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Biodegradable blends from bacterial biopolyester PHBV and bio-based PBSA: Study of the effect of chain extender on the thermal, mechanical and morphological properties

Patricia Feijoo^{1,2}, Amar K. Mohanty^{2,3,*}, Arturo Rodriguez-Uribe^{2,3}, José Gámez-Pérez¹, Luis Cabedo¹ and Manjusri Misra^{2,3,*}

¹ Polymers and Advanced Materials Group (PIMA), Universitat Jaume I (UJI), Avenida de Vicent Sos Baynats/n, 12071 Castelló, Spain

² Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, Guelph, Ontario, Canada

³ School of Engineering, University of Guelph, Thornbrough Building, 80 South Ring Road E, Guelph, Ontario N1G 1Y4, Canada

* Correspondence: mohanty@uoguelph.ca, mmisra@uoguelph.ca

Abstract: Being aware of the global problem of plastic pollution, our society is claiming new bioplastics to replace conventional polymers. Balancing their mechanical performance is required to increase their presence in the market. Brittleness of bacterial poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was attempted to be decreased by melt blending with flexible starch-based poly(butylene succinate-co-butylene adipate) (PBSA). An epoxy-functionalized chain extender was used to enhance interaction between both immiscible biopolyesters. Mechanical performance, morphology, rheology, and crystallization behavior of injection-molded PHBV-PBSA blends (70-30, 50-50, and 30-70 wt %) were assessed in the presence and absence of the chain extender. Crystallization of PHBV was hindered, which was reflected in the improvement of mechanical properties. When PBSA >50%, the homogeneity of results increased within the same sample while for PHBV-PBSA 70-30 wt % the elongation was 45% higher. During the flexural test, it changed from brittle to non-breakable. The additive did not change the type of morphology developed by each blend nor the toughening mechanisms, so impact strength was barely affected. However, it reduced the size of dispersed phase domains due to a viscosity change, improving their processability. The higher the PHBV in the blend, the higher the effect of the chain extender.

Keywords: poly-3-hydroxybutyrate-co-3-hydroxyvalerate; poly(butylene succinate-co-butylene adipate); chain extender; Joncryl®; polymer blend; reactive compatibilization.

1. Introduction

The scientific community has warned about the worldwide accumulation of plastic debris and their associated dangers for more than 10 years [1,2]. Despite this notice, plastic pollution is an up-to-date problem, and its forecast by 2040 promises an inauspicious scenario if the global production-disposal system does not change [3]. Many efforts have been devoted to aware all levels of the plastic industry, including society, about this environmental issue. However, although recovery and thermo-mechanical recycling improve every year, the waste management system remains inefficient and does not work globally [2,4,5].

Bearing in mind the transition towards a sustainable circular economy, the governments have banned single-use or short-shelf-life plastic products to boost alternative solutions to be developed [3,6,7]. Replacing commodities with bioplastics is one of the approaches considered to solve this environmental problem, among other complementary strategies like biotechnological upcycling [8,9]. The ambiguous terminology *bioplastic* comprehends either bio-based or biodegradable polymers, as well as those polymers that feature both characteristics. Moreover, to add more uncertainty to this nomenclature, the meaning of *biodegradable* is dependent on the environment considered (marine, compost, home-compost, soil, landfill) [7,10]. In the research field, the most common biodegradable polymers studied are poly(lactic acid) (PLA), poly(3-hydroxybutyrate) (PHB), and its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) as well as the petroleum-based poly(butylene adipate terephthalate) (PBAT), or other biopolyesters that could be bio-based such as poly(ϵ -caprolactone) (PCL), poly(butylene succinate) (PBS) and its copolymer poly(butylene succinate-co-butylene adipate) (PBSA) [8]. Although all of them are commercially available options, their presence in the market as consumer products (packaging, agriculture mulches, fabrics, etc) is mainly limited to flexible PBAT and rigid PLA, due to the more difficult processing of bioplastics [11]. Furthermore, biodegradable bioplastics can satisfy the technical requirements of only 35% of the current plastic applications [10]. This study is focused on bio-based PBSA and PHBV because under the literature they are considered biodegradable. Taking into account the complementary properties of both biopolymers as well as their commercial

availability, though PBSA is proposed to modulate the mechanical behavior of PHBV by improving its flexibility.

PHBV (see chemical structure in Fig. 1-A), along with its homopolymer PHB, are the most studied polyhydroxyalkanoates (PHA). PHAs are thermoplastics synthesized by bacteria as intracellular energy storage under nutrient-unfavorable conditions when carbon is in excess. Moreover, they can be potentially produced from renewable feedstocks such as dairy industrial wastewater [12]. Due to their full biodegradability, biocompatibility, and tunable mechanical performance, PHAs have been found suitable for packaging, pharmaceutical, and biomedical applications [13–16]. As a consequence of its highly crystalline nature, PHBV with low 3-hydroxyvalerate (3HV) content shows excellent barrier properties to oxygen and water [4], and balanced mechanical properties in terms of a tensile strength similar to polypropylene (PP) and relatively high Young's modulus (1-5 GPa) [17]. For the same reason, PHBV exhibits an inherent brittleness that progresses over time due to physical ageing [14,18]. In addition, its processability is limited by the closeness between its degradation temperature and its melting point [19,20], it narrowing its processing window in commonly used technologies like injection-molding or thermoforming [21].

PBSA is a copolyester synthesized by polycondensation of 1,4-butanediol with succinic and adipic acids (see chemical structure in Fig. 1-A). Nowadays, alternatives to the petrochemical production of succinic acid as the fermentation of glucose from biomass like corn/cassava starch among other sources, have led manufacturers to develop bio-based grades of PBS and PBSA [8,22]. PBSA possesses a ductile behavior and low crystallinity, with mechanical properties similar to polyolefins like polyethylene (PE), high impact strength as well as thermal and chemical resistance [23,24]. Thus, this thermoplastic shows excellent melt processability and re-processability by extrusion, injection molding, thermoforming, or film blowing [24].

Melt blending is a convenient method of combination of polymeric components, usually performed in extruders, to develop new materials with enhanced performance. Widely used in the industry, it is a simple and cost-effective way to tailor the properties of the polymers compared to the synthesis of new polymers [25,26]. For instance, Muthuraj et al. [27] and Pesaranhajiabbas et al. [28] demonstrated melt blending to be a successful method for PBS/PBAT and bioPBSA/PBAT systems respectively. In both blends, the formation of PBS(A)/PBAT copolymers by transesterification enhanced elongation at break along with the

tuning of morphology. However, simple blending in the melt state of immiscible polymers typically results in unsatisfactory physico-mechanical properties [29]. Actually, Kennouche et al. [30] reported the immiscibility of PHBV and PBS and showed that, although the crystallization rate of PHBV is hindered by the presence of PBS, the performance of the blends was modified according to the ratio of their components. Assuming a similar behavior with its copolymer PBSA, improvement of the miscibility (compatibilization) of the biopolymers is required to reach a synergistic performance by improving the interfacial adhesion between phases [29]. For this purpose, reactive extrusion (REx) allows the synthesis or modification of a polymeric material simultaneously with its processing [31].

REx technology has been demonstrated to be an effective way to improve the compatibility of polymer blends by chain extension, branching, grafting, or cross-linking [26,32]. For instance, Ma et al. [33] successfully used dicumyl peroxide (DCP) as a grafting initiator for blends of PHBV and PHB with PBS. Enhanced compatibility between polymers increased the elongation from <10 to 400% in 80PHBV-20PBS and the impact strength of 70PHB-30PBS was improved by 500%, while crosslinking did not affect their compostability. Rodriguez-Urbe et al. [34] studied the effect of maleic anhydride (MA) in PHBV/bioPBS system with hydrated magnesium silicate. In this case, grafted bioPBS-g-MA and PHBV/bioPBS-g-MA enhanced the dispersion of the components and their interaction with each other leading to increased tensile and flexural strength, elongation at break and barrier properties compared to non-compatibilized composites. Recently, Zytner et al. [35] effectively compatibilized PHBV and PCL using a mixture of a crosslinker (TAC) and a peroxide. The reduced particle size of PCL and the decreased interfacial gap between both phases resulted in improved toughness and increased elongation at break by 380%.

Typically, chain extenders have been used to improve thermal stability, the length of broken chains during processing, melt strength, and viscosity [36]. However, they also can act as compatibilizing agents by enabling branching and linking between polymer chains through their functional groups [37,38]. Specifically, chain extenders containing epoxy groups have been extensively used in polyesters. The epoxy groups may react with -OH and -COOH end-groups of the polyester promoting also the formation of copolymers [36]. It is noteworthy that their effectiveness depends on multiple factors such as their concentration in the blend, or the molecular weight (Mw) and carboxyl content of the polyesters [38,39]. Epoxy-based chain

extenders have been proven to be effective in PBS or PBSA blends that include PLA. However, their use in short-chain length PHA blends has been barely studied [37]. Palai et al. [40] produced PLA/PBSA blown films using an epoxy-functionalized styrene acrylate (ESA) as a compatibilizer, leading to improved mechanical behavior as well as optical and anti-slip properties. Wang et al. [41] improved the mechanical properties of 80/20 wt % poly(butylene succinate-butylene terephthalate) (PBST) and PLA blend by adding an epoxy-functionalized oligomeric acrylic copolymer (Joncryl® ADR-4370). By gel permeation chromatography (GPC), Wang et al. [41] determined the increase in Mw due to the formation of PBST-g-PBST, PLA-g-PLA and PBST-g-PLA copolymers. The optimal amount of the chain extender was found to be 0.3 phr while a higher amount promote the chain extension of the polymers with themselves. By contrast, Safont et al. [42] did not find the epoxy-based chain extender Joncryl® ADR-4368 the most effective additive to compatibilize PHBV and thermoplastic polyurethane (TPU) blends.

There is a lack in literature about PHBV and bio-based PBSA blends and further, about their compatibilization. To the best of our knowledge, this is the first ever report to the scientific literature on reactive extrusion of these two biodegradable and bio-based polyesters. Therefore, the purpose of this research was to study the compatibilizing effect of the presence and amount of the epoxy-based chain extender Joncryl® ADR-4468 on PHBV/PBSA blends ranging from 70% to 30% of PHEV. The materials obtained by reactive extrusion and injection molding, were studied via morphological, thermal, rheological, and mechanical behavior.

2. Materials and methods

2.1. Materials

PHBV (commercial grade ENMAT Y1000P) was acquired from Tianan Biologic Material Co. (Ningbo, China). The 3HV content of the material is 3 wt %. Bio-based PBSA (commercial grade bioPBS FD92PM, obtained from sugarcane, cassava or corn) was supplied by PTT MCC Biochem Co. (Bangkok, Thailand). The epoxy-based chain extender, with the trade name Joncryl® ADR-4468, was purchased from BASF (Germany). Joncryl® will be referred to as JON throughout the article.

2.2. Preparation of blends

The methodology followed was adapted from that previously described by our group elsewhere

[34].

2.2.1. Melt blending

Prior to processing, pellets of PHBV and PBSA were oven dried for 24 h at 80 and 60°C respectively. Blends containing 70, 50 and 30% of PHBV were prepared in a MIC27/GL-480 (Leistritz, Germany) co-rotating twin-screw extruder with a $\varnothing = 27$ mm and a L/D ratio = 48. Both polymers were manually mixed and added to the hopper. The extrusion was conducted at 100 rpm and the temperature processing profile was set at 165°C in all 12 zones and nozzle, reaching a melt temperature of the material at the die of around 175°C. The strands of the material were chilled in a water bath and pelletized. For the sake of comparison, neat polymers were also extruded using 180°C for PHBV and 160°C for PBSA. Alike polymer matrices were in situ reacted with two different concentrations of JON (0.3 and 0.5 phr) in the same equipment and conditions (165°C and 100 rpm) than non-compatibilized blends. However, the temperature reached by the materials at the die was lower, around 170°C. Previously to extrusion, powdered JON was manually mixed in a zip-lock plastic bag with dry PHBV (80°C) trying to adhere the compatibilizing agent to the hot surface of the pellets. Subsequently, covered PHBV is mixed with warm PBSA pellets (60°C) and added then to the hopper. The so-obtained samples were named as PHBV/PBSA/JON indicating the content of each component in weight percentage (wt %) for polymers and in parts per hundred rubber (phr) for the additive. Table 1 summarizes the compositions studied.

Table 1. Composition and nomenclature of studied blends

Sample code	PHBV (wt %)	PBSA (wt %)	JON (phr)
100/0/0	100	0	0
70/30/0	70	30	0
70/30/0.3	70	30	0.3
70/30/0.5	70	30	0.5
50/50/0	50	50	0
50/50/0.3	50	50	0.3
50/50/0.5	50	50	0.5
30/70/0	30	70	0
30/70/0.3	30	70	0.3
30/70/0.5	30	70	0.5
0/100/0	0	100	0

Previously to the following processing by injection molding, pelletized samples were dried at

60°C for 48 h to reach a moisture content <1%.

2.2.2. Injection molding

Using a Mini-Jector SSP-1 injection molder (MPM, Ohio, USA) the samples were shaped into tensile, flexural and impact specimens. Temperature profiles used are gathered in table 2. Pressures were applied to materials during 15 seconds of packing. Pressures needed to be increased as PBSA content was higher in the blend. Data are summarized in table 2.

Table 2. Temperature and pressure profiles used in injection-molding of the materials.

PHBV/PBSA/JON	Temperature (°C)		Pressure (psi)	
	rear barrel	front barrel-nozzle	1st fill	2nd fill-pack
100/0/0	180-180-180°C		400-350-200	
70/30/0			450-350-200	
50/50/0	170-170-170°C		500-400-250	
30/70/0			600-500-350	
70/30/0.3-0.5	175-175-175°C		500-400-300	
50/50/0.3-0.5	170-170-175°C		550-450-350	
30/70/0.3-0.5	160-170-175°C		650-550-450	
0/100/0	170-170-160°C		800-750-700	

2.3. Characterization of blends

2.3.1. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

FTIR spectra of the materials were collected in a Nicolet 6700 Thermo Scientific spectrometer in transmission mode and equipped with an attenuated total reflection accessory (ATR), using a resolution of 4 cm⁻¹ and 64 scans in the range of 400–4000 cm⁻¹.

2.3.2. Mechanical properties

Prior to testing, samples were conditioned according to ASTM D618 [43] for 48h at room temperature. Flexural and tensile properties were measured by an Instron universal testing machine model 3382 (Massachusetts, USA). Tensile tests were carried out at a crosshead speed between 5 and 50 mm/min according to ASTM D638 standard [44] while flexural properties were tested at 14 mm/min and 52 mm of span following ASTM D790 standard [45]. The notched Izod impact strength was measured by using a Zwick Roell Impact Tester model HIT25P (Ulm, Germany) with a 2.75 J pendulum. To determine statistical significance of chain extender (Joncryl) addition, mechanical performance data of each blend

(tensile/flexural modulus, elongation at break, and tensile/flexural/impact strength) were subjected to analysis of variance (ANOVA) using Statgraphics Centurion XVI version 16.1.17 (Manugistics Corp. Rockville, USA). Significant differences were determined using the least significant difference test ($p < 0.05$).

2.3.3. Morphological analysis

Morphology analysis of impact fractured surfaces of neat polymers and blends was carried out on a Phenom ProX (The Netherlands) microscope at a voltage of 10 kV. Prior to the analysis, samples were gold coated for 6 seconds.

2.3.4. Thermal properties

Thermogravimetric analysis (TGA) of blends and neat polymers studied was performed in a Q500 TG-analyzer (TA Instruments, New Castle, USA). Using a nitrogen atmosphere, extruded pellets were heated from 30 to 600°C at 10°C/min. The onset temperature ($T_{10\%}$), maximum degradation temperatures of each component (T_{max}) and ash residue at 600°C (R_{600}) were determined from TG and derivative (dTG) curves.

Differential scanning calorimetry (DSC) experiments were conducted in a Q200 DSC-calorimeter (TA Instruments, New Castle, USA) under a nitrogen flow of 50 mL/min and using samples of approximately 12 mg from injection molded specimens. All compositions studied were firstly heated from 40 to 200°C at 40°C/min, cooled to -70°C at 10°C/min and secondly heated to 200°C at 10°C/min. Melting and crystallization temperatures (T_m , T_c) and corresponding enthalpies (ΔH_m , ΔH_c) were determined from the second heating and cooling curves. The degree of crystallinity (X_c) was quantified by using equation 1:

$$X_c (\%) = \frac{\Delta H_m}{\Delta H_m^0 \cdot W_p} \cdot 100 \quad (1)$$

where ΔH_m represents the experimental melting enthalpy, W_p is the weight fraction of the polymer, and ΔH_m^0 is the theoretical melting enthalpy of 100% crystalline polymer. The theoretical melting enthalpies of 100% crystallized polymers used are 146 J/g for PHBV [46,47] and 135 J/g for PBSA [48].

2.3.5. Thermomechanical studies

Rheology of neat polymers and blends in the presence and absence of JON was studied using a 25 mm parallel-plate rheometer (MCR 302, Anton Paar, Germany) with a gap of 1 mm. Injection

molded samples were used. Frequency sweep experiments were conducted from 100 to 0.01 Hz at a fixed strain of 0.1% and 175°C.

Dynamic mechanical analysis (DMA) was performed from -70 to 80°C at a heating rate of 3°C/min at 1 Hz and 15 μm amplitude using a Q800 dynamic mechanical analyzer from TA Instruments (New Castle, USA). The heat deflection temperature (HDT) was measured on the same equipment with a 3-point bending clamp and setting a heating rate of 2°C/min. The test was conducted under a load of 0.455 MPa as indicated by ASTM D648 standard [49].

2.3.6. Melt flow index (MFI)

MFI of the neat polymers and their blends was measured in a melt flow indexer MFI-2000 Series (Qualitest, USA) according to ASTM D1238 standard [50], at 190°C and 2.16 kg load.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (ATR-FTIR)

FTIR spectra of PHBV and PBSA are plotted in Fig. 1-A with characteristic peaks marked. Their chemical structures are also displayed. According to literature, distinctive peaks of PHBV at 1261, 1452, 2932 and 2975 cm^{-1} correspond to C–O–C stretching, asymmetric deformation of CH_3 and –CH stretching of amorphous and crystalline phase respectively [30]. In the case of PBSA, C–O–C stretching is located at 1155 cm^{-1} and –CH stretching appeared as a single peak at 2946 cm^{-1} [51]. The most intense peak for both polyesters corresponds to carbonyl (C=O) of the ester groups, situated at 1711 cm^{-1} for PBSA and 1718 cm^{-1} for PHBV.

As can be seen in Fig. 1-B spectra of pristine blends were an overlapping of the typical peaks of the neat components (marked in grey for PHBV and black for PBSA), and their intensity progressively changed according to the proportion of each in the blend. No relevant interaction seemed to take place between PHBV and PBSA since no shifting of peaks was observed.

In Fig. 1-C, JON spectrum and its general structure are shown. As previously described by our group, the bands 1177, 907, 843 and 758 cm^{-1} were assigned to $\text{CH}_2\text{--O--CH}$ stretching of the epoxy group [52]. Chain extension of PHBV (PHBV–JON–PHBV) and PBSA (PBSA–JON–PBSA) could be possible due to the susceptibility of the epoxy group to react by ring-opening with both hydroxyl and carboxyl groups of the polyesters [53]. During melt blending, both polymers and the chain extender were in-situ reacted simultaneously which may lead also to the linking of PHBV and PBSA (PHBV–JON–PBSA), the additive acting in that case as a

compatibilizing agent [37].

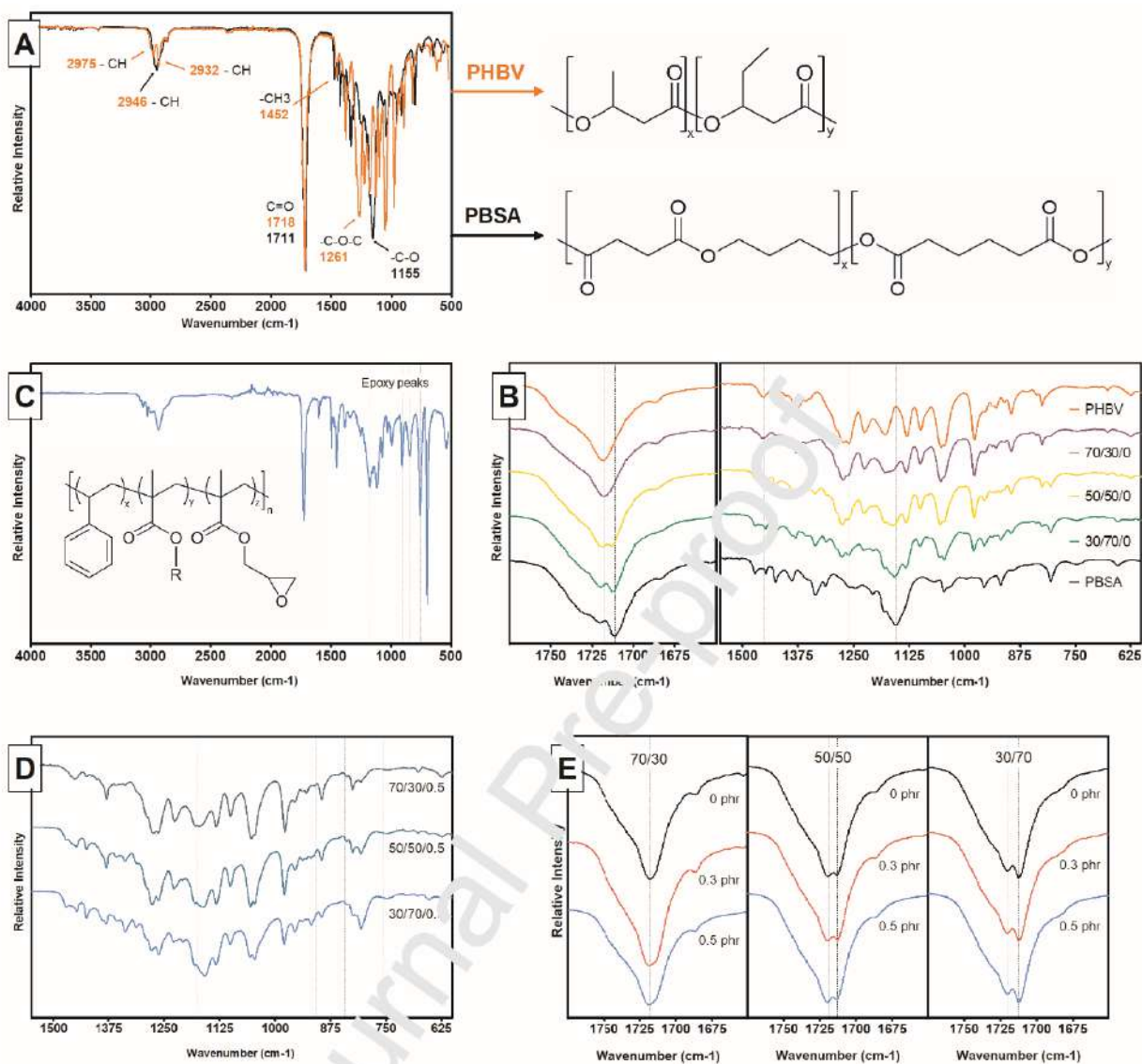


Figure 1. FTIR spectra of: A) PHBV and PBSA with their characteristic peaks indicated in grey and black respectively; B) Pristine blends vs neat polymers; C) Joncryl® ADR-4468 with characteristic peaks of epoxy marked; D) Fingerprint region of blends with 0.5 phr of compatibilizing agent added and epoxy peaks highlighted; and E) Detail of C=O peak of each blend with increasing amount of JON.

Even with the addition of the highest amount of the chain extender (0.5 phr), the peaks of the epoxy group were not observed (see Fig. 1-D), suggesting a complete reaction of the additive. However, there were no new bands or peak shifts with respect to the spectra of the blends without JON (see Fig. 1-D and 1-E). This may indicate no specific chemical interactions or, at least, not detectable by FTIR as Kennouche et al. [30] pointed out for grafted PHBV-PBS blends.

3.2. Mechanical properties

The mechanical behavior of binary PHBV-PBSA blends containing different amounts of the chain extender was studied by tensile, flexural and impact tests. Results are summarized in table 3.

Table 3. Mechanical properties of PHBV/PBSA/JON compositions

Formulation	Tens. strength (MPa)	Tens. modulus (GPa)	Elong. at break (%)	Flex. strength (MPa)	Flex. modulus (GPa)	Impact (J/m)
100/0/0	33.5 ± 1.3	3.26 ± 0.17	1.7 ± 0.3	68.1 ± 0.9	3.44 ± 0.08	20 ± 2
70/30/0	30.7 ± 1.1	1.95 ± 0.09	5.5 ± 1.4	45.9 ± 1.8	2.02 ± 0.08	22 ± 8
70/30/0.3	32.1 ± 0.6	2.44 ± 0.24	5.8 ± 0.2	35.4 ± 1.7	1.21 ± 0.06	26 ± 2
70/30/0.5	30.8 ± 0.8	1.87 ± 0.14	8.0 ± 1.9	30.5 ± 0.8	1.02 ± 0.03	23 ± 2
50/50/0	28.2 ± 0.8	1.57 ± 0.15	19.5 ± 11.7	37.9 ± 1.5	1.55 ± 0.03	42 ± 4
50/50/0.3	28.4 ± 0.7	1.62 ± 0.36	12.7 ± 2.9	27.5 ± 0.5	0.92 ± 0.02	34 ± 6
50/50/0.5	27.9 ± 0.5	1.63 ± 0.12	15.1 ± 7.4	26.7 ± 0.6	0.90 ± 0.02	38 ± 4
30/70/0	23.8 ± 0.4	0.97 ± 0.07	157.8 ± 65.9	27.5 ± 1.0	0.92 ± 0.03	260 ± 47
30/70/0.3	23.4 ± 1.1	1.11 ± 0.14	100.2 ± 37.6	18.9 ± 0.6	0.60 ± 0.02	261 ± 63
30/70/0.5	24.0 ± 0.6	1.06 ± 0.10	144.0 ± 41.5	19.2 ± 0.7	0.56 ± 0.03	249 ± 30
0/100/0	17.0 ± 2.7	0.31 ± 0.07	207.0 ± 43.3	14.3 ± 0.2	0.31 ± 0.005	409 ± 29

3.2.1. Tensile properties

The Young's modulus, tensile strength and elongation at break of all range formulations studied are compiled in Fig. 2. Crystallinity, morphology and interfacial adhesion play a significant role in mechanical behavior. Derived from its high crystallinity, PHAs like PHBV show an intrinsic fragile character that further progress with time [54]. Under tensile stress, neat PHBV exhibited a typical brittle fracture with a tensile strength of 33.5 MPa and an elongation at break lower than 2%. As PBSA content increased in pristine blends, elongation at break improved while tensile strength and modulus gradually decreased consequently by the addition of a softer polymer [55,56].

The ability of high ductile PBSA to confer mobility to the whole structure of the blends depended on the morphology developed in a specific PHBV/PBSA ratio. Morphology will be further discussed in section 3.3. Blend 70/30/0 showed no yielding, indicating that stiff PHBV still dominated the mechanical behavior because of the poor compatibility between both polymers. Blend 50/50/0 demonstrated slight yielding and whitening, indicating that tensile stress could be dissipated by the deformation of PBSA domains. However, fibrillary fracture led to premature failure of the sample indicating again poor compatibility between phases. As a

consequence of heterogeneous morphology, a great standard deviation was found for this blend. In the case of blend 30/70/0, the stress-strain curves showed distinct yielding, hardening and multiple yielding points in some specimens. Elongation at break was substantially improved by 93% compared to neat PHBV. However, compared to the major phase in this case (PBSA), elongation at break was decreased by 24% while modulus and tensile strength (stiffness) are increased by 313% and 106% respectively. Dispersed PHBV seemed to act like a stress concentrator for PBSA promoting the premature failure of the material.

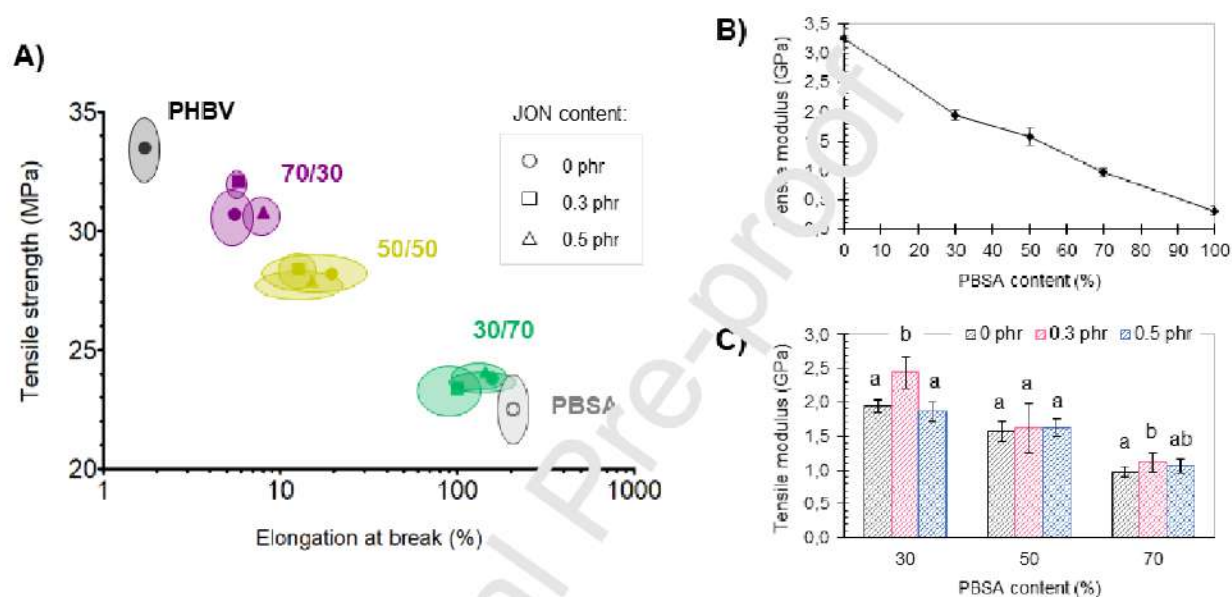


Figure 2. A) Tensile strength vs elongation at break of all compositions studied. B) Tensile modulus of neat polymers and pristine blends. C) Tensile modulus of blends in presence and absence of the chain extender. Different letters (a-b) within the same blend indicate significant differences ($p < 0.05$) due to effect of JON concentration.

In an attempt to improve the adhesion between both polymers by chemical bonding, JON was added in two different concentrations. The effect of the additive on the tensile properties was dependent on PHBV/PBSA ratio. The greatest improvement was exhibited by 70/30 which elongation at break increased by 5% with the addition of 0.3 phr of JON and 50% with 0.5 phr (significant influence of JON concentration, $p < 0.05$). In case of 50/50 blend, statistical analysis revealed that JON did not significantly affect ($p > 0.05$) either modulus, strength or elongation. In case of 30/70 blend, elongation at break was not significantly influenced ($p > 0.05$) by the presence and amount of JON. By contrast, there was statistically significant differences ($p < 0.05$) when tensile modulus was analysed. Taking into account only their

average values, elongation at break decreased approximately by 35% for both blends with the addition of 0.3 phr JON. However, with 0.5 phr JON, elongation is partially recovered until initial values of the non-compatibilized blend. Similarly, Przybysz et al. [57] found a decrease and increase in elongation at break of PHB/PCL blends using 0.5 and 1.0 phr of DCP as compatibilizer. Partial compatibilization may concentrate the stress on the new mobility restricted points of the molecular chains. In the same way, Wang et al. [41] reported that an excess of compatibilizer leads to crosslinking of the polymers affecting the free mobility of their molecular chains and thus, reducing their mechanical performance. Both authors exposed the importance of finding the suitable amount of additive for each type of blend. Furthermore, except for the 70/30/0.3 blend, tensile strength was barely affected by the presence of JON and tensile modulus was slightly increased.

The improvement of compatibility by chain extension seemed to allow certain synergy between PHBV and PBSA leading to homogeneous results between specimens and a higher yielding of the polymer matrix without compromising tensile strength and modulus. Entanglement between both polymers through JON may limit the crystallization of PHBV resulting in higher elongation. In addition, the linked structure of both polymers could provoke that PBSA transmits mobility to the whole molecular structure. Crystallization behavior will be further discussed in section 3.4.2.

3.2.2. Flexural properties

Flexural modulus and strength of neat polymers and blends are displayed in Fig. 3. Both parameters followed the same trend as tensile properties. As PBSA content increased, flexural modulus and strength of PHBV progressively decreased (increasing flexibility) as expected with the addition of a ductile polymer [33]. Mobility of PBSA chains at room temperature (low T_g) and its low crystallinity may allow the mobility of the whole matrix under a 3-point bending stress. Flexural modulus of PHBV was reduced by 41, 55 and 73% accordingly to 30, 50 and 70% of PBSA in the blend. However, although adding 30% PBSA led to the highest reduction of the modulus (or the highest increase of flexibility), it is noteworthy that 70/30/0 is the only blend that fractured during the test in the same brittle way as neat PHBV. This failure may indicate poor compatibility between phases and thus, stress could not be dissipated in the PBSA structure.

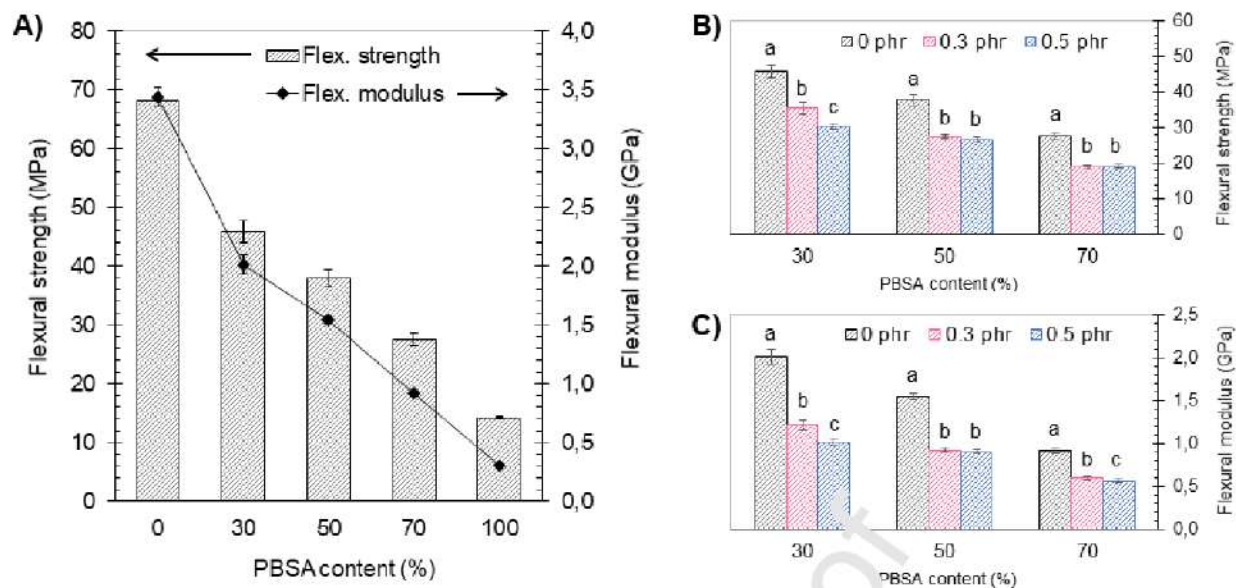


Figure 3. A) Flexural properties of neat polymers and pristine PHBV/PBSA blends. B) Flexural strength of PHBV/PBSA blends in presence and absence of chain extender. C) Flexural modulus of PHBV/PBSA/JON formulations. Different letters (a-c) within the same blend indicate significant differences ($p < 0.05$) due to effect of JON concentration.

Regarding the compatibilized blends, statistical analysis revealed no significant differences ($p > 0.05$) in flexural parameters regardless the concentration of JON for all blends. With exception of blend 70/30 and 30/70 modulus ($p < 0.05$), flexural modulus and strength decreased around 40% and 30% respectively. According to Liu et al. [58], flexural as well as tensile modulus are more sensitive to changes in matrix/surface than strength. In the case of 30%-PBSA blend, the addition of 0.5 phr of JON supposed an additional 10% reduction in both properties. Moreover, the presence of 0.3 phr was enough to change this blend into a non-breakable one under a constant 3-point bending load. As will be discussed in section 3.3, the addition of the chain extender resulted in better dispersion of the rubbery phase and smaller droplet size, which may enhance the interaction between both polymers because of the higher contact surface [59].

3.2.3. Impact

Impact strength and type of break of neat polymers and blends in presence and absence of JON are shown in Fig. 4. As expected, notched Izod impact strength increased with increasing PBSA content in blends [56], with intermediate values ranging from 20 J/m of PHBV to 409 J/m of PBSA. Nevertheless, the magnitude of this effect is different for each blend. Adding 30% of PBSA slightly increased impact strength to 23-26 J/m while adding 50% doubled the value of PHBV. Both blends showed a brittle complete break as that of neat PHBV. In the case of

phase reversed blend with 70% PBSA, impact strength is increased 10 times compared to neat PHBV and the blend exhibited hinge fracture. However, in comparison with neat PBSA, which was the major phase in this case, impact strength half decreased.

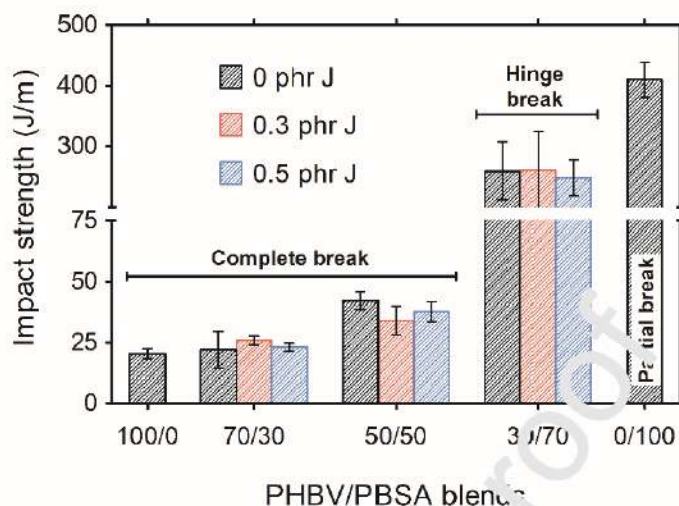


Figure 4. Impact strength of PHBV, PBSA and their blends in presence and absence of the chain extender.

Moreover, there was no statistically significant influence ($p > 0.05$) of the incorporation of the chain extender in impact strength of any blend. Not only interfacial adhesion but also phase morphology play an important role in impact and toughening [60]. In presence of a sudden load, JON was revealed as a poor compatibilizing agent for PHBV/PBSA blends. As will be mentioned in section 3.3, phase morphology changed with the addition of JON regarding the size of the domains of the dispersed phase. Nevertheless, non different toughening mechanisms were detected in comparison with pristine blends.

3.3. Morphological analysis

Morphology of the impacted fracture surface of neat polymers and blends was studied by SEM. Representative images of each formulation are displayed in Fig. 5. Neat PHBV presented localized thin cracks and a flat surface typical of a brittle fracture while neat PBSA showed smooth and wavy surface evidence of its resistance to break. Regarding pristine blends, all micrographs indicated that both biopolyesters were immiscible by showing discrete domains of each polymer. Up to 50% of PBSA content, PHBV is kept as the continuous phase while PBSA is the dispersed phase. Blend with 30% of PBSA showed drop-in-matrix morphology with voids and PBSA pulled-out droplets of a broad variety of sizes. Blend with 50% of PBSA showed a non-distinguishable globular morphology with fibrillary threads of

PBSA. After etching with chloroform, a heterogeneous transition structure to co-continuity was found composed of small spherical droplets and indeterminate-shaped curvy islands. These big PBSA domains may be the consequence of coalescence after increasing the volume fraction of the polymer and thus, reducing the distance between domains [28]. Blend with 70% of PBSA presented big cracks in a wavy surface at low magnification (x350) indicating the dominance of the continuous phase. At x3500 magnification, ellipsoidal PHBV domains can be seen homogeneously distributed but also diverse pull-outs were observed all over the surface.

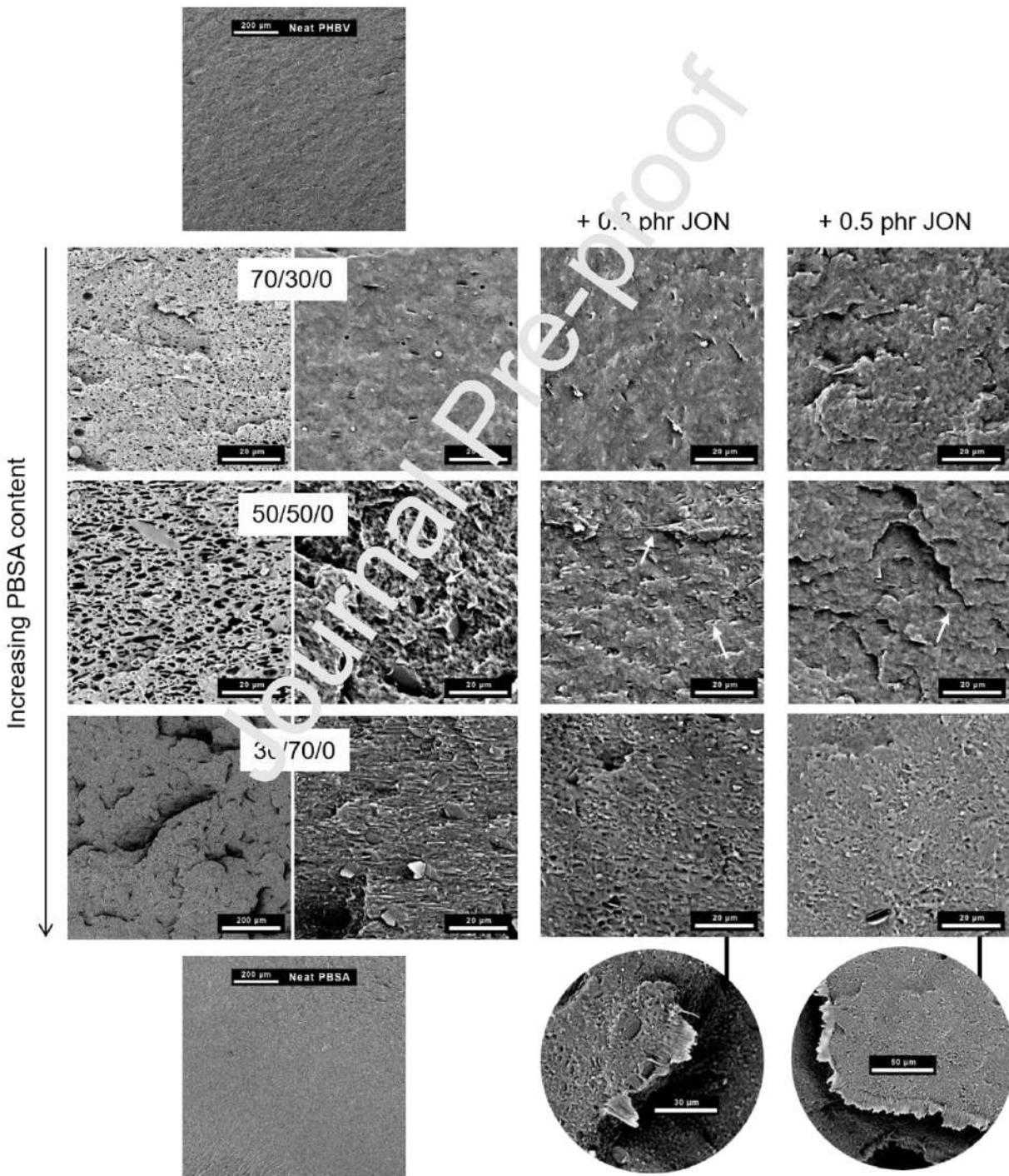


Figure 5. Representative SEM micrographs of neat polymers and pristine blends (top to

bottom), and blends with added JON (left to right). Left images show blends after selective etching of PBSA with CHCl_3 . Black zones correspond to PBSA domains. In the case of 30/70 PHBV/PBSA blend, general morphology at lower magnification (without etching) is displayed.

Regardless of the morphology, all formulations showed poor compatibility as can be distinguished by the presence of numerous pull-outs, voids and gaps at the interface of domains. Morphology correlates also with tensile behavior: brittle fracture for the blend with 30% of bioPBSA (drop-in-matrix or sea-island), heterogeneous failure and fibrous fracture for the blend with 50% of bioPBSA, and long yielding before fracture for the blend with 70% of bioPBSA. In a similar brittle/ductile blend composed by PHB/PC, Nishida et al. [61] reported that sea-island morphology led to high tensile strength while low tensile strength was associated with co-continuous morphology.

In presence of JON, the type of morphology was observed the same for each blend. More specifically, the voids found in the 70/30 PHBV/PBSA blend, are smaller in both 0.3 and 0.5 phr JON concentrations. It was necessary to zoom in until x5000 magnifications to find PBSA domains with the same size than in the blend without compatibilizer. This size reduction of the domains could be the consequence of a change in viscosity ratio. For instance, Nerkar et al. [56] improved drop-in-matrix morphology of PLA/PHO blends by increasing the viscosity of PHO using a peroxide crosslinker. Hongsriphan et al. [62] found that, when the difference of melt viscosities of PBS and polyamide11 was reduced by adding Joncryl® ADR-4300, the disperse phase was easily broken into smaller domains during processing and thus, more homogeneously distributed inside PBS matrix. Actually, the chain extender could not only act at the boundaries of immiscible polymers domains (interfacial bonding), but also inside the domains (intra-domain interactions). Bonding PHBV and PBSA with themselves changes the viscosity, crystallinity and thus, the morphology and mechanical performance [63,64]. Being the droplets smaller, the ductile PBSA is more homogeneously dispersed and the interfacial surface is higher for the same volume fraction. The higher the interfacial area of the dispersed phase exposed to the matrix, the higher the possibility of intermingling of their chains [59]. In addition, smaller droplet size also results in lower ligament thickness, which is associated with enhanced toughening and flexibility, as Safont et al. successfully achieved in PHBV/TPU/cellulose composites [42]. Both phenomena could explain the higher elongation at break and flexibility compared to the non-compatibilized blend. However, this enhanced

interaction was not strong enough under a sudden load to significantly improve the impact strength of the blend. In the 50/50 PHBV/PBSA blend, the addition of JON led to a more homogeneous and smooth surface with some PBSA domains connected by fibrils. Some PBSA droplets and voids were also found throughout the surface. With 0.3 phr of chain extender, slight debonding around PBSA domains could be found while in blend 0.5 phr JON this gap was reduced which may indicate a stronger adhesion between polymers as the compatibilizing agent increases. In case of the 30/70 PHBV/PBSA blend, similar morphology was found regardless of the amount of JON added. Compared to the non-compatibilized blend, PHBV domains were less deformed and some regions of matrix yielding were found, even larger as JON content increases.

In general, the addition of JON may create PHBV-JON-PBSA copolymers between both phases, reducing their surface tension. Therefore, the copolymer formed could act as a bridge to transfer the force received during impact, flexural or tensile tests. However, this transference was found to act in both directions. When brittle PHBV is the major phase, the force received is effectively transferred to the more dissipative energy PBSA domains, thus enhancing the tensile toughness and flexural behavior of PHBV. Wang et al. [65] found great improvement in toughness in PLA/PBAT blends ranging from 90 to 60% of brittle PLA after the reaction with the same epoxy-based chain extender. However, when PBSA is the major phase, the force received during tests is transferred from PBSA to rigid PHBV domains, thus reducing the elongation at break and impact strength of this system. Arruda et al. [36] pointed out that increased interfacial adhesion in 40%-PLA/PBAT blend compatibilized with JON was not enough to compensate the brittle behavior of the PLA phase.

3.4. Thermal properties

3.4.1. Thermogravimetric analysis (TGA)

Thermal stability of PHBV/PBSA blends and the effect of the incorporation of JON were studied by TGA. Thermal parameters (onset, temperature of maximum degradation and residue) are gathered in table 4.

Table 4. Thermal parameters of PHBV, PBSA and PHBV/PBSA/JON blends

PHBV/PBSA/JON	T _{10%} °C	T _{max PHBV} °C	T _{max PBSA} °C	R600 (%)
100/0/0	292	309	-	1.6
70/30/0	295	307	412	1.2
70/30/0.3	295	309	411	1.3
70/30/0.5	296	309	413	1.4
50/50/0	298	307	412	0.9
50/50/0.3	299	310	417	0.4
50/50/0.5	301	310	416	1.0
30/70/0	305	309	415	1.0
30/70/0.3	304	311	415	0.8
30/70/0.5	303	309	414	1.0
0/100/0	378	-	413	0.0

Additionally, Fig. 6 illustrates the trends of the dTG curves and the onset temperature. PHBV and PBSA showed a single-step decomposition at 309°C and 413°C, respectively. The polymer blends showed two degradation peaks, corresponding to their immiscible components ranging in intensity accordingly to their fraction in the blend.

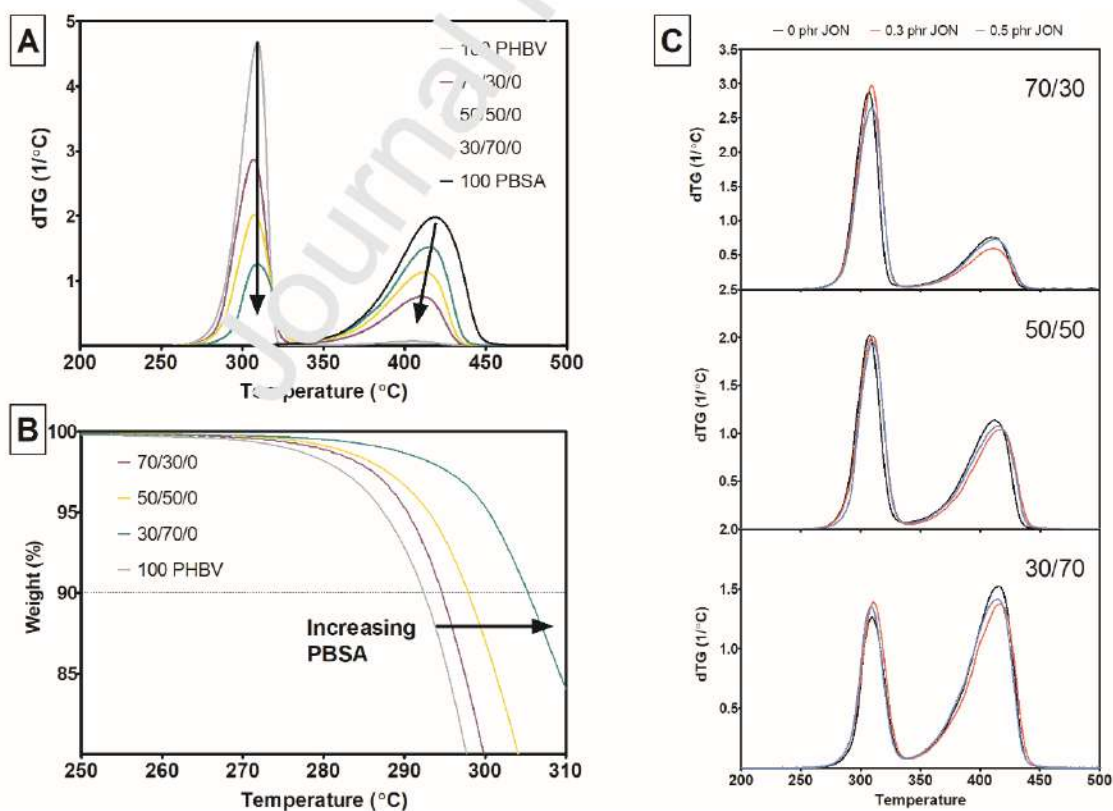


Figure 6. A) dTG curves of neat PHBV, neat PBSA and pristine blends. B) Onset detail of neat polymers and blends in TGA curve. C) DTG curves of blends with increasing amounts of JON.

As can be observed in Fig. 6-A, the degradation temperature of PHBV shifted to higher temperatures as PBSA increased in blends while the degradation temperature of PBSA progressively occurred at lower temperatures. Similarly, 10% weight loss temperature was found to raise towards higher temperatures as the PBSA fraction increased in the blend (Fig. 6-B). Blend 30/70/0 showed the highest enhancement, increasing the onset temperature of PHBV by 13°C. Blending PHBV and PBSA improved PHBV thermal stability as the stability of PBSA was reduced. Similar results were found by Kennouche et al. [30] in PHBV/PBS blends.

In contrast to the improved thermal stability of PHBV reported by Duangphet et al. [64], the incorporation of JON barely altered the thermal stability of blends. As can be observed in Fig. 6-C, dTG curves remained unchanged independently of the PHBV/PBSA blend and the amount of the chain extender added.

3.4.2. Differential scanning calorimetry (DSC)

Crystallization behavior of blends composed of semicrystalline polymers is of great importance to understand their thermal resistance, physical and mechanical properties. These properties substantially depends on crystallinity and morphology of the polymer matrix [66]. Table 5 summarizes the DSC parameters obtained in the thermograms.

Table 5. DSC parameters of PHBV, PBSA and their blends in presence and absence of JON

PHBV/PBSA/JON	Glass trans.	Melting point, °C			Melt. enthalpy, J/g		Crystalliz. point, °C		Crystallinity
	T _g , °C	T _{m1} PHBV	T _{m1} PBSA	T _{m2} PBSA	ΔH _{PHBV}	ΔH _{PBSA}	T _c PHBV	T _c PBSA	
100/0/0	Non detected	171	-	-	98	-	121	-	67
70/30/0	Non detected	171	77	85	60	13	118	52	51
70/30/0.3	Non detected	170	79	85	57	10	117	54	46
70/30/0.5	Non detected	172	77	84	57	9	117	54	45
50/50/0	-44	171	78	86	50	19	116	54	48
50/50/0.3	-47	170	77	86	43	18	114	51	43
50/50/0.5	-47	173	78	85	44	16	114	53	42
30/70/0	-47	170	77	85	24	25	118	53	35
30/70/0.3	-46	170	79	86	22	27	112	53	35
30/70/0.5	-46	170	78	86	18	23	112	53	29
0/100/0	-45	-	79	87	-	39	-	55	29

From the cooling curves at 10°C/min, a single exothermic peak was detected for both biopolymers. The crystallization temperature (T_c) of neat PHBV is located at 121°C, while T_c of neat PBSA is at 55°C. Both values are in accordance with those found in the literature [67,68]. After

blending, both T_c shifted to slight lower temperatures, it being this gap higher for PHBV peak in 50%-PBSA blend. The slight effect on each other crystallization point may be the consequence of their phase-separated morphology, the boundaries of their domains being the only location of interference by restricting the mobility of the polymer chains. The 5°C lower temperature of PHBV crystallization peak in 50/50/0 blend could be explained by the morphology observed in SEM. The transition morphology maximized the interface area between both biopolyesters, which may increase the mobility restriction of PHBV chains by low-crystalline PBSA. The presence of JON shifted T_c to lower temperatures. By enhancing the chemical interaction between both polymers, the ability of polymer chains to be part of the crystals seemed to be reduced. T_c of PHBV decreased by 1°C, 2°C and 6°C to lower temperatures compared to pristine blends with 30%, 50% and 70% of PBSA, respectively. JON seemed to have a higher influence on crystallization as the PBSA fraction increased in the matrix. However, T_c of PBSA was barely affected by the presence of the chain extender except for the 70/30/0 blend, in which the domains of this dispersed phase had the maximum surface/volume ratio. In this case, enhanced interaction at the boundaries seemed to allow PHBV to slightly promote PBSA crystallization. Restricted alignment of PHBV may act as nuclei for PBSA. The amount of JON added seemed not to be critical in T_c value.

From the second heating curves at 10 °C/min, a single endothermic peak was observed for PHBV at 171°C, whereas PBSA showed a double peak at 79°C and 87°C. According to the study about the melting behavior of PBSA carried out by Wang et al. [68], when T_c is between 55°C and 75°C, the imperfect and unstable crystals formed are susceptible to melt-recrystallizing during heating. In pristine blends, the melting enthalpies (ΔH_m) and the degree of crystallinity (X_c) showed intermediate values according to the weight fraction of each polymer. With the increasing addition of JON, the degree of crystallinity progressively decreased until a maximum 6% reduction in each blend. However no clear trend was found in T_m , that varied 1-2°C maximum throughout all of the compositions studied. These results suggested that the reaction with the chain extender interrupted the chain mobility of the polymer chains in separated domains, decreasing the fraction of both types of crystals without changing the crystal structures. The slight variation in T_m may indicate that crystallization underwent in each domain by separate and barely effect of one polymer over the other was present.

3.5. Thermomechanical studies

3.5.1. Rheology

The rheological characterization of PHBV, PBSA and their blends was performed at 175°C. Fig. 7 summarizes the storage modulus (G'), loss modulus (G'') and complex viscosity of all compositions studied as a function of frequency. According to the linear viscoelastic theory, the G' and G'' of a polymer increase with increasing frequency. The storage modulus (G') reflects a non-time-dependent elastic response while the loss modulus is related to a time-dependent viscous behavior [20]. In addition, the shear-thinning phenomenon was observed in all materials, which complex viscosity decreased as angular frequency increased [69].

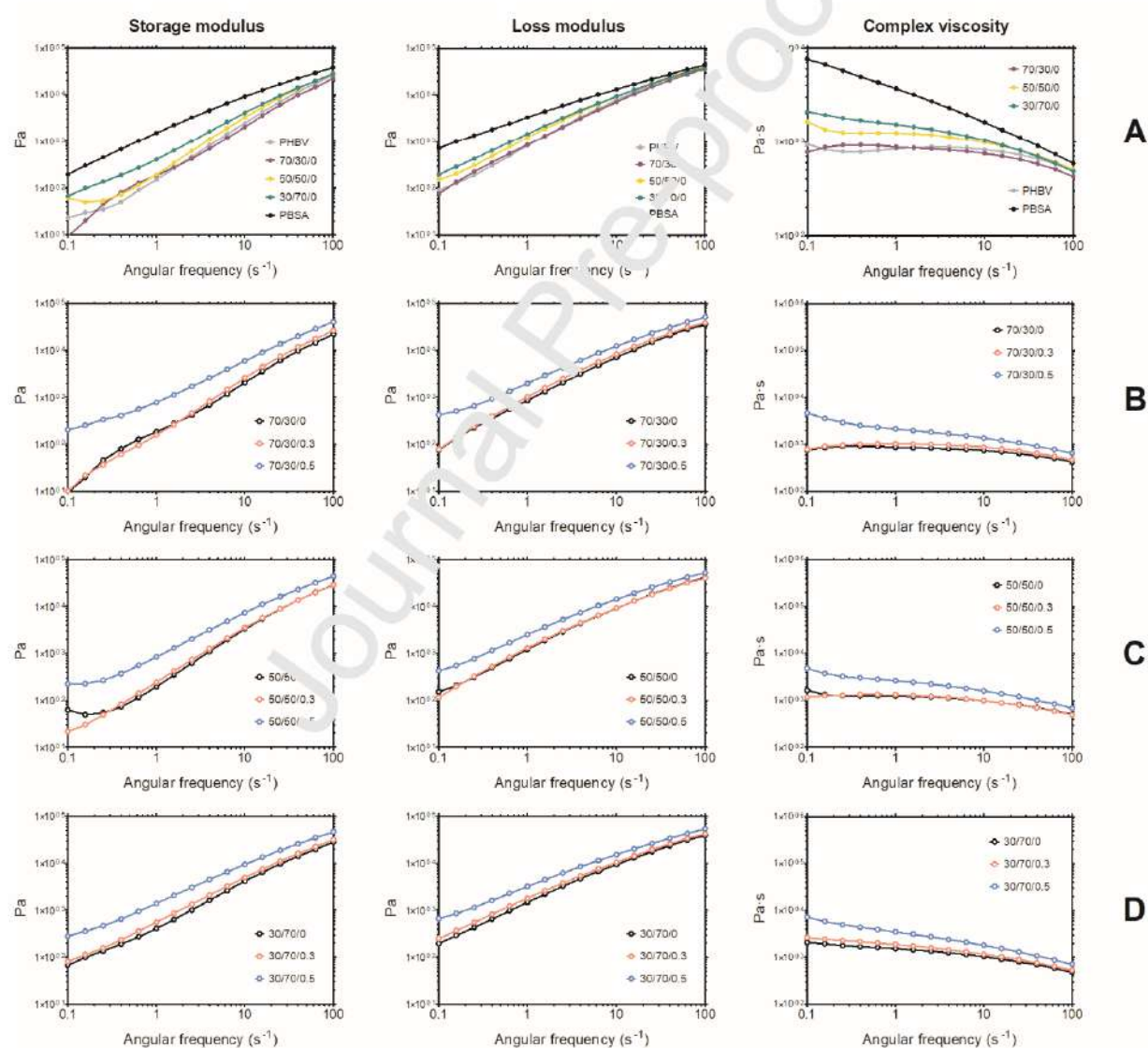


Figure 7. From left to right column: storage modulus, loss modulus and complex viscosity of A) Neat PHBV, neat PBSA and their pristine blends, B) Blend 70/30 with JON, C) Blend 50/50 with JON, and D) Blend 30/70 with JON

Generally speaking, the values of both moduli and complex viscosity of the pristine blends (Fig. 7-A) lay between those of their pure components. More specifically, blend 70/30/0 showed very similar behavior to neat PHBV, particularly in loss modulus. However, this blend showed a storage modulus plateau in the low-intermediate frequency region, around 0.5-1.0 rad/s, which is also reflected in higher complex viscosity. This suggests that the structure formed in the 70/30/0 blend was difficult to relax even at a long timescale [69]. Bousmina [70] attributed these secondary plateaus of immiscible blends to the shape relaxation of the deformed droplets of the dispersed phase, although it can also be a consequence of room conditions storage of the samples [71]. The subsequent drop in G' at the lowest angular frequency may be ascribed to the thermal degradation of the material due to the long residence time in the rheometer [71]. In the case of blend 50/50/0, there was also an increase in G' at low frequencies. Despite their equal presence in the blend, rigid chains of PHBV still dominated the rheological behavior of the material, hindering their relaxation at long-timescale. Moreover, the higher presence of PBSA seemed to protect PHBV from thermal degradation. Blend 30/70/0, in which PBSA is the major phase, exhibited an intermediate behavior according to the weight fraction of its components.

In all compatibilized blends, the addition of 0.3 phr of JON slightly increased all rheological parameters while 0.5 phr JON was found to be the optimal amount to greatly improve the interaction between both polymers. In a similar flexible/rigid blend composed of PBST/PLA 80/20, Wang et al. [41] reported increasing viscosity as the content of the epoxy-based chain extender increased in the blend. They attributed this strengthening effect to the longer molecular chains created by chemical bonding. In the 70%-PHBV blend (Fig. 7-B), G' plateau disappeared with the addition of 0.3 phr JON. This suggests that the enhanced interaction between both polymers decreased their interfacial tension [70]. Similarly, the increase of G' at low frequencies in the 50%-PHBV blend (Fig. 7-C), was also eliminated by adding 0.3 phr of the chain extender. As mentioned in morphology section (see 3.3), there was no difference in size of PBSA domains between 0.3 and 0.5 phr JON compatibilized blends. The contrasting rheological behavior of both amounts of JON may result from the competition of chain extension against the thermal degradation of PHBV [64].

As a whole, all rheological parameters (G' , G'' and complex viscosity) significantly increased with 0.5 phr addition of JON. Branching and chain extension decreased the mobility of polymer chains as well as reduced the difference in melt viscosity of the biopolyesters. Therefore, the

processability in the molten state was enhanced, the scale of this effect being higher according to increasing PHBV content in the blend [62,64]. This behavior suggests higher reactivity of JON with PHBV together with more proportion of intra-domain linkages (chain extension) than PHBV-JON-PBSA copolymer formation (compatibilization).

3.5.2. Dynamic mechanical analysis (DMA)

Fig. 8 shows the storage modulus (G') and $\tan \delta$ curves of neat biopolyesters and their pristine and compatibilized blends. The storage modulus gives information about the elastic behavior and stiffness of the materials, whereas the peaks found in $\tan \delta$ curves are attributed to their glass transition temperatures (T_g) [72]. For the sake of comparison, the storage modulus at room temperature (25°C) have been considered. It is noteworthy that PHBV was still in a glassy state at room temperature.

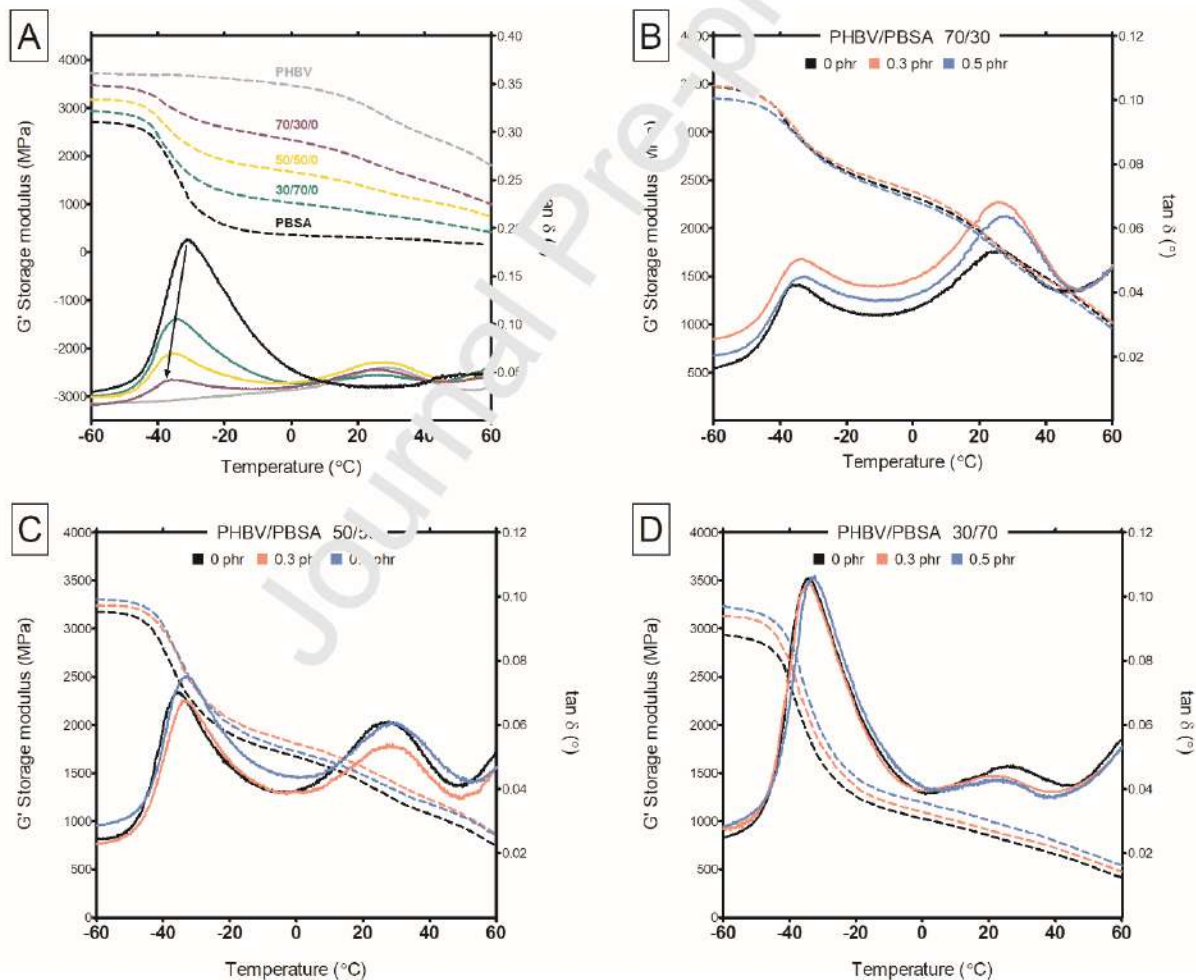


Figure 8. G' (dotted line) and $\tan \delta$ (solid line) curves of A) Neat biopolyesters and their pristine blends, B) Blend 70/30 with JON, C) Blend 50/50 with JON, and D) Blend 30/70 with JON.

As can be seen in Fig. 8-A, the pristine blends showed intermediate G' values between 2958 and 294 MPa, those corresponding to neat PHBV and PBSA. G' of PHBV and thus, its stiffness, progressively decreased by 38, 56 and 73% by the addition of 30, 50 and 70% of PBSA respectively. The magnitude of this effect concerning the PBSA weight fraction in the blend was higher in the 70/30/0 sample. As expected, the incorporation of an amorphous phase increased the ductility of the blend, broadening the temperature processing window of PHBV [20].

The effect of the chain extender in the PHBV-PBSA blends was more complex. On the one hand, the storage modulus of the 70/30 blend (Fig. 8-B) remained practically unchanged irrespective of the JON content. On the other hand, G' of 50/50 (Fig. 8-C) and 30/70 blend (Fig. 8-D) increased by 6-12% and 8-19% respectively by growing JON content. As reported by Sahoo et al. [73], the no modification of the thermomechanical behavior by a compatibilizing agent could be due to two competitive effects: higher interaction between polymers (higher G' and T_g) and plasticizing (lower G' and T_g). From 50% of PBSA, when phase dominance is transiting to PBSA, the higher interaction of PBSA with stiff PHBV restricted the mobility of the polymer matrix. Thus, the stiffness and storage modulus were increased with the addition of JON.

Tan delta ($\tan \delta$) represents the ratio between storage modulus (G' , elastic behavior) and the loss modulus (G'' , viscous behavior). Peaks are obtained when G' decreases at a higher rate than G'' as a consequence of the drastic increase of molecular mobility. These peaks are attributed to the glass transition (T_g) of the materials [72]. PBSA showed a single peak at about -32°C whereas T_g of PHBV was located at 28°C . Both peaks were distinguished in all blends (Fig. 8-A), confirming the immiscibility of PHBV and PBSA [74]. T_g of PBSA shifted to lower temperatures as PHBV content increased in the blend and its intensity decreased accordingly to the PBSA fraction. By contrast, T_g of PHBV slightly shifted to lower temperatures as PBSA content increased in the blend. However, its intensity was not proportional to PHBV content. T_g of PBSA was greater affected which can be attributed to a decrease in its molecular mobility by the presence of PHBV.

With the addition of the chain extender, it would be expected that longer polymer chains difficult their mobility, increasing the T_g of the polymers [41]. However, in presence of JON, no clear effect was detected except for the 30/70 blend. When PHBV is the minor phase, the improved interaction between both polymers led to the decrease of T_g of PHBV.

3.5.3. Heat deflection temperature (HDT)

HDT can be defined as the maximum service temperature at which a material can maintain its dimensional stability under a certain load [75]. High heat resistance is preferred for certain applications such as food packaging (hot beverages containers, straws, etc) [76]. HDT values of neat biopolymers, and their compatibilized and non-compatibilized blends are shown in Table 6. For a clearer understanding, data are also plotted in Fig. 9.

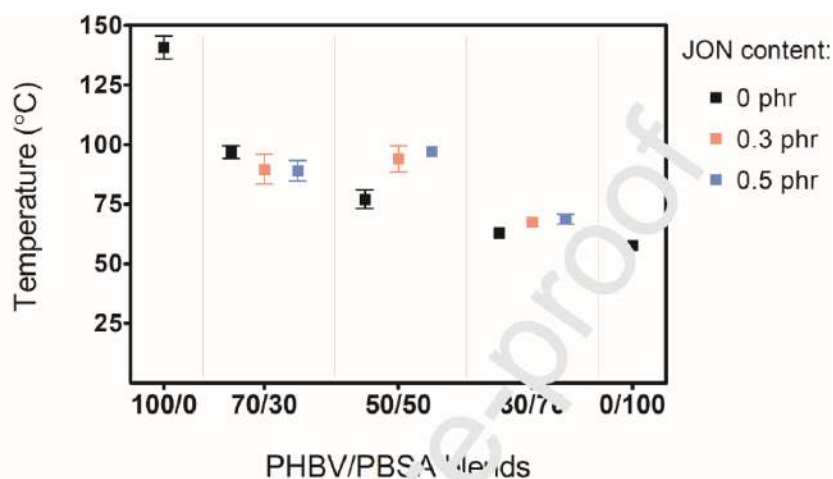


Figure 9. Heat deflection temperature of neat biopolyesters and their blends in the presence and absence of the chain extender.

HDT values of PHBV and PBSA were 141°C and 58°C, respectively, which are consistent with those found in literature [28,24]. As expected, the heat deflection temperature of blends decreased as PBSA content increased. Crystallinity plays an important role in softening. Crystallinity is progressively reduced as increasing the amorphous fraction in the blend, and thus, the material is easier to soften.

With the addition of JON, the effect on HDT was different depending on which polymer was the continuous phase. For blends with at least 50% of PBSA, HDT was increased as the content of the chain extender also increased. In these cases, the enhanced interaction between both biopolymers reduced the mobility of polymer chains. For blend 70/30, in which the main component is the heat-resistant PHBV, HDT values decreased as JON content was higher. The improved compatibility between polymers allowed PBSA to promote the mobility of PHBV chains. This behavior is in accordance with previously reported rheological measurements.

3.6. Melt flow index (MFI)

MFI is a parameter that gives information about flowing behavior during processing like injection

molding, which typically requires MFI values above 8g/10 min [34]. MFI values of all compositions studied are summarized in Table 6. MFI of non-compatibilized blends progressively decreased as the fraction of low-crystalline PBSA increased.

Table 6. MFI and HDT values of all compositions studied.

PHBV/PBSA/JON	MFI g · 10 min ⁻¹	HDT °C
100/0/0	27.1 ± 0.8	141 ± 5
70/30/0	19.5 ± 0.5	97 ± 3
70/30/0.3	16.1 ± 1.4	90 ± 6
70/30/0.5	14.9 ± 1.0	90 ± 4
50/50/0	14.7 ± 0.9	71 ± 4
50/50/0.3	12.0 ± 0.7	94 ± 6
50/50/0.5	11.3 ± 0.6	97 ± 1
30/70/0	10.2 ± 0.3	63 ± 0.5
30/70/0.3	9.7 ± 0.4	67 ± 0.1
30/70/0.5	9.5 ± 0.5	69 ± 2
0/100/0	4.4 ± 0.3	58 ± 0.4

The increasing presence of JON led to an additional decrease in the MFI of blends. This may be attributed to an enhanced entanglement of both components. Flowing of the blends is reduced as viscosity increases [28]. However, the scale of reduction was higher as higher the PHBV content in the blend.

4. Conclusions

Developing biodegradable polymer blends plays an important role in the fight against plastic pollution. In the present study, limited compatibilization of PHBV/PBSA blends was achieved by reactive extrusion with an epoxy-based chain extender (JON). The experimental results showed that simple binary blending did not significantly improve the mechanical performance of PHBV further than what corresponded to the PBSA weight fraction in the blend. The immiscibility of PHBV and PBSA was confirmed by SEM and DMA (two different T_g) in both pristine and compatibilized blends. Neither the incorporation of JON nor the amount (0.3 or 0.5 phr) changed the type of morphology developed in the three compositions studied: drop-in-matrix for 30%-, heterogeneous transition for 50%- and ellipsoidal sea-island for 70%-PBSA. However, it did change the size of PBSA domains, the homogeneity, and the yielding of the PBSA matrix, respectively, indicating increased interaction between both polymers. Formation

of PHBV-JON-PBSA copolymers are a key factor to reach synergistic performance. Chain extension could create bondings at the boundaries of both immiscible phases and also intra-domains, what would modify also the viscosity. Actually, the processability of all blends was improved. MFI drastically decreased with the addition of JON especially as PHBV content was higher in the blend system. Crystallinity progressively decreased by a maximum of 6% in all blends with the increasing addition of JON that prevented longer molecular chains from being included in the crystal lattice of PHBV or PBSA. Compatibilization allowed the minor phase of each blend to magnify its effect. The greatest improvement in mechanical performance was found in 70/30 PHBV/PBSA with 0.5 phr of JON. Enhanced interaction improved the elongation at break by 45% and turned the material into a non-breakable one under flexural stress. By contrast, in 50%- and 70%-PBSA compatibilized blends, the enhanced interaction allowed PHBV to act as a stress concentrator hindering the ability of the PBSA matrix to dissipate the stress. For the same reason, HDT decreased up to 8°C in the 30%-PBSA blend, and increased up to 20°C in the 50%-PBSA blend and up to 6°C in the 70%-PBSA blend with the progressive addition of the chain extender. Nonetheless, under a sudden impact load, JON was revealed as a poor toughening agent in respect of the blend and the amount of the additive used. In absolute terms, that is, compared to conventional polymer blends, the restricted compatibilizing effect of JON supposes a limitation to develop competitive biodegradable alternatives to conventional plastics in terms of performance. Nonetheless, this study is one step further to make the replacement of conventional plastics a reality. This research can provide references for the design, processing and promotion of new PHBV/PBSA materials in the future.

CRedit authorship contribution statement

Patricia Feijoo: Methodology, Investigation, Formal analysis, Writing—Original Draft Preparation. **Amar K. Mohanty:** Project Conceptualization, Methodology, Administration, Funding acquisition, Supervision, Writing—Review and Editing. **Arturo Rodriguez-Uribe:** Methodology, Formal analysis, Writing—Review and Editing. **José Gámez-Pérez:** Writing—Review and Editing. **Luis Cabedo:** Writing—Review and Editing. **Manjusri Misra:** Project Conceptualization, Methodology, Administration, Funding acquisition, Supervision, Writing—Review and Editing. All authors contributed to the discussion, reviews, and approval of the manuscript for publication.

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Abbreviations

The following abbreviations are used in this manuscript:

3HV	3-Hydroxyvalerate units
DCP	Dicumyl peroxide
ESA	Epoxy functionalized styrene acrylate
GPC	Gel permeation chromatography
JON	Joncryl® ADR-4468
MA	Maleic anhydride
Mw	Molecular weight
PBAT	Poly(butylene adipate terephthalate)
PBS	Poly(butylene succinate)
PBSA	Poly(butylene succinate-co-butylene adipate)
PBST	Poly(butylene succinate-butylene terephthalate)
PCL	Poly(ϵ -caprolactone)
PE	Polyethylene
PHA	Polyhydroxyalkanoate
PHB	Poly(3-hydroxybutyrate)
PHBV	Poly(3-hydroxybutyrate-co-3-valerate)
PLA	Poly(lactic acid)
PP	Polypropylene
REx	Reactive extrusion
TPU	Thermoplastic polyurethane

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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