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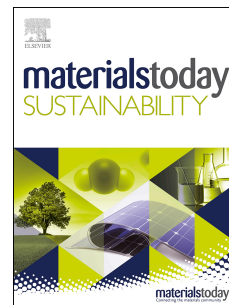
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# Fully bio-based ternary polymer blends: structural characterization and mechanical behavior

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## Abstract

In this work, ternary immiscible blends based on poly(lactic acid) (PLA) as major phase and polybutylene succinate (PBS) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHH) as minor phases were prepared through melt blending, aiming at obtaining fully biobased materials with enhanced ductility and toughness as compared to the inherently brittle matrix. Thermodynamic considerations based on the calculation of the interfacial tensions predicted the achievement of a partial encapsulation between the domains of the two minor components embedded in the PLA matrix. The rheological characterization revealed higher melt viscosity and elasticity for all the ternary blends as compared to the PLA matrix and a growing level of interfacial interactions between the different phases when increasing amounts of PBS are incorporated. This last was confirmed through morphological observations, which allowed demonstrating the achievement of an improved homogeneous microstructure for the blends containing 30 and 40 wt.% of PBS, notwithstanding the relatively good interfacial adhesion obtained in all the explored materials. The combined effect of the strong established interfacial interactions and of the uniform morphology resulted in the obtainment of dramatic increments of ductility, tensile toughness and impact strength for all formulated ternary blends as compared to the PLA matrix, and especially for those containing 30 or 40 wt.% of PBS, while maintaining satisfactory levels of stiffness and tensile strength.

**Keywords:** biobased polymers; ternary blends; PLA; rheological behavior; mechanical properties

## 1. Introduction

In recent years, the environmental concerns related to the massive accumulation of plastic wastes and to the high carbon footprint of petroleum-derived polymers have stimulated a rising interest from

both academia and industry towards the development of eco-friendly and renewable plastics, which are possibly either biobased or biodegradable [1-3]. The data about the market of biobased polymers showed that in the last decade the global production of biopolymers is continuously increasing, forecasting a production of about 2.43 million tons in 2024, with a prominent role of starch-based blends, followed by poly (lactic acid) (PLA) and polybutylene adipate terephthalate [4]. In particular, PLA is experiencing a very fast growth in the market, due to its interesting properties such as high mechanical strength, good biodegradability or compostability and large-scale availability at a competitive price [5-7]. Furthermore, it has been demonstrated that the production of PLA involves lower CO<sub>2</sub> emissions and lower energy consumption (ca. 25-55% less than fossil fuel-based polymers) as compared to the traditional plastics, thus contributing to the mitigation of the carbon footprint and the environmental impacts associated with the productive processes of polymeric materials, opening new perspectives for a sustainable development of the plastic industry [8-9]. Owing to these attractive characteristics, the market of PLA is steadily widening from the production of unexpensive commodities and single-use packaging products towards several applications areas typically dominated by conventional petroleum-based polymers, such as automotive, biomedical and electric sectors [10]. However, PLA suffers from a series of shortcomings, such as brittleness, slow crystallization rate, low melt strength and low impact strength, which still limit its utilization for durable and engineering applications, hence restricting the possibility of attaining a strong commercial standpoint [11-13]. In particular, the inherent low ductility (typically low elongation at break, ca. 2-7%) and the limited toughness are the major bottlenecks preventing the widespread application of PLA, especially in areas in which good deformability and impact resistance are required [14]. Therefore, there is an urgent need to modify the properties of PLA to solve its aforementioned hurdles, hence making this biobased polymer unquestionably competitive with conventional fossil fuel-based commodities. For these reasons, current research on PLA modification is focused on the development of strategies effectively improving its ductility and toughness [15-17]. So far, the most exploited methods involve the incorporation of plasticizing agents [18-19], blending with rubbery elastomers or polymers [20-21], copolymerization [22-23] and the formulation of nanocomposites [24]. Among the different strategies, melt blending is considered the most economical, versatile and industrially viable route, since it does not require any preventive chemical functionalization of the base polymer components, thus avoiding the use of chemicals and solvents potentially increasing the environmental impact of the whole process [25]. Additionally, differently from the introduction of plasticizers that usually results in a detrimental decrease of the elasticity modulus, a proper selection of the modifier polymer allows the achievement of a satisfactory toughness/stiffness balance [26]. However, in the case of melt blending a good compatibility between

the polymer pair components is mandatory for achieving the desired mechanical properties [27]. This is usually achieved through the introduction of physical compatibilizer systems [28], which enhance the interfacial adhesion between the polymer components, or exploiting reactive compatibilization strategies, in which the selected compatibilizing agent is able to react *in-situ* (during the processing) with the polymer functionalities, leading to improvements of the interfacial polymer/polymer interactions [29]. Furthermore, it is important considering that the final properties of a blend strongly depend, apart from the inherent characteristics of the components, also on the final multiphase morphology. From a general point of view, PLA-based blends with finer morphologies, characterized by small and well-distributed domains of the minor phase into the matrix, show significantly enhanced ductility and toughness [30]. Therefore, a further important issue in melt blending concerns the optimization of the processing conditions in such a way that effectively improved performance as compared to those of polymer components are achieved.

PLA-based ternary blends, involving the incorporation of two polymers as minor phases, have also been studied [31-33]. Compared to binary blends, usually the introduction of a third phase allows the achievement of more balanced properties, taking advantage from the synergistic interactions obtainable from the combination of different polymers having complementary properties [34]. In this context, Andrezejewski et al. [35] reported PLA modification through reactive mixing with poly(butylene adipate-co-terephthalate) copolymer and an epoxy-functionalized chain extender, demonstrating the achievement of increased elongation at break and impact strength, especially in the blends containing 30 wt.% of copolymer. Similarly, Liu et al. [36] exploited a reactive extrusion process to produce PLA-based ternary blends containing an epoxy-functionalized elastomer and a zinc ionomer. The obtained results revealed that an effective interfacial compatibilization was achieved at elevated extrusion temperatures (namely, 240 °C), resulting in final materials with super-toughness properties and moderate levels of stiffness and tensile strength. Interestingly, the introduction of poly(methyl methacrylate) (PMMA) was demonstrated successful in enhancing the interfacial interactions between PLA and a polybutadiene-g-poly(styrene-co-acrylonitrile) impact modifier [37]. In particular, increasing contents of PMMA promoted the phase adhesion and the dispersion state of the impact modifier droplets in the blends, inducing the obtainment of highly toughened blends showing incomplete breakage of the impact specimens. A physical compatibilization method involving the use of epoxidized vegetable oils as compatibilizers was exploited by Garcia-Campo et al. [38] in PLA, poly(3-hydroxybutyrate) and poly(butylene succinate) (PBS) or poly(butylene succinate-co-adipate) ternary blends. Also in this case, the incorporation of both flexible polyesters positively contributed to increasing the ductility of the blends, with

consequent enhancements of the impact toughness, especially in the compatibilized systems which showed improved ductile properties as compared to their uncompatibilized counterparts.

Although the vast literature reporting the development of PLA-based ternary blends with improved toughness, some aspects are worth noticing from the above research. Firstly, PLA-based ternary systems showing highly enhanced ductility are mostly obtained through the incorporation of toughened elastomers or of a third polymeric phase which are not bio-based, hence adversely sacrificing the biobased content of the final product. On the other hand, it has been shown that effective toughening is usually achieved when a compatibilizer (working either with physical or chemical mechanism) is introduced in the system for enhancing the interfacial adhesion between PLA and the other components, while only few studies have explored the final properties of fully biobased ternary blends without the use of any compatibilizer [30, 34, 39].

In this work, highly toughened ternary blends based on PLA as major phase and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHH) and polybutylene succinate (PBS) as minor phases were formulated through melt blending. The phase behavior, the microstructure and the mechanical behavior of ternary blends characterized by various compositions were thoroughly investigated, aiming at disclosing the effect of the incorporation of different contents of dispersed phases and of the final morphology of the blends on the achievement of impressively improved toughness and ductility.

## 2. Materials and Methods

### 2.1 Materials

The materials used in this work were:

- Polylactic acid (PLA) 3251D by Ingeo™ Natural Natureworks, having density = 1.24 g/cm<sup>3</sup>, Melt Flow Index of 80 g/10 min (210 °C, 2.16 kg);
- Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHH) with a content of hydroxyhexanoate of 11 mol%, manufactured by Aonilex, KANEKA Biopolymer under the trade name PHBX151A. Main properties: density = 1.19 g/cm<sup>3</sup>, Melt Flow Index of 3 g/10 min (165 °C, 5 kg);
- Polybutylene succinate (PBS) PBE003 by Natureplast. Main properties: density = 1.26 g/cm<sup>3</sup>, Melt Flow Index of 5 g/10 min (190 °C, 2.16 kg).

All the biopolymers were used as-received, without any further purification.

## 2.2 Preparation of the blends

The polymers were first dried for 5 h at 80 °C in a vacuum oven and then the ternary blends (whose composition is reported in Table 1) were prepared using a co-rotating twin screw extruder with a Thermo Fisher Process 11 twin-screw extruder. The parameters adopted for the processing of the blends were: flat temperature profile at 170 °C, feed rate of 400 g/h, screw rotation speed of 350 rpm. Neat polymers were subjected to the same processing.

The composition of the formulated blends and the names used hereinafter are reported in Table 1.

| Sample   | wt.% PLA | wt.% PBS | wt.% PHBHH |
|----------|----------|----------|------------|
| 70/15/15 | 70       | 15       | 15         |
| 60/30/10 | 60       | 30       | 10         |
| 50/20/30 | 50       | 20       | 30         |
| 50/30/20 | 50       | 30       | 20         |
| 50/40/10 | 50       | 40       | 10         |

**Table 1.** Compositions and names of the formulated blends

## 2.3 Characterizations

### 2.3.1 Contact angle analyses

Contact angle measurements were carried out using a Phoenix 300 contact angle system (Kromtek Co., Malaysia) at room temperature. The results were further evaluated using image processing software (ImageJ). The measuring liquids were high-performance liquid chromatography (HPLC) grade water and diiodomethane.

### 2.3.2 Thermal analyses

The thermal behavior of all the investigated materials was investigated through differential scanning calorimetry (DSC) analyses, performed using a QA1000 TA Instruments apparatus. All the tests were carried out under dry N<sub>2</sub> atmosphere, using samples of about 8 mg sealed in aluminum pans. The samples underwent the following thermal cycle: a first heating from -50 to 200 °C, a cooling step from 200 to -50 °C and a final heating ramp to 200 °C. During all the ramps, the heating/cooling rate was fixed at 10 °C/min. The glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_{cc}$ ), melting temperature ( $T_m$ ), melting enthalpy ( $\Delta H_m$ ) and cold crystallization enthalpy ( $\Delta H_{cc}$ ) were evaluated from the second heating-up trace. The crystallinity content of the different phases in the ternary blends was evaluated according to Equation 1:

$$\text{Cristallinity degree} = X_c = \frac{\Delta H}{\Delta H_0 \cdot w} \cdot 100 \quad \text{Equation 1}$$

where:  $\Delta H$  is the melting enthalpy for PBS and PHBHH while is the difference between melting and cold crystallization enthalpies for PLA,  $\Delta H_0$  is the theoretical melting enthalpy of 100% crystalline polymer (93.7 J/g for PLA [7], 110.3 J/g for PBS [40], and 146 J/g for PHBHH [41]) and  $w$  is the weight fraction of the polymer in the blend.

### 2.3.3 Rheological behavior

An ARES (TA Instrument) strain controlled rotational rheometer equipped with a parallel-plates geometry (plate diameter = 25mm; typical gap during the measurements = 1mm) was exploited for the determination of the rheological behavior of the formulated materials. Frequency sweep test were performed at  $T = 170$  °C and frequency = 100-0.1 rad/s. For each material, the strain amplitude was determined through preliminary strain sweep measurements allowing assessing the linear viscoelasticity range. All the rheological measurements were performed in inert ( $N_2$ ) atmosphere, to avoid oxidative degradation of the samples during the test. Prior to the measurements, the samples were vacuum-dried at 80 °C for 4 h. Specimens for the rheological characterization, having diameter of 25 mm and thickness of 1 mm, were obtained through a compression molding step, using a hot-plate press operating at 100 bar, 190 °C for 3 min.

### 2.3.4 Morphological observations

An EVO 15 scanning electron microscope (SEM) from Zeiss was exploited for the evaluation of the morphologies of the formulated blends. The samples (taken from the extrudates) were fractured in liquid nitrogen and the obtained surfaces were gold metalized prior to the observations.

### 2.3.5 Mechanical tests

Tensile tests were performed using an Instron® dynamometer, according to the ASTM D638 standard. A 5 kN load cell was used, working at 1 mm/min until 0.25% deformation was achieved and 10 mm/min till the specimen fracture. Five specimens (ISO 527 standard type 5A) were tested for each system and the results averaged. Dumbbell specimens for tensile tests were obtained through injection molding using a Babyplast 6/10P Cronoplast press, operating at 180 °C (prior to the processing the materials were vacuum dried at 80 °C for 4h).

The impact strength was evaluated through Charpy tests performed with a pendulum impact HIT5P (Zwick/Roll) according to UNI EN ISO 179-1/1Eu standard, employing 2 J impact energy, impact speed 2.9 m/s (specimen dimensions: 80 mm x 10 mm x 4 mm). All the measurements have been carried out at room temperature. Five specimens were tested for each system and the results averaged.



Specimens for the impact tests were obtained through a compression molding step (after a vacuum drying at 80 °C for 4h), using a hot-plate press operating at 100 bar, 190 °C for 3 min.

### 3. Results and discussion

#### 3.1 Interactions between the components: calculation of the spreading coefficients

As widely reported in the literature [42-44], the morphology of multiphase polymer-based systems is governed by the interfacial interactions established between the different polymer components. Therefore, the microstructure of the blends after the melt compounding process can be profitably predicted through the calculation of the interfacial interaction values. To this aim, the values of the surface tensions of PLA, PBS and PHBHH were calculated through contact angle measurements using the OWRK-method, which allows the assessment of the polar ( $\gamma^p$ ) and dispersive ( $\gamma^d$ ) components and of the total energy surface ( $\gamma$ ) [45-46]. The obtained values (which are reported along with the measured contact angles in Table 2) were then used to evaluate the interfacial tensions between the polymer pairs (i.e. PLA/PBS, PLA/PHBHH and PBS/PHBHH) using the Equation 2 [47]:

$$\alpha_{12} = \gamma_1 + \gamma_2 - 4 \left( \frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad \text{Equation 2}$$

where:  $\alpha_{12}$  is the interfacial tension between polymers 1 and 2, and  $\gamma_1$  and  $\gamma_2$  are the surface tension of the two components (total and dispersive or polar components). The obtained values (reported in Table 3) demonstrated that in PLA/PBS/PHBHH ternary blends, the PBS/PHBHH interfacial tension is lower as compared to those of PLA/PBS and PLA/PHBHH, indicating that the interactions between PBS and PHBHH are more intense than those established between the other polymer pairs. At variance, a similar extent of interfacial interactions is expected for PLA/PBS and PLA/PHBHH.

A widely exploited thermodynamic model for the prediction of the phase morphology of immiscible ternary blends involves the calculation of the spreading coefficients on the basis of the interfacial tensions between the polymer components [48-50]. This methodology establishes the thermodynamic tendency of one component to engulf a second component, when embedded in a matrix constituted by a third component, depending on the values of the spreading coefficients, calculated as follows:

$$\lambda_{123} = \alpha_{13} - \alpha_{12} - \alpha_{23} \quad \text{Equation 3}$$

where:  $\lambda_{123}$  is the spreading coefficient and  $\alpha_{ij}$  are the interfacial tensions between the components [51-52]. According to this theory, a positive value of the spreading coefficient indicates the achievement of a complete wetting morphology, in which the component 2 is prone to completely spread at the interface between components 1 and 3. Conversely, a partial wetting morphology is obtained for negative values of the spreading coefficient. In this case, none of the components spreads

at the interface, but the three phases meet at a three-phase line of contact. As observable from the calculated values of the spreading coefficients reported in Table 3, the thermodynamic calculations predict partial wetting for PLA/PBS/PHBHH blends, as all the spreading coefficients are negative. In other words, the most thermodynamically stable morphology for the formulated ternary blends is when all the phases are assembled at the interface in the form of a three-phase line of contact. In particular, since the ternary blends object of this work are composed of one major phase (i.e. PLA) and two minor phases, a partial encapsulation between the droplets of the two minor components embedded in the PLA matrix can be predicted.

| Sample | Contact angle [deg] |               | Surface tension [mN/m]  |                         |       |
|--------|---------------------|---------------|-------------------------|-------------------------|-------|
|        | water               | diiodomethane | Dispersion              | Polar                   | Total |
|        |                     |               | component<br>$\gamma^d$ | component<br>$\gamma^p$ |       |
| PLA    | 57                  | 45            | 19.7                    | 27.7                    | 47.3  |
| PBS    | 69                  | 34            | 8.9                     | 36.2                    | 45.2  |
| PHBHH  | 72                  | 40            | 8.2                     | 33.8                    | 42.1  |

**Table 2.** Contact angle and surface tension values for the base polymer

| Polymer pair | Interfacial tension [mN/m] | Spreading coefficient [mN/m]            |
|--------------|----------------------------|---|
|              | $\alpha_{ij}$              | $\lambda_{ij}$                          |
| PLA/PBS      | 5.21                       | $\lambda_{\text{PHBHH-PLA-PBS}}$ -10.24 |
| PLA/PHBHH    | 5.34                       | $\lambda_{\text{PHBH-PBS-PLA}}$ -0.17   |
| PBS/PHBHH    | 0.31                       | $\lambda_{\text{PLA-PHBH-PBS}}$ -0.44   |

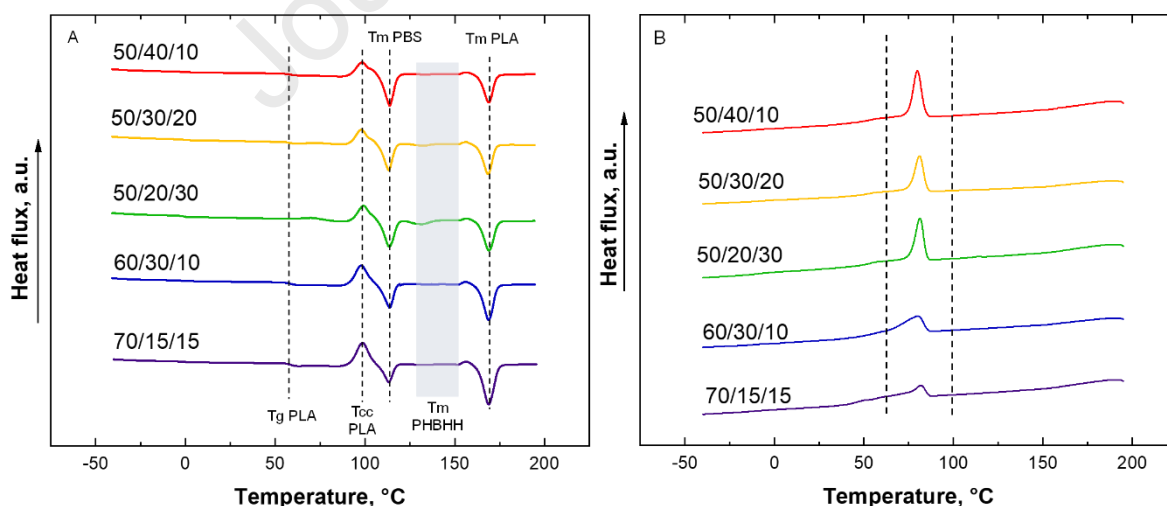
**Table 3.** Values of interfacial tensions and spreading coefficients

### 3.2 Thermal behavior

Figures 1 A-B report the DSC thermograms for all ternary blends collected during the second heating and cooling scans, respectively; the related crystallization/melting properties are listed and compared with those of the base polymers in Table 4. Calorimetric analyses performed on the neat components (DSC thermograms reported in Figure S1 in Supplementary Information) confirmed a typical semicrystalline behavior for all three polymers. As observable in Figures 1, all the ternary blends show a quite similar thermal behavior during both the cooling and the heating ramps. Furthermore, no significant differences between the glass transition, cold crystallization, melting and crystallization temperatures of the blends and those of the neat components are observed, as already reported for similar biobased ternary blends [38]. In particular, looking at the heating-up traces reported in Figure 1A, in all the ternary blends the glass transition temperature of the PLA phase remains unchanged at 58 °C, as well as the cold crystallization peak at 98 °C and the endothermic peaks at 114 and 169 °C, which can be attributed to the cold crystallization of PLA and melting of PBS and PLA phases, respectively. Besides, for the blends containing high amount of PHBHH (i.e. 50/20/30 and 50/30/20)

an exothermic peak, associable with the melting phenomena occurring in this phase, appears at 132 °C. During the cooling stage, neither PLA nor PHBHH show visible exothermic peak, indicating slow crystallization kinetics for both polymers. As observable in figure 1B, all the ternary blends exhibit a peak at 80 °C, which can be attributed to crystallization phenomena occurring in PBS.

Interestingly, the crystallization of both PLA and PBS phases was promoted in the ternary blends. In fact, as indicated by the calculated values of the crystallinity degree reported in Table 4, for both polymers the content of crystalline phase is higher in the ternary blends than in the neat materials. Similar results have been obtained by Zhang et al. [30] for PLA-based ternary blends containing PBS and poly(3-hydroxybutyrate-co-hydroxyvalerate). In particular, they found a promoted crystallization for PLA and attributed this result to the activation of the chain mobility of the matrix phase in presence of the inclusions of the minor phases. Furthermore, as already demonstrated by Yazawa et al. [53] in PLA/polycaprolactone blends, the phase interface can play a fundamental role in inducing nucleation events at the interface between the matrix and the domains of the minor phases, leading to an increase of the matrix crystallinity. In the ternary blends studied here, for PLA a significant increment of the crystallinity content is observed in the ternary blend containing 30 wt.% of PHBHH, whereas PBS shows higher tendency in crystallizing when its content in the blends is lower than 20 wt.%. Since the physical properties of semicrystalline polymers are strongly dependent on the solid-state morphology and on crystallinity, the obtained results in terms of different crystallinity degree are expected remarkably influencing the mechanical properties of the blends, as deeply discussed below.



**Figure 1.** DSC thermograms recorded during second heating (A) and cooling (B) scans for all formulated ternary blends.

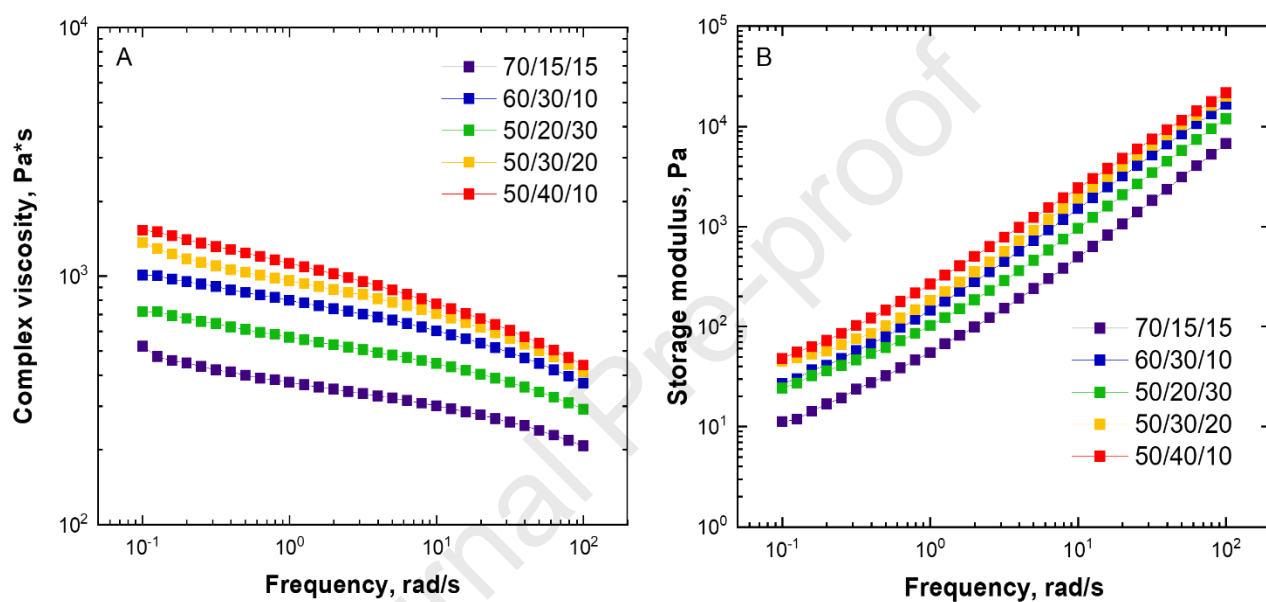
| Sample   | $\Delta H_m$ | $\Delta H_{cc}$ | $\Delta H_m$ | $\Delta H_m$ | $\Delta H_{cc}$ | $X_c$ | $X_c$ | $X_c$ |
|----------|--------------|-----------------|--------------|--------------|-----------------|-------|-------|-------|
|          | PLA          | PLA             | PBS          | PHBHH        | PHBHH           | PLA   | PBS   | PHBHH |
|          | [J/g]        | [J/g]           | [J/g]        | [J/g]        | [J/g]           | [%]   | [%]   | [%]   |
| PLA      | 39           | 23              | -            | -            | -               | 17    | -     | -     |
| PBS      | -            | -               | 49           | -            | -               | -     | 44    | -     |
| PHBHH    | -            | -               | -            | 35           | 32              | -     | -     | 2     |
| 70/15/15 | 34           | 18              | 11           | -            | -               | 24    | 66    | -     |
| 60/30/10 | 30           | 16              | 18           | -            | -               | 25    | 54    | -     |
| 50/20/30 | 25           | 11              | 14           | -            | -               | 30    | 63    | -     |
| 50/30/20 | 22           | 12              | 16           | -            | -               | 21    | 48    | -     |
| 50/40/10 | 22           | 12              | 21           | -            | -               | 21    | 47    | -     |

**Table 4.** Thermal properties of PLA/PBS/PHBHH ternary blends. Data for the neat polymer components are also reported.

### 3.3 Rheological behavior and morphology

It is widely documented in the literature that the interfacial interactions established in multiphase polymer systems, as well as the phase morphology of these materials, can be profitably evaluated through the study of their dynamic rheological properties, being these last very sensitive to the evolution of the microstructure and of the dispersion state of the components resulting from the blending process [54-55]. Therefore, dynamic rheological measurements were performed to gain some insights into the microstructure of the formulated ternary blends and the obtained frequency dependence of the complex viscosity and of the storage modulus are displayed in Figures 2 A and B, respectively. The correspondent curves of the neat components are reported in Figures S2 (A-B). As far as the complex viscosity is concerned, neat PLA exhibits a Newtonian behavior extending for the whole investigated frequency range, whereas PHBH and, especially, PBS show higher complex viscosity values with respect to PLA and a more pronounced shear thinning behavior at intermediate and higher frequencies. All the ternary blends reveal higher complex viscosity values as compared to the neat PLA matrix; in particular, the complex viscosity values of the blends progressively increase as a function of the content of PBS phase, which presents higher melt viscosity as compared to the other two components. For 60/30/10 and 50/30/20 systems, containing the same PBS loading, an increment of the amount of PHBHH phase induces the achievement of increased viscosities. Furthermore, as observable from the curves reported in Figure 2A, a shear thinning behavior developing for the whole tested frequency interval can be observed for all the ternary blends. The incorporation of different amounts of PHBHH and PBS, thus, induced not only an increase of the complex viscosity values, but also the disappearance of the Newtonian plateau in the low-frequency region. This feature highlights the occurrence of interactions at the interface between the different components, which affect the dynamics of the polymer macromolecules, hence leading to a

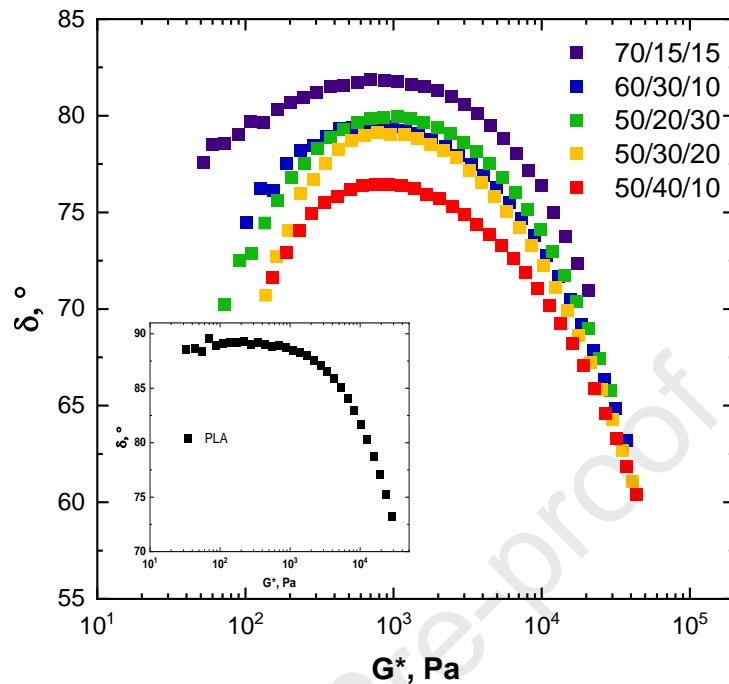
continuous relaxation of the macromolecular network, from short to long relaxation times [56]. According to the storage modulus data reported in Figure 2B, all ternary blends exhibit a non-terminal behavior recognizable in the flattening of the moduli curves in the low frequency zone, showing a deviation from the liquid-like relaxation of the neat components (see Figure S2B) which arises from the multi-relaxation behavior of the different phases and domains dispersed in the matrix. Similarly to what noticed for the complex viscosity, also in this case the values of the modulus of the ternary blends are governed by the content of PBS, which present higher melt elasticity as compared to the other two components.



**Figure 2.** Complex viscosity curves (A) and storage modulus as a function of frequency (B) for all formulated ternary blends.

The increased melt elasticity of the ternary blends upon the incorporation of increasing contents of PBS is further confirmed by the analysis of the van Gurp-Palmen (vGP) plot, displaying the trend of the phase angle ( $\delta$ ) as a function of the logarithmic complex modulus ( $G^*$ ). According to the curves depicted in Figure 3, all the formulated ternary blends exhibit a very different behavior with respect to the PLA matrix, whose vGP plot is reported in the inset in Figure 3. In fact, neat PLA shows a trend quite similar to those expected for a linear homopolymer (characterized by a completely viscous terminal behavior), with a plateau approaching  $\delta = 90^\circ$  in the low  $G^*$  region. For the ternary blends, a remarkable decrease of  $\delta$  at low  $G^*$  is observed; this behavior indicates a prominent elastic response for all formulated blends, arising from the interfacial interactions between the different phase domains embedded within the matrix and the PLA itself. Once again, it can be noticed that the increase of the melt elasticity is even more pronounced in the blends containing high content of PBS, thus confirming

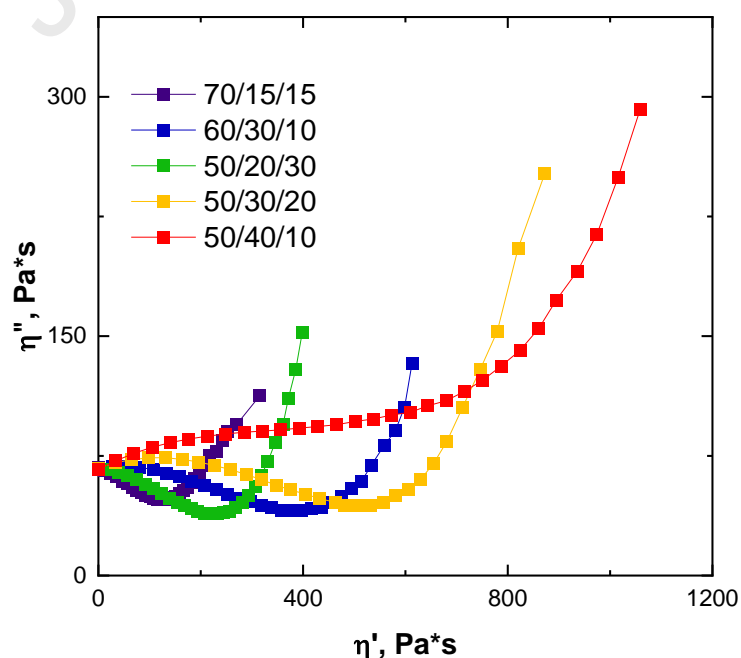
that the introduction of PBS ensures improved interfacial interactions within the materials, thereby influencing the phase adhesion and the final blend microstructure, as discussed in detail below.



**Figure 3.** Van Gurp–Palmen plot for all formulated ternary blends (the plot for the neat PLA matrix is reported in the inset).

All the noticed modification of the material rheological properties resulting from the introduction of different contents of the minor phases reflect a change of the relaxation dynamics of the polymer macromolecules of the different blend constituents. A more detailed analysis of the different relaxation phenomena occurring in the blends (stemming from the presence of a variety of dynamic species characterized by dissimilar shape, state of dispersion and extent of interfacial interactions) can be made through the arrangement of the data coming from dynamic frequency sweep measurements in the so-called Cole-Cole plot (Figure 4). Such kind of representation, which combines the imaginary ( $\eta''$ ) and real ( $\eta'$ ) components of the complex viscosity, was demonstrated to be sensitive in assessing phase separation in multiphase polymer-based systems and in revealing different relaxation mechanisms [57]. According to the literature, polymer-based systems having a single-phase structure and characterized by a single relaxation time present a smooth and semicircular arc. Conversely, the presence of different phases inducing additional relaxation mechanisms causes a deviation from the full arc shape, with the formation of a second arc or of a linear tail [58]. Generally, the arc appearing in the low  $\eta'$  region is related to the intrinsic relaxation of the main component, while the region at higher  $\eta'$  represents the relaxation related to the deformation of the domains of the dispersed phases [59].

All the PLA/PBS/PHBHH ternary blends studied here show significant deviations from the semicircular shape expected for homogeneous systems, indicating the achievement of typical heterogeneous multi-phasic microstructure. In particular, for the systems containing up to 30 wt.% of PBS, the semicircular arc appearing in the low  $\eta'$  region and the subsequent tail (which could be the sign of a second arc not fully completed in the tested frequency range) suggest the achievement of a drop-matrix phase morphology. The observed sudden increase of  $\eta''$  in the high  $\eta'$  (i.e. low frequency) region reflects the additional long-time relaxation processes stemming from the relaxation of the inclusions of the dispersed phases, as well as from the interfacial interactions between the polymer components; both these phenomena significantly hinder the system complete relaxation. Furthermore, it can be observed that the incorporation of increasing amounts of PBS causes significant modifications of the relaxation mechanisms of all ternary blends. In fact, a progressive retardation of the relaxation dynamics as a function of the PBS content can be observed, indicating that increasing amounts of PBS result in longer relaxation process, likely due to the more pronounced solid-like behavior and elasticity of this phase. The obtained results also suggest that a high level of interaction between the different phases is achieved when increasing amounts of PBS are incorporated in the ternary blends, and this feature is expected remarkably influencing the achieved phase morphology. On the other hand, 50/40/10 ternary blend exhibits a different behavior as compared to the other materials, also in the low  $\eta'$  region; for this system, indeed, the continuous increase of  $\eta''$  seems indicate a modification of the relaxation mechanism as compared to the other blends. In this case, the dispersed phases are able to continuously relax over a long time, inducing a continuous spectrum of relaxation times.

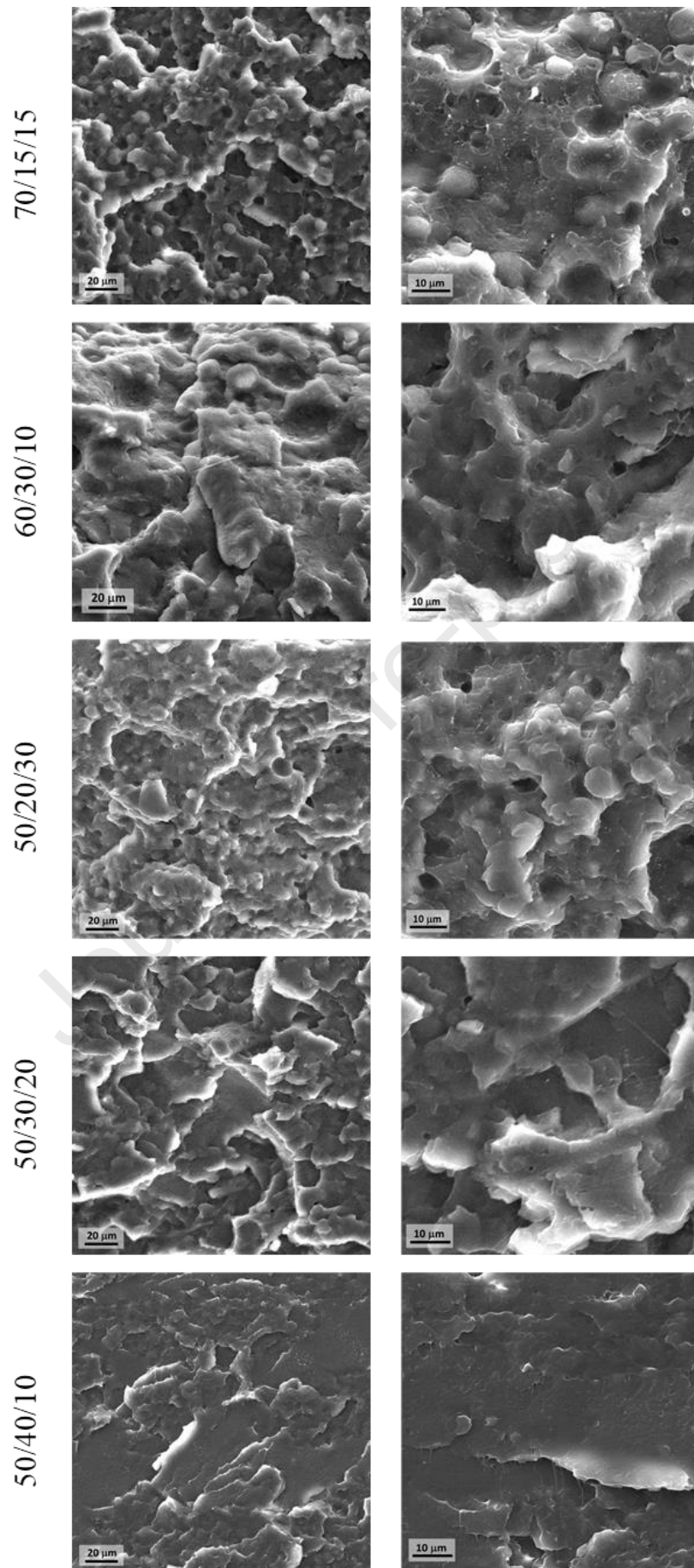


**Figure 4.** Cole-Cole plot for all formulated ternary blends.

Figure 5 reports some representative morphological observation at different magnifications of all the formulated ternary blends obtained through SEM microscopy. Blends containing low amounts of PBS (i.e. 70/15/15 and 50/20/30 systems) show a clear drop-matrix separate phase morphology, indicating the immiscibility of the polymer components. Nevertheless, a relatively good interfacial adhesion can be observed, as also testified by the absence of obvious debonding, highlighting a good compatibility between the different phases and a certain extent of interfacial interaction. As the content of PBS phase increases, an improved homogeneous morphology is achieved. In fact, ternary blends containing 30 and, even more, 40 wt.% of PBS exhibit much finer phase microstructure and a more uniform morphology, with possibly enhanced interfacial interactions between dispersed phases and PLA matrix. In the 50/40/10 ternary blend in particular, the minor phase domains are completely embedded in the matrix phase, making difficult distinguishing the dispersed phase inclusions, at least at the considered magnifications.

As reported in the literature, in a non-reactive ternary blend with two minor components, three different morphologies can be expected: separately dispersed minor phases, partial encapsulation and core-shell structures [60]. For the PLA/PBS/PHBHH blends studied here, thermodynamics calculations reported in section 3.1 predicted partial wetting for all investigated systems. Furthermore, from the results of the rheological analyses an improvement of the interfacial interactions in the blends containing high amounts of PBS was expected. Therefore, morphological observations seem confirm what already inferred, indicating that, when the content of PBS is higher than 30 wt.%, a beneficial effect in the morphology homogeneity and in phase adhesion is achieved.





**Figure 5.** SEM micrographs at different magnification for all PLA/PBS/PHBHH ternary blends.

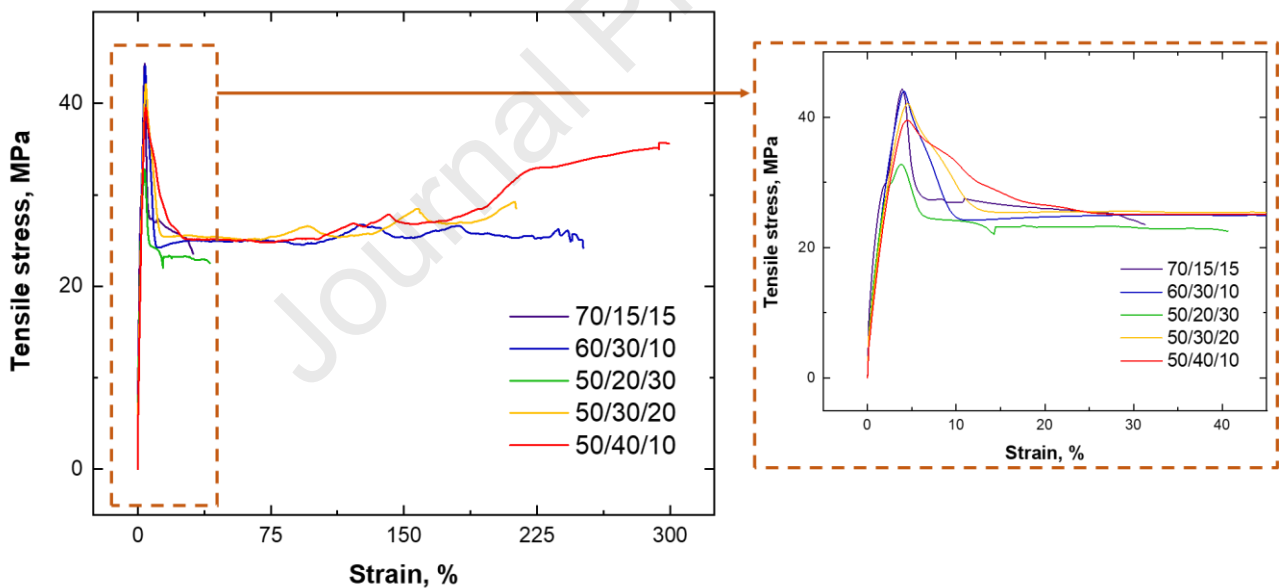
### 3.4 Mechanical properties

The stress-strain curves obtained by the tensile tests performed on all the formulated ternary blends are depicted in Figure 6. Furthermore, the values of the evaluated elastic modulus, tensile strength, elongation at break and tensile toughness values are displayed in Figures 7 (A-C). The curves obtained for the neat polymer components are also reported for comparative purposes in Figure S3, whereas Table S1 listed their main tensile properties. Neat PLA matrix shows a brittle behavior, failing at very low values of elongation at break ( $4.8 \pm 0.6$ ). Similarly, neat PHBHH exhibit brittle fracture, reaching a slightly higher value of failure strain ( $8 \pm 1.6$ ) with respect to PLA. Differently, PBS is characterized by a ductile behavior, showing significantly improved elongation at break ( $244 \pm 3.0$ ) as compared to the other base polymer samples.

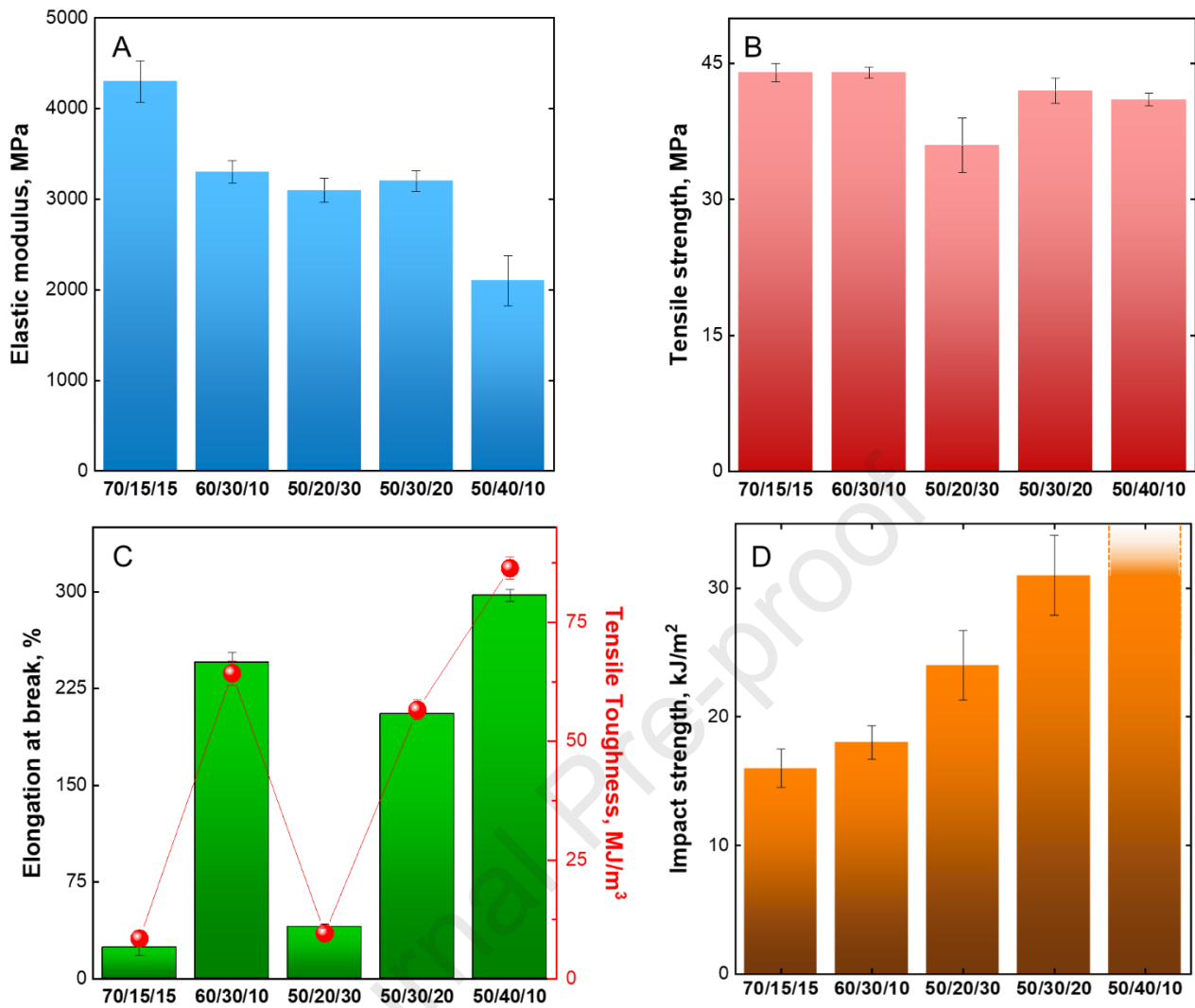
Interestingly, the PLA/PBS/PHBHH ternary blends exhibited a great balance in tensile properties as compared to the neat components. In fact, differently from the PLA matrix, all the blends underwent yielding followed by a significant drawing, indicating the occurrence of a brittle-to-ductile fracture transition. In particular, the introduction of PBS phases, especially at content higher than 30 wt.%, induces a dramatic increment of the elongation at break and of the tensile toughness as compared to both brittle PLA and PHBHH phases, while causing a moderate decrease of the stiffness and of the tensile strength. More specifically, the elongation at break of the 70/15/15 and 50/20/30 ternary blends reaches 24 and 40 %, respectively, increasing by about 5 and 8 times with respect to neat PLA. At the same time, these systems show considerably high elastic moduli and values of tensile strength moderately lower with respect of PLA. For the systems containing 30 or 40 wt.% of PBS the elongation at break is further increased, and reaches 297% for the 50/40/10 blend, showing an impressive increment as compared to neat PLA. Once again, it should be noticed that the excellent increment of the blend ductility does not significantly compromise the stiffness and the tensile strength of the materials. Undoubtedly, the incorporation of increasing amounts of PBS soft phase induces some reduction of the material elastic modulus and tensile strength, but a great balance between the tensile properties is still maintained even for the systems containing high PBS contents. This result seems suggest a beneficial effect of the increased crystallization of PLA that could be favorably keep the strength of the blends also in presence of high contents of soft phase [5].

In addition to the tensile ductility, the introduction of different ratios of PBS and PHBHH into PLA is able to affect also the material impact strength. As reported in the literature, neat PLA show a completely brittle failure mode, with an impact strength of about  $3.8 \text{ kJ/m}^2$  [61]. The values recorded for the ternary blends (depicted in Figure 7D) highlight the achievement of significantly improved impact strength values (for the 50/40/10 blend it was not possible reaching the sample breakage at the selected test conditions), showing a transition from brittle to fully ductile fracture mode.

It is well established that the blend morphology, the dispersion state of the domains of the dispersed phases and the interfacial interactions established at the interface considerably affect the final mechanical properties of multiphasic materials. For the PLA/PBS/PHBHH ternary blends studied here, better results in terms of increased ductility were showed by the blends containing 30 or 40 wt.% of PBS. Actually, the evaluation of the rheological behavior of these materials suggested a high level of interfacial interactions for these systems. Furthermore, morphological analyses demonstrated that for 60/30/10, 50/30/20 and 50/40/10 ternary blends improved homogeneous microstructure, characterized by a much finer phase morphology with respect to the other formulated materials, and a good extent of phase adhesion, were achieved. In all, the obtained results indicate that the introduction of high contents of PBS has a beneficial effect in improving the interfacial interactions between the blend components, and in promoting the achievement of a great extent of interfacial adhesion, thereby positively influencing the final properties of the obtained blends, especially in terms of increased ductility and toughness, which represent two main drawbacks of PLA, still severely limiting the exploitation of this biopolymer for structural applications.



**Figure 6.** Stress-strain curves for all PLA/PBS/PHBHH ternary blends.



**Figure 7.** Elastic modulus (A), tensile strength (B), elongation at break and tensile toughness (C), and impact strength (D) for all investigated ternary blends.

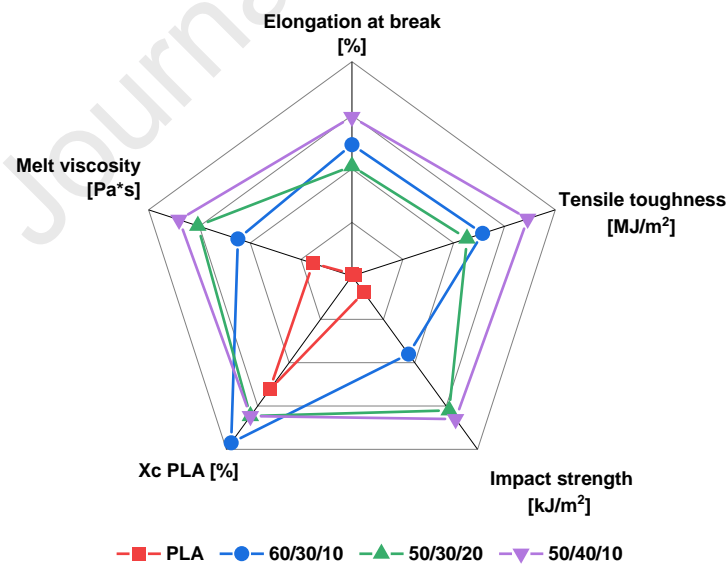
#### 4. Conclusions

In this work PLA/PBS/PHBHH immiscible ternary blends were formulated through melt blending, aiming at improving the intrinsic brittleness and low impact strength of PLA, while maintaining unaltered the sustainability characteristics and the biobased content of the matrix. The results coming from microstructural and mechanical characterizations demonstrated the possibility of achieving fully biobased materials with greatly balanced properties. In particular, the main achievements of the present study are summarized in the radar plot depicted in Figure 8, which compares the ternary blends containing 30 or 40 wt.% of PBS with the neat PLA matrix in terms of elongation at break, tensile toughness, impact strength, crystallinity of PLA phase and melt viscosity.

More in details:

- the characterization of the mechanical behavior (in terms of both tensile and impact properties) of the obtained ternary blends demonstrated the possibility of achieving impressive enhancements of the toughness and of the impact strength as compared to neat PLA, without significantly compromising its typical high stiffness and tensile strength;
- the incorporation of PBS and PHBHH phases resulted in a beneficial effect on the crystallinity behavior of the PLA matrix, leading to an enhancement of its crystalline degree that, in turn, contributed achieving relatively high values of tensile strength and stiffness also in presence of high contents of soft phase;
- owing to the introduction of PBS and PHBHH phases, all formulated ternary blends exhibited higher melt viscosity than neat PLA, hence ensuring high melt strength values which are usually required for the processing of polymeric materials through some industrially relevant technologies, such as thermoforming or film blowing.

In all, the obtained results revealed the possibility of obtaining fully biobased materials with greatly balanced and tunable properties, through the exploiting of an effective strategy, such as melt blending, that present the advantages of cost-effectiveness and facile large-scale production, opening new perspectives for the massive utilization of PLA as an alternative to conventional fossil fuel-based polymers also for applications requiring high levels of toughness and ductility.



**Figure 8.** Radar plot showing balanced properties for PLA/PBS/PHBHH ternary blends as compared to PLA matrix.

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- Fully biobased PLA/PBS/PHBHH ternary blends were prepared through melt blending
- Ternary blends showed significantly higher toughness and impact strength than PLA
- A satisfactory ductility/stiffness balance was obtained for all ternary blends
- The incorporation of high content of PBS positively affected the blend morphology
- Ternary blends exhibited high melt viscosity and elasticity than neat PLA

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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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