by MA to initiate the compatibilization. All the blends are prepared with a fixed ratio of PLA and PBSA (85 wt.% / 15 wt.%).

Table 2 displays the compositions of the blends, which are abbreviated as PLA/PBSA/X/Y. The values of X and Y represent the weight percentage of DCP and MA, respectively, with respect to the total mass of PLA/PBSA (85 wt.% / 15 wt.%). For example, PLA/PBSA/0.25/1 indicates that the blend contains 0.25 wt.% DCP and 1 wt.% MA based on the weight of PLA and PBSA.

Table 2: Composition of the blends prepared by direct compatibilization

Name	X = DCP (wt %)	Y = MA (wt %)
Blend compatibilized by DCP		
PLA/PBSA/0,25/0	0,25	0
PLA/PBSA/0,5/0	0,5	0
Blend compatibilized by MA		
PLA/PBSA/0,25/1	0,25	1
PLA/PBSA/0,25/2	0,25	2
PLA/PBSA/0,5/1	0,5	1
PLA/PBSA/0,5/2	0,5	2

Indirect compatibilization

In the initial step, two distinct Maleic anhydride grafted polyesters are synthesized. The first one is PLA-g-MA, and the second one is PBSA-g-MA. The maleation process involves mixing the respective polymer with MA and DCP inside an extruder. The grafting of MA, initiated by DCP, takes place during this process. Varying amounts of MA and DCP are used.

Next, two different methods are employed for blend compatibilization. In the first method, PLA is substituted with PLA-g-MA (PLA/PBSA/PLA-g-MA, 75/15/10). The second method replaces PBSA with PBSA-g-MA (PLA/PBSA/PBSA-g-MA, 85/10/5).

Table 3 presents the blend compositions, denoted as PLA/PBSA/Grafted Polymer/X/Y. Here, X and Y represent the weight percentages of DCP and MA, respectively, used in the preparation of the grafted polyester compatibilizers. For example, PLA/PBSA/PLA-g-MA/0,25/1 signifies that the blend with a fixed ratio of 75/15/10 was compatibilized using PLA-g-MA prepared with 0.25 wt.% DCP and 1 wt.% MA, with respect to PLA mass used in that preparation.

Table 3: Composition of the blends prepared by indirect compatibilization

Name	Composition of the maleated PLA		Composition of the maleated PBSA	
	X = DCP (wt %)	Y = MA (wt %)	X = DCP (wt %)	Y = MA (wt %)
Blend compatibilized by PLA-g-MA *PLA/PBSA/PLA-g-MA (75/15/10)*				
PLA/PBSA/PLA-g-MA/0,25/2	0,25	2	X	X
PLA/PBSA/PLA-g-MA/0,25/6	0,25	6	X	X
PLA/PBSA/PLA-g-MA/0,5/2	0,5	2	X	X
PLA/PBSA/PLA-g-MA/0,5/6	0,5	6	X	X
Blend compatibilized by PBSA-g-MA *PLA/PBSA/PBSA-g-MA (85/10/5)*				
PLA/PBSA/PBSA-g-MA/0,25/2	X	X	0,25	2
PLA/PBSA/PBSA-g-MA/0,25/6	X	X	0,25	6
PLA/PBSA/PBSA-g-MA/0,5/2	X	X	0,5	2
PLA/PBSA/PBSA-g-MA/0,5/6	X	X	0,5	6

Pure PLA and PBSA, and the non-compatibilized PLA/PBSA blend were prepared as well for comparison.

4.2.2. Extrusion

To avoid any possible hydrolytic degradation of the biodegradable polymers during the melt processing, both PLA and PBSA were thoroughly dried in a dehumidifier at 80 °C for 24 hours prior to the processing. Likewise, MA was dried in an oven at 50 °C for 24 hours to eliminate any moisture traces, while DCP was used as received.

A co-rotating twin-screw extruder-kneader (Collin ZK 25T SCD 15 Teach-Line, Ebersberg, Bavaria, Germany) was employed.

Image 5: Co-rotating twin-screw extruder

The extrusion temperature was maintained at 180°C and a screw speed of 50 rpm was employed. The components are placed together in a plastic container and shaked, before being introduced in the feeding hopper. It is to avoid the aggregation in the feeding hopper due to size and mass difference. As the extrudate goes out of the nozzle, it passes through a cooling water bath and is finally pelletized.

In the case of indirect compatibilization, the obtained PLA-g-MA and PBSA-g-MA pellets were dried overnight, and the same procedure was applied the next day to prepare the final blend.

4.2.3. Injection molding

Samples for mechanical characterization were acquired through the process of injection molding. The process was carried out using a reciprocating screw injection molding machine (Battenfeld PLUS 350/75, Kottingbrunn, Austria), which employed a 25 mm diameter and a 14 L/D ratio screw.

To prevent hydrolytic degradation caused by shear stress, the pellets of the various blends obtained through reactive extrusion were dried overnight before performing the injection molding.

The injection molding press had a closing force of 350 kN. The processing temperature was set at 180°C. Samples for tensile testing (sample thickness = 2 mm, ASTM D-638, type IV) and impact testing (sample thickness = 3,2 mm, ASTM D-256) were obtained.

4.3. Characterization techniques

4.3.1. Mechanical analysis

To evaluate the mechanical properties of the material, tensile tests were performed using a universal testing equipment (Instron 5569, Norwood, USA) on dumbbell samples at a strain rate of 10 mm/min. From the stress-strain curves, we obtained values for Young's modulus (E), yield strength (σ_y) and deformation at break (ε_b). At least five tensile samples were examined for each reported value.

In addition, we measured the impact strength of the material using injection molded specimens with a cross section of 12.7 × 3.2 mm. To create notches in the injection molded

bars, we machined the surface to a depth of 2.54 mm with a radius of 0.25 mm. We conducted Izod impact tests using a Ceast pendulum, following the ASTM D-256 standard. To obtain the average impact strength, we tested at least eight samples.

4.3.2. Thermal analysis and phase behavior

To investigate the thermal properties of the material and phase behavior, we conducted Dynamic Mechanical Analysis (DMA) using rectangular specimens in a TA Q800 viscoelastometer in single cantilever bending was employed. The temperature range was set from -100 °C to 120 °C with a heating rate of 4 °C/min, and the tests were performed at a frequency of 1 Hz and amplitude of 15 μm.

Results allow us to determine the glass transition temperatures from the maximum of the tan delta curve as a function of the temperature.

Differential Scanning Calorimetry (DSC) using a Perkin-Elmer DSC-7 calorimeter calibrated with an indium standard as a reference was also employed in the thermal characterization. The samples were obtained from previously injection molded specimens and were heated from 30 °C to 200 °C at a rate of 20 °C/min under a nitrogen atmosphere. Two heating scans were conducted to ensure the reproducibility of the results.

From the analysis of the first heating scan, we were able to determine the melting and crystallization temperatures of PLA at the maxima and minima of the corresponding endothermic and exothermic peaks, respectively, and the melting temperature of PBSA was presented as well. Melting and crystallization enthalpies of PLA (ΔH_m and ΔH_c respectively) were measured from the areas under the peaks. The degree of crystallinity was calculated using the equation shown below:

$$X_c = \frac{\Delta H_m - \Delta H_c}{PLA\ wt.\ \% \times \Delta H_m^0} \times 100 \qquad \textit{Equation 1}$$

Where ΔH_m^0(PLA) is the enthalpy of melting per gram of 100% crystal (perfect crystal) PLA (93 J/g), and PLA $wt.$ % is the weight fraction of PLA in each blend.

4.3.3. Microstructure

The microstructure was examined through transmission electron microscopy (TEM). Ultrathin sections of approximately 100 nm were prepared from injection-molded specimens using a Leica EMFC 6 ultramicrotome fitted with a diamond knife. Micrographs were captured using a Tecnai G2 20 twin apparatus (FEI, Waltham, MA, USA), operating at an acceleration voltage of 200 kV.

5. Results and discussion

This chapter is focused on analyzing the blends' mechanical, thermal, and microstructural properties. It is structured as follows:

First, the main results obtained for the reference blend PLA/PBSA (85 wt.% / 15 wt.%) are presented.

Subsequently, the various compatibilizing techniques employed will be reviewed. Each technique will be discussed individually, highlighting its respective results and implications.

5.1. PLA/PBSA

The mechanical properties of the reference blend, consisting of 85 wt.% PLA and 15 wt.% PBSA, as well as the pure PLA and PBSA were measured by tensile and Izod impact tests. The parameters determined from it are summarized in Table 4. As it can be observed, the reference blend exhibits a ductile behavior, resulting in a significant increase in elongation at break, reaching a value of 164%, while brittle PLA shows a value of 3 %. Prior to failure, a yielding phenomenon is observed. Nevertheless, the addition of PBSA does not drastically impact the yield strength. Although there is a decrease of 9% in the elastic modulus, this reduction can be expected when blending brittle and ductile polymers. However, it should be noted that this decrease is moderate. Furthermore, the impact resistance remains unchanged.

Table 4: Mechanical results of PLA, PBSA and reference blend PLA/PBSA (85 wt.% / 15 wt.%) , N.B. states for Not Breakable

Composition	Modulus (MPa)	Yield strength (MPa)	Elongation at break (%)	Impact strength (J/m)
Pure PLA	3190 ± 124	59,8 ± 0,8	3 ± 0	26 ± 1
Pure PBSA	349 ± 25	25,8 ± 0,7	133 ± 22	N.B.
PLA/PBSA	2890 ± 70	51,8 ± 3,4	164 ± 24	27 ± 1

The results from the Dynamical Mechanical Thermal Analysis (DMTA) are presented in Table 5 for both pure polymers and the reference blend. As can be seen, two glass transitions, close to those corresponding to the pure polymers, appeared, indicating that the blend is not miscible.

Table 5: DMTA results of PLA, PBSA, and the reference blend PLA/PBSA (85 wt.% / 15 wt.%)

Composition	T_g (PLA) (°C)	T_g (PBSA) (°C)
Pure PLA	72	X
Pure PBSA	X	-22
PLA/PBSA	69	-22

In view of the obtained results, the immiscibility of the uncompatibilized blend has been stated. With respect to the mechanical performance, it is evident that the addition of PBSA in PLA enhances its ductility. However, the impact strength of the material remains considerably low, presenting a constraint for various applications. This preliminary investigation led us to explore reactive extrusion as a viable approach to enhance the blend's compatibility and thereby improve its overall mechanical and thermal characteristics.

5.2. PLA/PBSA/DCP

The first attempt to improve the compatibility between PLA and PBSA involves the incorporation of Dicumyl peroxide (DCP) as a radical initiator. This peroxide is intended to

serve as an efficient crosslinking agent during the reactive compatibilization process, facilitating the formation of PLA-g-PBSA copolymers at the interface of the two phases.

● *Mechanical properties*

The mechanical results obtained from the tensile test and Izod impact tests are presented in Table 6.

Table 6: Mechanical results of PLA/PBSA/X/0 blends and the reference blend

Composition	Modulus (MPa)	Yield strength (MPa)	Elongation at break (%)	Impact strength (J/m)
PLA/PBSA	2890 ± 70	51,8 ± 3,4	164 ± 24	27 ± 1
PLA/PBSA/0.25/0	2720 ± 100	48,5 ± 1,9	164 ± 5	36 ± 3
PLA/PBSA/0.5/0	2800 ± 48	X	8 ± 6	29 ± 2

In the case of PLA/PBSA/0.25/0 blend, it can be observed that the modulus is lower compared to the uncompatibilized blend, which could be an indication of an improved compatibility between the components according to the rule of mixture. However, the elongation at break remains unchanged, suggesting that the addition of DCP to improve surface adhesion may not be sufficiently effective. Regarding the impact strength, while there is an increase of 9 J/m, pointing towards improved compatibility between the two phases, this increment is not significant enough to definitively state that the material's resistance to high-strain rates has been notably enhanced. Consequently, while the observed increase suggests a positive effect on compatibility, it does not provide substantial evidence to firmly establish the compatibility between the phases.

In the case of PLA/PBSA/0.5/0, the resulting elastic modulus and impact strength are close to those of the uncompatibilized blend. The impact strength shows the same tendency. More importantly, no yielding phenomenon is observed for this blend, which demonstrates a brittle fracture with an elongation at break highly reduced by 88% with respect to the uncompatibilized PLA/PBSA blend. These results suggest that higher DCP contents do not help to the compatibilization of the blend.

The proposed mechanism in the presence of DCP is depicted in Figure 4. In the presence of DCP radicals, PLA and PBSA can potentially generate macroradicals, through hydrogen abstraction. As a result, at the interface of the PLA/PBSA blends, crosslinking reactions can occur through the combination of PLA and PBSA macroradicals.
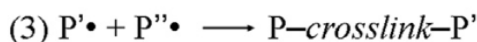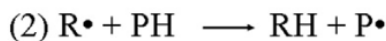
$$(1)\ R\text{-}O\text{-}O\text{-}R \longrightarrow 2R\bullet$$

$$(2)\ R\bullet + PH \longrightarrow RH + P\bullet$$

$$(3)\ P'\bullet + P''\bullet \longrightarrow P\text{-}crosslink\text{-}P'$$

Figure 4: Proposed reaction mechanism in the presence of DCP [43]

When comparing with the bibliography, similar results as ours were obtained by Semba *et al.* [37], who studied the PLA/PCL (80 wt.% / 20 wt.%) blend compatibilized by DCP addition during reactive extrusion. The tensile modulus and yield strength of the blend aligned with the rule of mixture. Furthermore, they observed minimal influence on the ultimate strain when incorporating PCL compatibilized with low amounts of DCP. Additionally, they observed a detrimental effect on the elongation at break when the amount of DCP was increased in the PLA/PCL blend.

According to another study [44], this may be attributed to chain-scission events that take place during the reactive processing involving DCP. These chain-scission events lead to the presence of shorter-length chains with fewer entanglements, ultimately resulting in a decrease in the strain at break because of the loss of structural integrity.

In another study, Ma *et al.* [43] compatibilized PLA with PBAT (80 wt.% / 20 wt.%) with DCP. They displayed similar results as ours. The impact strength and elongation at break are not effectively improved by the addition of 0.2 wt. % of DCP, compared to the uncompatibilized blend. However, the analysis of the microstructure by SEM revealed that adding DCP led to an enhancement in interfacial tension, evident through a more uniform and reduced size of the dispersed phase domain. Meanwhile, the interface appeared less discernible, indicating a strong interface. These results imply an improvement of the compatibility between the two polymers in the blend.

● *Thermal properties*

Table 7: DMTA results of PLA/PBSA/X/0 blends and the reference blend

Composition	T_g PLA (°C)	T_g PBSA (°C)
PLA/PBSA	69	-22
PLA/PBSA/0,25/0	70	-22
PLA/PBSA/0,5/0	69	-22

By employing Dynamic Thermal Mechanical Analysis (DMTA), we determined the glass transition temperatures of the different blends. The results are presented in the Table 7.

As can be seen, two different glass transition temperatures appeared in the two compatibilized blends, indicating phase separation as in the case of the uncompatibilized one. Moreover, the position of both T_{gs} was similar to that of the reference blend (and to those of the pure polymers) indicating that the compatibilization method is not effective enough to significantly modify either the T_{gs} or the mechanical properties.

Finally, Differential Scanning Calorimetry (DSC) allowed us to understand the thermal history of the blends. The thermograms corresponding to the first heating scan are presented on Figure 5 and the thermal parameters extracted from it are shown in Table 8.
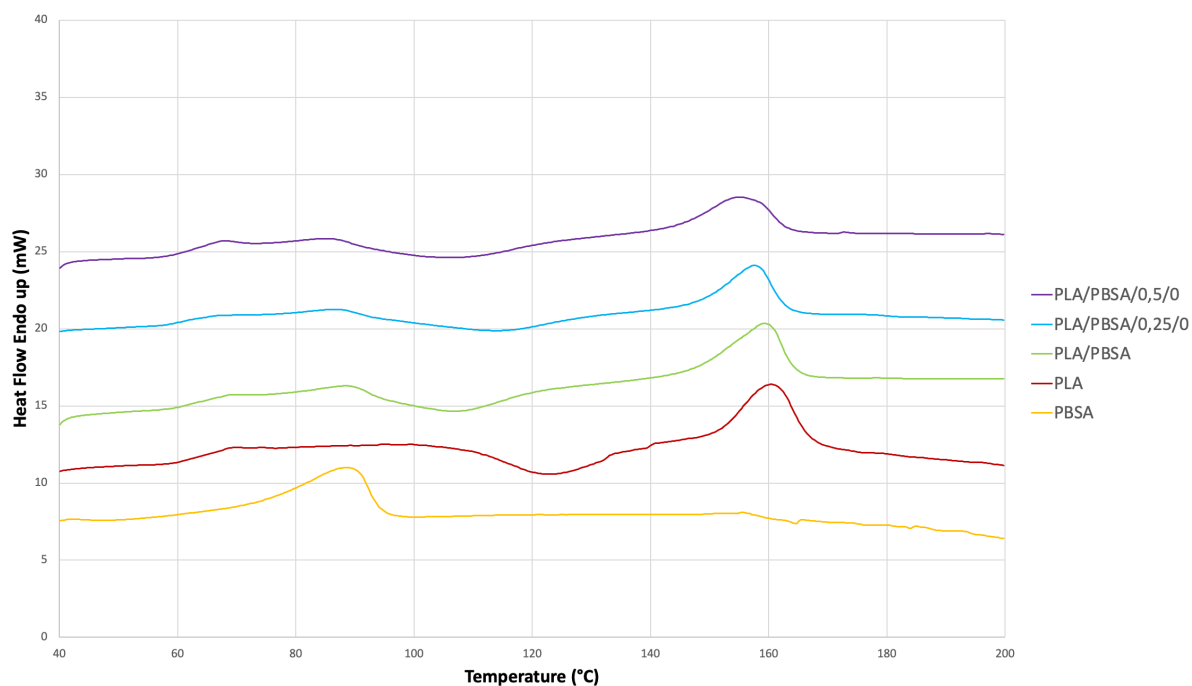

Figure 5: Thermogram for the pure polymers, the reference blend and the PLA/PBSA/X/0 blends

Table 8: Thermal transition for the pure polymers, the reference blend and the PLA/PBSA/X/0 blends

Composition	T_m PBSA (°C)	T_{cc} PLA (°C)	T_m PLA (°C)	X_c PLA (%)
Pure PLA	X	122 ± 2	160± 1	10 ± 4
Pure PBSA	88 ± 0	X	X	X
PLA/PBSA	88 ± 0	107 ± 1	159 ± 1	10 ± 0
PLA/PBSA/0,25/0	87 ± 0	114 ± 0	158 ± 0	11 ± 4
PLA/PBSA/0,5/0	85 ± 0	106 ± 0	155 ± 1	9 ± 1

Both PLA and PBSA are semi crystalline polymers. On the thermograms, the first heating scan is depicted. For the reference blend (PLA 85 wt.% / PBSA 15 wt.%) and the compatibilized blends by DCP it can be see a first endothermic peak corresponding to the melting of the PBSA phase, overlapping with the exothermic cold crystallization of PLA, and finally the last endothermic peak corresponding to the melting of the PLA phase.

It is worth highlighting that the addition of PBSA in PLA results in a notable reduction in the cold crystallization temperature (T_{cc}) of PLA. This phenomenon can be attributed to the presence of the molten PBSA phase, which facilitates chain motion. In other words, PBSA serves as a nucleating agent for PLA. Consequently, the PLA chains are able to crystallize at lower temperatures, as reported by Lee *et al.*. [45]

The incorporation of 0.25 wt% DCP into the blend (PLA/PBSA/0.25/0) leads to a slight elevation in the cold crystallization temperature (T_{cc}). This finding provides further evidence of the compatibilizing effect of DCP in this particular blend. The presence of DCP, which induces crosslinking, restricts the mobility of the polymer chains, impeding the rearrangement of PLA chains into an ordered structure at lower temperatures, as observed in the uncompatibilized blend. In contrast, the PLA/PBSA/0.5/0 blend does not show an increase in T_{cc}, confirming that the presence of DCP in this specific proportion does not have a positive effect on the blend.

Lascano *et al.* [23] obtained similar behavior for PLA/PBSA blend compatibilized by the addition of an epoxy styrene-acrylic oligomer (ESAO). They observed a shift of cold

crystallization of PLA in the pure PLA/PBSA blend but the addition of ESAO finally led to an increase in the T_{cc} value.

The observed crystallinity of the blends is found to be nearly negligible. This can be ascribed to the molding processing technique employed, which is known to impede the crystallization of PLA, due to its high cooling rate.

- *Overview*

Finally, based on a comparative analysis of our results with those of other studies, it can be inferred that there is some level of interaction between the two polymers in the blend compatibilized with 0.25 wt. % of DCP, as indicated by the mechanical and DSC test results. However, the DMTA analysis reveals that the blend remains immiscible after the addition of DCP, as evidenced by the presence of two distinct glass transition temperatures (T_g). Therefore, it can be hypothesized that the achieved compatibility for this blend is not substantial enough to create a miscible blend or a significant compatibilization effect. This could explain that there is no significant enhancement in toughness compared to the uncompatibilized blend.

For the blend with higher DCP content, the resulting decrease in mechanical properties, specifically the ductility, is attributed to main-chain scissions occurring during the reactive processing. For this reason, the attempt to effectively compatibilize PLA/PBSA blend by direct addition of DCP has shown non-effective.

5.3. PLA/PBSA/DCP/MA

In the second approach to enhance compatibilization, a one-step extrusion process is employed using Maleic Anhydride (MA) as a compatibilizer in the presence of Dicumyl Peroxide (DCP) as a free-radical initiator. The aim is to facilitate the formation of PLA-g-MA-g-PBSA in the blend. These grafted polyesters are expected to position themselves at the interface between the two phases, facilitating improved compatibility.

- *Mechanical properties*

The mechanical results obtained by tensile and Izod impact tests are presented in the Table 9.

On one hand, the modulus decreases in all the blends except for PLA/PBSA/0.5/1, which shows an increase in modulus. On the other hand, all the blends exhibit a brittle fracture at low deformation prior to the occurrence of yielding. Furthermore, the addition of MA with DCP does not appear to have any effect on the blend's impact resistance. The lower modulus observed in comparison to the uncompatibilized blend may suggest an enhanced compatibility between the components, as indicated by the rule of mixture. However, the considerable decrease in elongation at break observed after adding MA, along with the unchanged impact resistance, indicates a failure in achieving effective compatibilization.

Table 9: Mechanical results of PLA/PBSA/X/Y blends and the reference blend

Composition	Modulus (Mpa)	Yield strength (Mpa)	Elongation at break (%)	Impact strength (J/m)
PLA/PBSA	2890 ± 70	51,8 ± 3,4	164 ± 24	27 ± 1
PLA/PBSA/0,25/1	2740 ± 79	X	5 ± 2	26 ± 4
PLA/PBSA/0,25/2	2675 ± 35	X	6 ± 3	25 ± 1
PLA/PBSA/0,5/1	2950 ± 114	X	2 ± 0	27 ± 0
PLA/PBSA/0,5/2	2640 ± 106	X	4 ± 1	27 ± 0

In comparison, Wang *et al.* [46] investigated the compatibility of dry thermoplastic starch (DTPS) with PLA using MA as a compatibilizer during one-step reactive extrusion in order to increase the strength of the thermoplastic starch. Results showed that MA-compatibilized blends with starch as the major phase and PLA as the minor phase exhibited higher tensile strength compared to uncompatibilized blends. Morphological analysis confirmed improved microstructure of the blends, with reduced DTPS granule size even at high content. These findings support the efficacy of MA as a compatibilizer, leading to improved blend strength.

However, in our case, the results we obtained for elongation at break demonstrates the ineffectiveness of the use of MA as a compatibilizer. This reduction can be attributed to the degradation of PLA during the reactive process. [47, 48] The grafting reaction of MA onto the polymer backbone aims to form MA-grafted-PLA (or PBSA-g-MA), where maleic anhydride can further react with the hydroxyl-end groups of the other polyester through esterification, resulting in improved surface adhesion.

The proposed mechanism for MA-grafting onto PLA is illustrated in Figure 6. It starts by the homolytic scission of the peroxide. Once the radical is formed, hydrogen abstraction can occur, producing a PLA which may react with the MA. The resulting polymer radical may then combine with another radical (MA, peroxide, or polymer radicals or hydrogen) or terminate. However, side reactions may also take place, including β-scission following MA grafting, as well as back-biting and thermohydrolysis of PLA due to its thermal instability. This results in PLA degradation leading to the decrease in molecular weight of PLA.
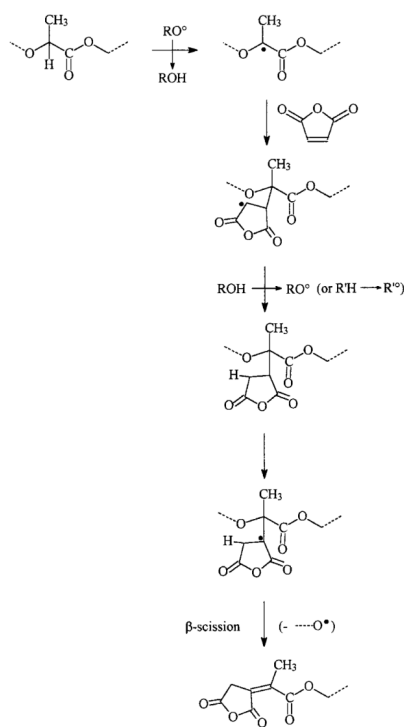

Figure 6: Proposed reaction mechanism of MA grafting onto PLA

Supporting that information, during the reactive extrusion process of our blends, the extrudates exhibited a yellowish color, indicating the degradation of PLA. This clearly suggests that the loss of structural integrity is the primary cause for the significant decrease in

elongation at break observed in the blends containing MA when compared to the uncompatibilized blend.

The study conducted by Nezamzadeh *et al.* [49], presented the effect of MA as a compatibilizer in a PLA/thermoplastic starch blend prepared using an internal mixer. They controlled the mixing order by adding MA during a first step or a second step as well as the MA content. Interestingly, they demonstrated that the addition of MA during a second step allows a better interfacial adhesion. This led to an increase in elongation at break and a decrease in both yield strength and elastic modulus. These findings highlight the importance of controlling the processing of MA, especially when working with thermally unstable polymers.

● *Thermal properties*

Table 10: DMTA results of PLA/PBSA/X/Y blends and the reference blend

Composition	T_g PLA (°C)	T_g PBSA (°C)
PLA/PBSA	69	-22
PLA/PBSA/0,25/1	69	-20
PLA/PBSA/0,25/2	67	-25
PLA/PBSA/0,5/1	68	-24
PLA/PBSA/0,5/2	67	-24

DMTA results presented in the Table 10 confirm the presence of two immiscible phases with distinct glass transition temperatures for PLA and PBSA. Therefore, from these results, it can be said that the blends are immiscible. Similar to the previous case, the glass transition temperatures in the compatibilized blend remains the same that those in the reference blend and pure polymers. This indicates that the compatibilization method does not alter the T_{gs}.

Regarding the DSC analysis, Figure 7 shows the first heating scan of the studied blends and Table 11 the thermal parameters extracted from them.
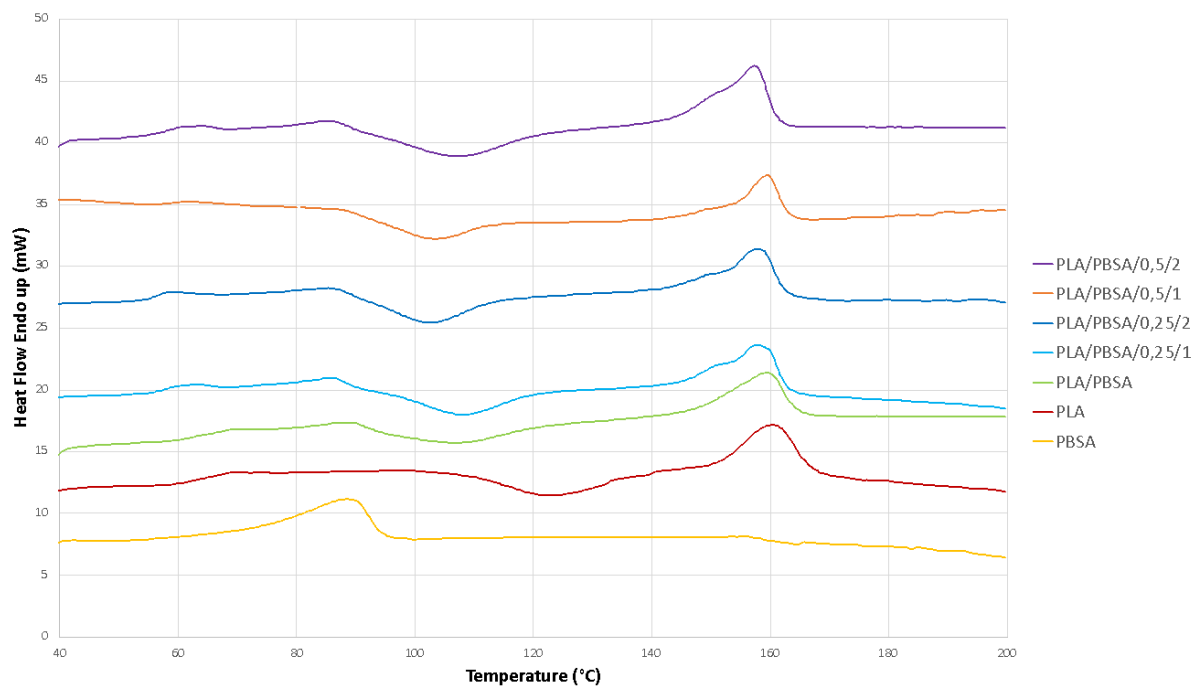
Figure 7: Thermogram for the pure polymers, the reference blend and the PLA/PBSA/X/Y blends

Table 11: Thermal transition for the pure polymers, the reference blend and the PLA/PBSA/X/Y blends

Composition	T_m PBSA (°C)	T_{cc} PLA (°C)	T_m PLA (°C)	X_c PLA (%)
Pure PLA	X	122 ± 2	160± 1	10 ± 4
Pure PBSA	89 ± 0	X	X	X
PLA/PBSA	88 ± 0	107 ± 1	159 ± 1	10 ± 0
PLA/PBSA/0,25/1	85 ± 1	108 ± 0	158 ± 1	9 ± 2
PLA/PBSA/0,25/2	86 ± 1	103 ± 0	159 ± 2	8 ± 3
PLA/PBSA/0,5/1	84 ± 1	103 ± 0	159 ± 2	5 ± 3
PLA/PBSA/0,5/2	86 ± 0	107 ± 0	159 ± 2	6 ± 2

The addition of MA in the blends, specifically in PLA/PBSA/0.25/2 and PLA/PBSA/0.5/1, appears to decrease the T_{cc} of PLA. However, this is not observed in PLA/PBSA/0.25/1 and PLA/PBSA/0.5/2 blends. The lack of consistent trends observed in these results prevents us from drawing conclusions regarding the nucleating effect of MA in the blends. Additionally, it can be seen that the use of 0.5 wt.% DCP seems to reduce the overall crystallinity of the blend.

Comparably, Nezamzadeh *et al.* [49] revealed that the addition of MA reduces the crystallinity and T_{cc} of PLA in the blend.

The overall low crystallinity is also due to the processing conditions, as stated in the previous section.

- *Overview*

From the mechanical and thermal analyses conducted, it can be deduced that the attempt to enhance the compatibility of the blend was compromised by the concurrent degradation of PLA in the presence of MA and DCP.

Based on our findings as well as the relevant literature, it becomes clear that meticulous control of the reaction conditions is crucial in this method to effectively manage polymer degradation. This involves precise control of the quantities of MA and DCP utilized, as well as fine-tuning the reactive extrusion parameters. By maintaining optimal conditions, it could become feasible to mitigate polymer degradation and potentially attain the desired compatibilization effects in the blend.

5.4. PLA/PBSA/PLA-g-MA

The results obtained from the two direct compatibilization techniques emphasize the challenges associated with controlling direct reactive processes to enhance the final properties.

A more feasible approach for achieving interfacial modification is to modify the polymer matrix itself and use that modified polymer as the compatibilizing agent. This leads to more controlled reactions.

Therefore, in this third technique, we will use PLA-g-MA as a compatibilizer replacing 10 wt.% of PLA in all the blends. The objective was to induce the grafting of a portion of PBSA onto the PLA-g-MA backbone, thereby promoting increased interactions between the two polymers. The preparation of PLA-g-MA is monitored by varying the amount of MA and DCP used in the first reactive extrusion process.

● *Mechanical properties*

The mechanical test results are presented in Table 12.

Table 12: Mechanical results of PLA/PBSA/PLA-g-MA/X/Y blends and the reference blend

Composition	Modulus (MPa)	Yield strength (MPa)	Elongation at break (%)	Impact strength (J/m)
PLA/PBSA	2890 ± 70	51,8 ± 3,4	164 ± 24	27 ± 1
PLA/PBSA/PLA-g-MA/0,25/2	2600 ± 140	48,9 ± 3,1	192 ± 6	28 ± 1
PLA/PBSA/PLA-g-MA/0,25/6	2830 ± 119	50,2 ± 2,6	191 ± 18	27 ± 1
PLA/PBSA/PLA-g-MA/0,5/2	3083 ± 89	58,1 ± 3,2	151 ± 41	28 ± 0
PLA/PBSA/PLA-g-MA/0,5/6	2850 ± 55	54,2 ± 2,0	175 ± 22	27 ± 0

Among the blends, the ones with lowest amount of DCP initiator used in the preparation of PLA-g-MA show the highest increase in elongation at break of the final blend. The yielding phenomenon is observed for both and the yield strength is not significantly impacted by the addition of PLA-g-MA. Noteworthy, the modulus of PLA/PBSA/PLA-g-MA/0.25/2 is reduced while for PLA/PBSA/PLA-g-MA/0.25/6, the decrease with respect to the uncompatibilized blend is not significant.

While increasing the amount of DCP initiator to 0.5 wt.% in PLA-g-MA reactive processing, the elongation at break of the blend compatibilized with this PLA-g-MA is slightly reduced, this reduction being more important in the case of low MA content (PLA/PBSA/PLA-g-MA/0.5/2), resulting in a less ductile material compared to the uncompatibilized blend. Additionally, for this last one, the modulus and the yield strength show the highest values. The reasons behind the unexpected results for the PLA/PBSA/PLA-g-MA/0.5/2 blend remain unexplained and unclear. Experimental errors might have contributed to these findings. Finally, the decrease in modulus as well as the increase in yield strength for PLA/PBSA/PLA-g-MA/0.5/6 are not significant.

The proposed mechanism for the formation of PLA-g-MA is the same as the one presented in the method before.

Based on the results, it can be inferred that incorporating a lower amount of DCP initiator during the PLA-g-MA processing is more beneficial for enhancing elongation at break and improving the ductility of the final blend compatibilized by this PLA-g-MA. This can be attributed to the reduced likelihood of PLA degradation during the initial grafting process when using lower amounts of the initiator.

No such conclusive trend can be inferred from the variation of mechanical parameters with respect to the MA content used to prepare PLA-g-MA, as the data do not exhibit a consistent pattern.

In a study on the compatibilization of polylactide (PLA) and thermoplastic starch blends, PLA-g-MA (PLA modified with maleic anhydride) was prepared using three different amounts of free radical initiator. [50] These PLA-g-MA samples were then used as compatibilizers in a second step reactive extrusion with the blend. The researchers performed SEM analysis and found that in all cases, the size of the thermoplastic starch (TPS) phase was reduced compared to the unmodified blend. Notably, the blend with the lowest peroxide level showed the smallest and most uniform TPS phase size. The researchers explained that the reason for not achieving further reduction in the TPS phase size with a higher peroxide level and grafting degree is the increased occurrence of PLA chain scission. In simpler terms, although a higher peroxide level resulted in higher grafting, it also had undesirable effects on the PLA polymer chains, which compromised the reduction of the TPS phase size and therefore the final mechanical properties. Carlson *et al.* [47] determined the grafting level of maleic anhydride (MA) onto PLA using reverse titration. They confirmed that a higher amount of initiator led to higher grafting levels. Specifically, using 2 wt.% of MA with peroxide levels of 0.25 wt.% and 0.5 wt.%, the MA grafting levels were found to be 0.48 wt.% and 0.65 wt.%, respectively.

Considering the effect of MA content, according to a study conducted by John *et al.* [51], the graft content was decreased as the monomer concentration increased, while Mani *et al.* [48] show the opposite trend.

Above all, it is worth mentioning that the resulting extrudates of the maleation process were all presenting a yellowish color, indicating degradation of the PLA. Therefore, even if

the effect seems less important at low initiator content, the degradation of PLA is still a limiting factor in that process. This can explain the impact strength results obtained for all the blends, for which regardless of MA and DCP content used in the first extrusion step, there was no significant improvement.

- *Microstructure*

As the mechanical results presented good achievement in improving the ductility of the blend, the microstructure of the PLA/PBSA/PLA-g-MA/0.25/2 was analyzed by TEM. For comparison, the reference blend PLA/PBSA was also observed.

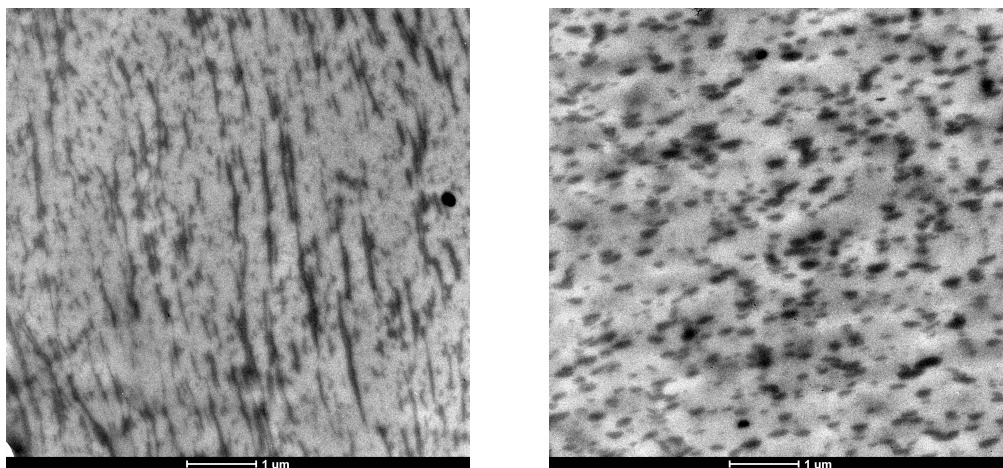The TEM images of the microstructure of these blends are presented on the Image 6.

**Image 6: TEM images of the microstructure of PLA/PBSA (on the left) and
PLA/PBSA/PLA-g-MA/0.25/2 (on the right)**

Interface modification in the molten state is anticipated to reduce interfacial tension, resulting in a smaller scale of segregation and to improve interfacial adhesion in the solid state. This improvement in the microstructure is expected to have an impact on the overall mechanical properties.

As seen in the Image 6, smaller-sized droplets of the PBSA phase are evident in the compatibilized blend, whereas in the uncompatibilized blend, the dispersed PBSA phase exhibits larger and more longer droplet size. These findings indicate an improvement in phase compatibility achieved through a reduction in surface tension for the compatibilized blend.

This enhancement in surface tension is believed to contribute to the increased ductility but is apparently not enough to provoke an improvement in the impact resistance of the blend.

- *Thermal properties*

The DMTA results confirm the immiscibility of the phases in the blend. This is evident from the observation of two glass transition temperatures, as presented in Table 13. In that case as well, the glass transition temperatures of PLA and PBSA are not changed by the addition of PLA-g-MA.

Table 13: DMTA results of PLA/PBSA/PLA-g-MA/X/Y blends and the reference blend

Composition	T_g PLA (°C)	T_g PBSA (°C)
PLA/PBSA	69	-22
PLA/PBSA/PLA-g-MA/0,25/2	70	-24
PLA/PBSA/PLA-g-MA/0,25/6	69	-23
PLA/PBSA/PLA-g-MA/0,5/2	70	-22
PLA/PBSA/PLA-g-MA/0,5/6	69	-22

Regarding the DSC analysis, the thermograms of the first heating scans and thermal parameters extracted from them are presented on Figure 8 and in Table 14, respectively.
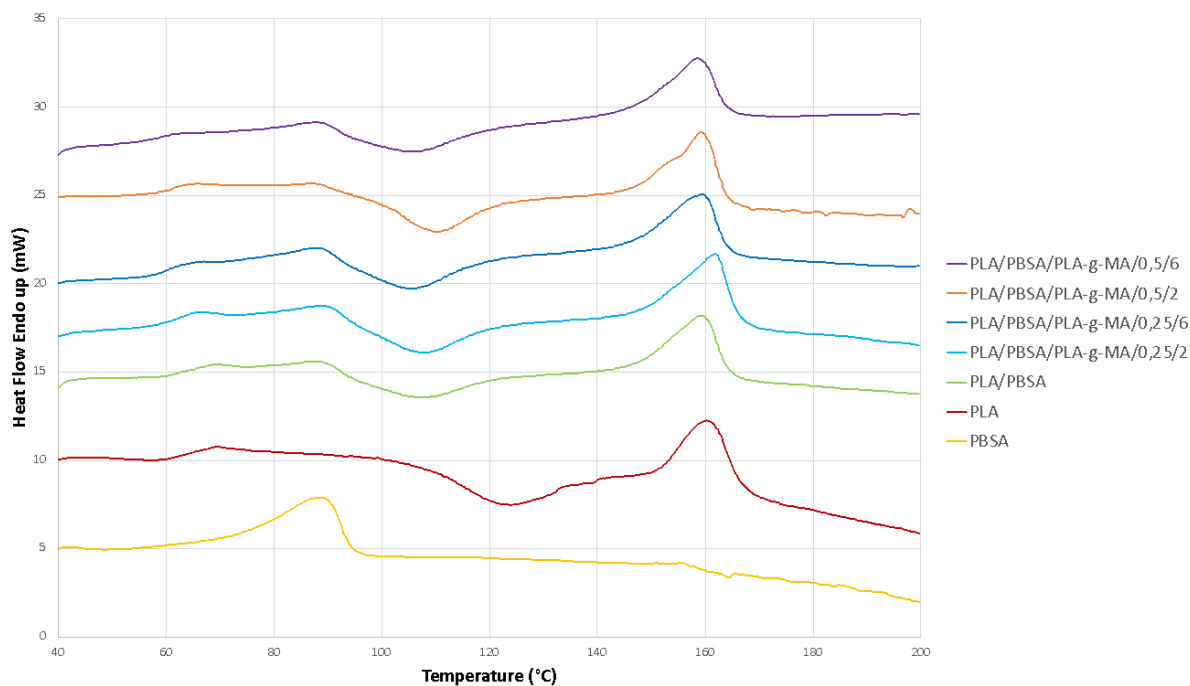
Figure 8: Thermogram for the pure polymers, the reference blend and the PLA/PBSA/PLA-g-MA/X/Y blends

Table 14: Thermal transition for the pure polymers, the reference blend and the PLA/PBSA/PLA-g-MA/X/Y blends

Composition	T_m PBSA (°C)	T_{cc} PLA (°C)	T_m PLA (°C)	X_c PLA (%)
Pure PLA	X	122 ± 2	160± 1	10 ± 4
Pure PBSA	89 ± 0	X	X	X
PLA/PBSA	88 ± 0	107 ± 1	159 ± 1	10 ± 0
PLA/PBSA/PLA-g-MA/0 ,25/2	89 ± 0	108 ± 1	162 ± 1	9 ± 1
PLA/PBSA/PLA-g-MA/0 ,25/6	88 ± 0	105 ± 1	159 ± 1	10 ± 0
PLA/PBSA/PLA-g-MA/0 ,5/2	86 ± 3	110 ± 1	160± 1	8 ± 1
PLA/PBSA/PLA-g-MA/0 ,5/6	88 ± 0	106 ± 1	159 ± 1	8 ± 1

No particular trend can be observed. The melting of PBSA, followed by the cold crystallization and finally the melting of PLA are identified. While adding PBSA to PLA, the cold crystallization temperature of PLA is reduced, as explained in Section 5.2. The addition of MA does not seem to have more impact on that reduction. Additionally, the overall

crystallinity of the blends seems to remain unchanged by the addition of PLA-g-MA. Yet a slight decrease can be observed in the case of the blend mixed with maleated PLA prepared with high amount of DCP.

In the study conducted by Gardella *et al.* [38], it was observed that the incorporation of PLA-g-MA into PLA/PCL blends had a notable impact on the crystallization and melting behavior of PLA. Increasing the amount of PLA-g-MA in the blends resulted in a shift of the cold crystallization peak of PLA to lower temperatures and an increase in crystallization enthalpy. The researchers suggested that this enhancement of PLA crystallization in the presence of PLA-g-MA as a compatibilizer could be attributed to the reduced chain size of PLA-g-MA caused by small degradation, which facilitated easier crystallization compared to pure PLA. Furthermore, the PCL domains present in the blend served as nucleating agents, promoting crystallization. This effect was more pronounced when the size of the PCL domains was significantly reduced due to the improved morphology achieved through compatibilization.

- *Overview*

In summary, compatibilization efforts have shown some positive effects on the blends PLA/PBSA/PLA-g-MA/0.25/2, PLA/PBSA/PLA-g-MA/0.25/6, and PLA/PBSA/PLA-g-MA/0.5/6, as evidenced by an increase in elongation at break. Additionally, the decrease in modulus may imply some compatibility enhancement according to the rule of mixture. However, these improvements seem more efficient when low amount of DCP is used in the preparation of PLA-g-MA, attributed to less chain-scissions. Yet, these improvements have not translated into enhanced toughness, as the impact strength remains unchanged. The microstructure analysis of the blend PLA/PBSA/PLA-g-MA/0.25/2 indicates improved compatibility between the phases through a reduction in surface tension. Nevertheless, the thermal results provide further insights and reveal the immiscibility of the blend, as indicated by the presence of two glass transition temperatures. Additionally, the degradation of PLA during maleation impacts the final mechanical properties of the blend.

In conclusion, the low impact resistance in the blends can be attributed to the presence of an unstable microstructure and degraded PLA. However, it is worth noting that the current technique demonstrates better control over degradation compared to the previous one-step reactive extrusion method.

5.5. PLA/PBSA/PBSA-g-MA

In this last attempt to compatibilize the PLA/PBSA blend, we replaced 5 wt. % of PBSA by PBSA-g-MA, whose aim is to increase interaction between PLA and PBSA. As the results of the previous method were enthusiastic but the degradation of PLA during the maleation process remained problematic, we decided to maleate PBSA as it is thermally more stable. It is anticipated that the maleic anhydride groups present in PBSA-g-MA will react with the hydroxyl end groups of PLA, similar to the reaction between PLA-g-MA and PBSA in the previous method.

- *Mechanical properties*

Mechanical results from tensile and Izod impact tests are presented in Table 15.

Table 15: Mechanical results of PLA/PBSA/PBSA-g-MA/X/Y blends and the reference blend

Composition	Modulus (MPa)	Yield strength (MPa)	Elongation at break (%)	Impact strength (J/m)
PLA/PBSA	2890 ± 70	51,8 ± 3,4	164 ± 24	27 ± 1
PLA/PBSA/PBSA-g-MA/0,25/2	2580 ± 35	52,0 ± 1,0	175 ± 14	31 ± 1
PLA/PBSA/PBSA-g-MA/0,25/6	2590 ± 67	51,4 ± 2,6	162 ± 5	30 ± 0
PLA/PBSA/PBSA-g-MA/0,5/2	2840 ± 29	52,0 ± 2,0	174 ± 16	28 ± 0
PLA/PBSA/PBSA-g-MA/0,5/6	3000 ± 25	58,3 ± 0,6	160 ± 22	27 ± 0

The elongation at break is increased for the blends with low amounts of MA, i.e., PLA/PBSA/PBSA-g-MA/0.25/2 and PLA/PBSA/PBSA-g-MA/0.5/2, while it is not the case for the two others which show almost the same elongation at break as the reference blend. A decrease in the modulus is observed for PLA/PBSA/PBSA-g-MA/0.25/2 and PLA/PBSA/PBSA-g-MA/0.25/6, as well as for PLA/PBSA/PBSA-g-MA/0.5/2, even though the decrease is less important for this last one than the two previous ones. Yield strength does

not seem impacted by the addition of PBSA-g-MA in the three first cases. Additionally, blends with low amounts of DCP demonstrated a slight increase in the impact strength. It is not observed in the blends with high DCP amounts. In the last blend, that is PLA/PBSA/PBSA-g-MA/0.5/6, the modulus and yield strength increased.

Based on these findings, it can be concluded that the concentration of MA in the maleated PBSA preparation influences the ductility of the blend that is compatibilized with this maleated PBSA. Specifically, when a low concentration of MA (2 wt.% in our case) is used to prepare PBSA-g-MA, it leads to enhanced ductility in the final blends. Furthermore, the modulus of these blends decreases according to the rule of mixture, which may be suggestive of an improved compatibility between PLA and PBSA.

In contrast, the impact test results reveal that the concentration of DCP in the preparation of maleated PBSA plays a crucial role. Using a low amount of DCP in the PBSA-g-MA compatibilizer preparation results in increased impact strength of the final blends. However, it is important to note that this increase is not significant enough to claim an overall improvement in toughness and therefore to claim a real effect of DCP.

The proposed mechanism for the grafting of MA onto the PBSA backbone begins with the organic peroxide undergoing homolytic scission. This process involves the peroxide abstracting a hydrogen atom from an α-carbon atom adjacent to the ester carbonyl group of the PBSA macromolecule. As a result, macroradicals are formed, which are capable of reacting with MA molecules. Additionally, these macroradicals can undergo β-scission, leading to the creation of an inactive vinylidene end chain and another radical species.

Following the grafting of MA, several termination reactions can take place. These include recombination with a radical originating from the β-scission reaction or through reaction with a radical present in the environment.

Mani *et al.* [48] indicates that the concentration of maleic anhydride (MA) has a lesser impact on the percent grafting onto the PBSA backbone compared to the initiator concentration. This is attributed to the high monomer concentration, which improves grafting efficiency by reducing the likelihood of radical termination reactions before MA grafting occurs. On the other hand, the initiator concentration directly affects the overall concentration of free radicals, which consequently influences the termination rate as well as the chain-scission occurrence.

Based on these findings, one would expect that a higher MA content in the initial extrusion process would lead to more successful grafting of MA onto PBSA, resulting in a greater amount of MA being available to interact with PLA in the subsequent extrusion process. This, in turn, would enhance the ductility. However, contrary to this expectation, our results demonstrate the opposite trend. It appears that a smaller amount of MA used in the preparation of PBSA-g-MA is more effective in improving the ductility.

Furthermore, the study proposes that increasing the concentration of DCP in the PBSA-g-MA preparation would affect grafting. Specifically, it suggests that a higher DCP concentration would result in more chain-scission, leading to a decrease in the molecular weight of PBSA and potentially compromising its structural integrity. Consequently, this would be expected to result in poorer mechanical properties in the final blend. However, our findings do not provide support for this hypothesis. The only notable difference observed is a slight decrease in impact strength, which is not significant enough to attribute a substantial effect to the concentration of DCP.

- *Microstructure*

PLA/PBSA/PBSA-g-MA/0.25/2 microstructure was analyzed by TEM and compared to the one of the uncompatibilized blend. The TEM images are shown on the Image 7.
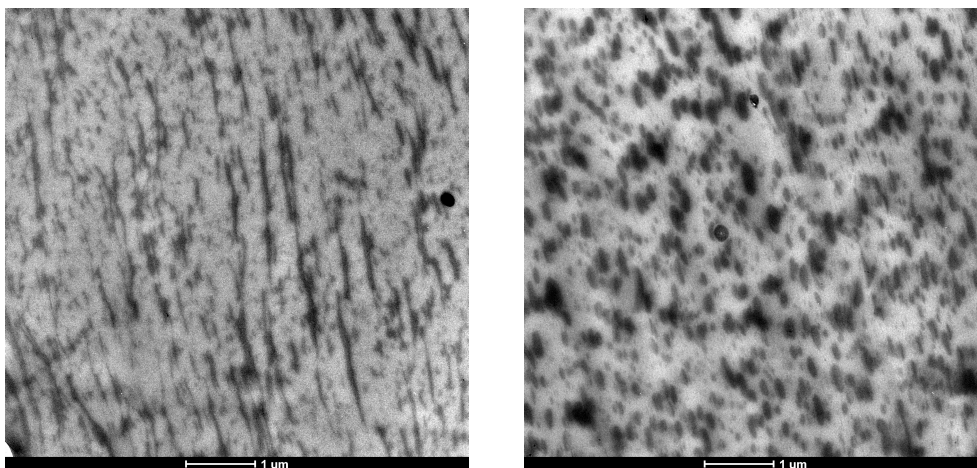

Image 7: TEM images of the microstructure of PLA/PBSA (on the left) and PLA/PBSA/PBSA-g-MA/0.25/2
(on the right)

As previously shown, PLA/PBSA blend microstructure shows that the PBSA dispersed phase is well distributed but the particles shows elongation. The addition of PBSA-g-MA results in smaller droplets. These results demonstrate an enhancement in the surface tension and therefore on the compatibility. As mentioned, this is translated in a better ductility of the blend, while it does not ameliorate the impact resistance of the blend.

- *Thermal properties*

The consistent trend observed in the previous techniques is upheld by the DMTA results, as depicted in Table 16. It reveals the presence of two glass transition temperatures in the blends, which are similar to those of the PLA/PBSA blend and the pure polymers. These observations indicate the existence of two immiscible phases within the blends.

Table 16: DMTA results of PLA/PBSA/PBSA-g-MA/X/Y blends and the reference blend

Composition	T_g PLA (°C)	T_g PBSA (°C)
PLA/PBSA	69	-22
PLA/PBSA/PBSA-g-MA/0,25/2	69	-20
PLA/PBSA/PBSA-g-MA/0,25/6	69	-22
PLA/PBSA/PBSA-g-MA/0,5/2	70	-21
PLA/PBSA/PBSA-g-MA/0,5/6	70	-21

Lastly, in terms of the DSC analysis, Figure 9 illustrates the first heating scan of the investigated blends, while Table 17 presents the extracted thermal parameters derived from these scans.
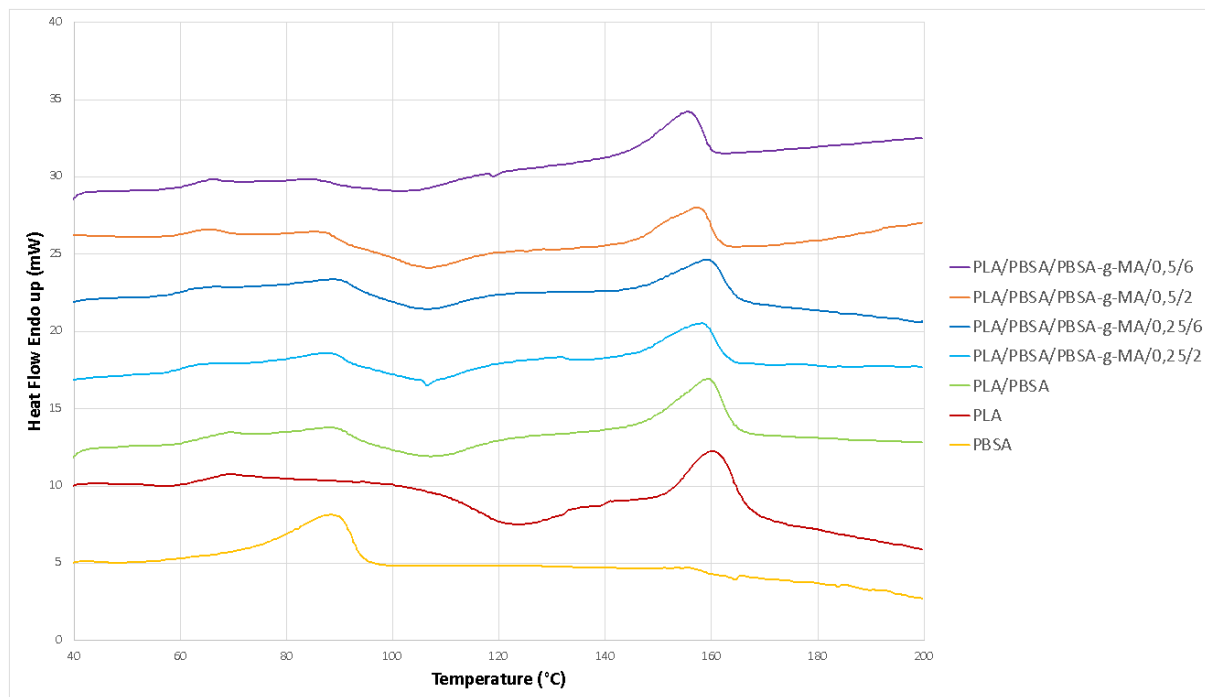
Figure 9: Thermogram for the pure polymers, the reference blend and the PLA/PBSA/PBSA-g-MA/X/Y blends

Table 17: Thermal transition for the pure polymers, the reference blend and the PLA/PBSA/PBSA-g-MA/X/Y blends

Composition	T_m PBSA (°C)	T_{cc} PLA (°C)	T_m PLA (°C)	X_c PLA (%)
Pure PLA	X	122 ± 2	160 ± 1	10 ± 4
Pure PBSA	89 ± 0	X	X	X
PLA/PBSA	88 ± 0	107 ± 1	159 ± 1	10 ± 0
PLA/PBSA/PBSA-g-MA/0 ,25/2	88 ± 0	107 ± 0	158 ± 1	7 ± 1
PLA/PBSA/PBSA-g-MA/0 ,25/6	88 ± 1	105 ± 2	159 ± 1	11 ± 1
PLA/PBSA/PBSA-g-MA/0 ,5/2	85 ± 0	107 ± 1	157 ± 1	8 ± 2
PLA/PBSA/PBSA-g-MA/0 ,5/6	85 ± 1	105 ± 4	157 ± 2	9 ± 1

The findings indicate that the thermal transition of PLA remained unaffected by the presence of PBSA-g-MA. It also had a minimal impact on the melting behavior of PBSA in the first two blends, whereas in the latter two blends with higher amounts of DCP, a shift of PBSA melting temperature to lower temperatures was observed.

This result could be attributed to the statements made by Mani *et al.* [48]. They support the notion that a higher concentration of DCP leads to an increase in chain scission and a decrease in the molecular weight of PBSA. Consequently, when PBSA is replaced by PBSA-g-MA in the blend to improve compatibility, the resulting shorter PBSA macromolecules have more mobility. This, in turn, leads to a reduction in the melting temperature of the blend.

Overall, the crystallinity of the blends remained relatively unchanged when compared to the uncompatibilized blend. This result is again attributed to the processing conditions.

- *Overview*

From our results, it appears that the use of a low amount of MA in the preparation of PBSA-g-MA promotes better ductility of the final compatibilized blends. The analysis of the microstructure of PLA/PBSA/PBSA-g-MA/0.25/2 confirms that the blend surface tension has been improved as seen by the reduction of the dispersed phase size. This is in favor of saying that some compatibility has been achieved between the two phases. However, considering the DMTA results, immiscibility remains and that is the case for all the blends. This could explain that there is not significant improvement in the impact strength of the blends.

The effect of DCP in the preparation of PBSA-g-MA doesn't seem to affect the mechanical properties. However, it seems to affect the melting temperature of PBSA, demonstrating a reduction in molecular weight appearing at high initiator concentration.

Conclusion

The efforts to improve the toughness of the PLA/PBSA blend through reactive extrusion have not yielded successful results. Notably, the impact resistance, the primary mechanical parameter targeted for enhancement, remained unchanged throughout all attempted methods. However, it is worth noting that the ductility, which was already favorable in the uncompatibilized blend, showed signs of improvement in the two last attempts, which are regarded as the most promising compatibilization approaches of this work.

Nevertheless, this work allowed to identify the strengths and difficulties of each approach.

The first attempt using Dicumyl peroxide (DCP) as a reactive agent to compatibilize the blend through a one-step reactive extrusion showed no improvement in ductility or impact resistance. Nevertheless, a slight enhancement in the interaction between the polymers was hypothesized at low DCP concentrations, from the comparison of the results with the bibliography. It was also determined that only low amounts of DCP could promote this enhancement, as higher concentrations result in chain-scission.

The second method, involving also a one-step reactive blending using Maleic anhydride (MA) to enhance blend compatibility in the presence of DCP, failed to improve the blend properties. In fact, it led to a decrease in the overall mechanical properties of the blends, attributed to chain-scission occurring during the process.

To address the challenges related to the concurrence of degradation over interfacial bonding, the use of a two-step reactive extrusion was tried. The objective was to achieve a more precise regulation of the reaction in order to promote compatibility. In both scenarios, utilizing PLA-g-MA and PBSA-g-MA, prepared in an initial extrusion process, as compatibilizers for the blend, the results demonstrated increased ductility compared to the blend without compatibilization. The analysis of the morphology demonstrated that the dimension of the dispersed phase domains was reduced resulting in more homogeneous blends. However, despite these improvements, the impact resistance of the blends did not experience any noticeable enhancement, resulting in an overall low toughness material. Additionally, the degradation, specifically in the case of PLA-g-MA preparation, remained a concern. However, it is worth noting that the impact of this degradation was reduced compared to the direct extrusion attempt with MA.

Moreover, it was demonstrated through thermal analyses, that the blends exhibited significantly low crystallinity, indicating their amorphous nature. That was attributed to the fast cooling rate of the injection molding process, inhibiting the crystallization of PLA.

Given the promising results observed with PLA/PBSA/PLA-g-MA/X/Y and PLA/PBSA/PBSA-g-MA/X/Y blends, there are potential avenues for future research. First, it would be interesting to investigate the grafting level of MA onto PLA or PBSA using techniques such as Fourier-transform infrared spectroscopy (FTIR) or titration. Then, exploring different processing conditions could be valuable to optimize interactions between the polymers and the reactive agent. Additionally, working on the injection molding process to induce crystallinity could be a solution for the enhancement of the toughness of the blend.

Overall, this study provided valuable insights into the difficulties encountered when blending polymers with reactive agents through the process of reactive extrusion. The control of factors such as reactive agent concentrations is crucial for achieving compatibility. Additionally, the selection of appropriate processing conditions, including temperature, screw speed, residence time, and shear rate, play a critical role in determining the extent of reaction between the polymers and the reactive agent. Improper control of these parameters can result in incomplete reactions or polymer degradation, negatively impacting the quality and performance of the resulting blend.

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