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Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch

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Abstract

In this study binary and ternary blends of polylactide (PLA), polycaprolactone (PCL) and thermoplastic starch (TPS) are prepared using a one-step extrusion process and the morphology, rheology and physical properties are examined. The morphology and quantitative image analysis of the 50/50 PLA/TPS blend transverse phase size demonstrate a bimodal distribution and the addition of PCL to form a ternary blend results in a substantial number of fine dispersed particles present in the system. Focused ion beam irradiation, followed by atomic force microscopy (AFM) shows that dispersed PCL forms particles with a size of 370 nm in PLA. The TPS phase in the ternary blends shows some low level coalescence after a subsequent shaping operation. Dynamic mechanical analysis indicates that the temperature of the tan δ peak for the PLA is independent of TPS blend composition and that the addition of PCL in the ternary blend has little influence on the blend transitions. Both the α and β transitions for the thermoplastic starch are highly sensitive to glycerol content. When TPS of high glycerol content is blended with PLA, an increase in the ductility of the samples is achieved and this effect increases with increasing volume fraction of TPS. The ternary blend results in an even greater ductility with an elongation at break of 55% as compared to 5% for the pure PLA. A substantial increase in the notched Izod impact energy is also observed with some blends demonstrating three times the impact energy of pure PLA. The mechanical properties for the ternary blend clearly indicate a synergistic effect that exceeds the results obtained for any of the binary pairs. Overall, the ternary blend approach with PLA/TPS/PCL is an interesting technique to expand the property range of PLA materials.

Keywords: Thermoplastic starch; Polylactide; Polycaprolactone

1. Introduction

Environmental concern over the use of traditional petroleum-based polymers has stimulated the development of polymers from renewable resources as an alternative. Starch, as the main reserve polysaccharide of higher plants, is a naturally occurring biopolymer and is of low cost. Starch consists of two main polysaccharides, amylose and amylopectin, based on chains of 1 → 4 linked α-D-glucose [1]. Amylose is essentially linear, amylopectin, often the major part (about 72% in wheat and maize starches), is highly branched containing on average one branch point which is 1 → 4 → 6 linked for every 20–25 straight chain residues [1]. The starch granule is partially crystalline, and various crystalline forms are reported, depending on the proportion of the two main polysaccharides and the regions in the starch granules. Since the melting temperature (T_m) of pure dry starch is close to 220–240 °C and the onset temperature of starch degradation is around 220 °C [2], native starch has to be modified in order to be melt-processed as a thermoplastic.

The addition of water to starch is known to have a strong plasticizing effect, causing a large decrease in the glass transition temperature (T_g) [3]. When starch is usually heated in the presence of water the native crystalline structure is disrupted, a phenomenon known as gelatinization. In an excess of water, above the gelatinization temperature, the starch granule loses

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its native crystalline order and swells irreversibly to many times its original size [1]. In native wheat starch the granule size distribution is bimodal [4] and the different sizes display somewhat different gelatinization behavior [5,6]. Although water is a ubiquitous plasticizer of starch, it is volatile, and cannot be used to produce utilizable plastic-like materials. For this reason, the use of other, non-volatile, plasticizers, such as glycerol, are often used in combination with water. Glycerol appears to be a less effective plasticizer than water [7]. However, Perry and Donald [8] have shown that gelatinization proceeds even when no water is present: there is no chemical requirement for water, the only requirement being mobility, induced by some low molecular weight plasticizer. However, without water the temperature for the onset of gelatinization by glycerol increased [9,10]. Upon heating, starch granules become solvated, with the amorphous regions of the plasticized starch granule. This transformation of granular starch into a thermoplastic-like material allows it to be processed in a similar fashion to conventional polymers. At glycerol contents in the TPS lower than 10–15%, the plasticization leads to reduced mechanical properties [11]. A more effective plasticization can be obtained at higher glycerol contents, in a range where glycerol demixing can occur in the thermoplastic starch. Thermoplastic starch itself is characterized by moisture sensitivity and weak mechanical properties as compared with other thermoplastic polymers. Blends of other polymers with thermoplastic starch represent an important route to overcome these limitations.

Crop-based polylactide (PLA) is an example of a promising biopolymer prepared through a combination of biotechnology and chemistry. Polylactide is prepared from 100% renewable resources such as corn, sugar beets or rice [12]. Blending thermoplastic starch with PLA is a route to reduce raw material costs, energy consumption and also to increase its rate of biodegradation. Avérous and Martin [13] and also Park et al. [14] were the first to study TPS/polylactide blends. The gelatinized starch was prepared with various water/glycerol ratios and was then dried. After that, the dry blend was mixed using a batch mixer or extruded with a single-screw extruder. Martin and Avérous [13] observed that the modulus decreased when the TPS fraction increased. In comparison to the pure TPS and PLA materials, all the blends showed a marked decrease in the elongation at break, tensile strength and impact resistance. They explained the poor mechanical properties by the lack of affinity between the two phases. The morphology of their TPS/PLA 75/25 (wt.%) blends was characterized by a TPS continuous phase with large and non-uniform PLA domains exhibiting phase sizes in the 10–100 μm range.

Poly(ε-caprolactone) (PCL) is a well-known synthetic, biodegradable, semi-crystalline polyester, characterized by a high elongation at break. Its low melting point of around 60 °C is often perceived as an impediment for use as a common thermoplastic. However, since PCL and PLA have complementary strengths and weaknesses as polymer materials, PCL could be an interesting candidate to moderate the brittle behavior of PLA.

Previous work from this laboratory has shown that a one-step extrusion process can be used to prepare polyethylene/TPS blends with excellent properties [15]. In that process, the plasticization of starch (from a suspension of starch, glycerol and water), devolatilization of water and blending of TPS with the carrier polymer were all achieved in one single extrusion operation. The PE/TPS blends prepared in this fashion demonstrate levels of ductility and modulus similar to the virgin polyethylene even at very high loadings of TPS. This blend preparation approach is particularly effective at achieving high loadings of the glycerol plasticizer in starch and it has been shown [15–17] that loadings in excess of 28% glycerol are necessary in order to achieve a TPS phase that is sufficiently deformable to carry out morphology control protocols in blend systems.

The objectives of this research are to examine the morphology and properties of PLA/PCL/TPS binary and ternary blends prepared via a one-step melt processing operation.

2. Experimental

2.1. Materials

The wheat starch was obtained from ADM, while the glycerol was provided by MAT Laboratories. Polylactide was supplied by Cargill LLC (non-commercial grade 5729B) and polycaprolactone by Solvay-Interox ($M_w = 80{,}000$ g/mol, MFI = 3 g/10 min at 160 °C). Throughout this paper the designations TPS36 and TPS24 refer to 36% and 24% glycerol in the thermoplastic starch respectively.

2.2. Processing

The extrusion system was composed of a single-screw extruder connected to a co-rotating twin-screw extruder. The starch/excess water/glycerol suspension was fed in the first zone of the twin-screw extruder set at 150 rpm, while polylactide was fed in the single-screw extruder. After gelatinization and plasticization of the starch followed by extraction of the volatiles, TPS was mixed with the molten polylactide on the twin-screw extruder. The temperature in the zones crossed by polylactide was set at 150 °C. The draw ratio of the strands exiting the die was held at 1. All the blend compositions are given in weight fractions. More details concerning the extrusion process are reported elsewhere [15,18].

The starch suspensions destined to be fed to the twin-screw extruder were prepared in the following proportions: 48.5 wt.% of starch, 28.15 wt.% of glycerol and 23.35 wt.% of excess water for TPS36, and 48.5 wt.% of starch, 15.65 wt.% of glycerol and 35.85 wt.% of excess water for TPS24. The starch is used as-received, without drying. The water used for gelatinization was subsequently removed through venting in the zone just before the connection with the single screw. TPS36 and TPS24 contained about 36 and 24 wt.% glycerol after extrusion, respectively.

The various compositions were extruded under the same conditions, and granulated after air cooling. Pure PLA was also re-extruded. The feeding rate of the starch slurry was approximately the same for all the compositions and was held to obtain 40–45 g/min of TPS. The feeding rate of PLA + PCL was adjusted for each blend composition. For terblends and also for PLA/PCL blends, binary dry blends of PLA and PCL were prepared by initially dry blending the corresponding pellets. True compositions were measured from the thermal decomposition of the pellets using thermal gravimetric analysis (TGA) as reported previously [19].

The compounded pellets were then used to prepare ASTM D638 Type I standard tensile dog-bone specimens and Izod type test specimens by injection molding on a Sumitomo SE50S machine. The temperature profile was 150/150/155/160 °C from the feeder to the mold. The nominal width and thickness of the tensile bars were 10 and 3 mm, respectively. The dimensions of the Izod impact bar were 63 × 12.6 × 4.7 mm. The cross-section surface at the 3 mm-depth notch was around 47 mm^2. No demolding agent was used in injection molding.

2.3. Blend morphology and image analysis

The specimens were microtomed to create a perfect plane face using a cryogenic Leica microtome with a glass knife. To increase the contrast between the polymer phases, selective solvent extractions were performed at room temperature. The TPS was extracted for 3 h in 3N HCl. The specimens were soaked in water and then dried in a vacuum oven. After coating with a gold–palladium alloy, the microtomed specimens were observed under a Jeol JSM 840 scanning electron microscope. Morphologies in the center of the microtomed cross section of the strands after extrusion and Izod impact bars are presented. Image analysis was carried out using a digitizing table from Wacom to evaluate the volume and number average diameters, d_v and d_n respectively. SEM micrographs of ×500 and ×1000 magnification were used.

2.4. Atomic force microscopy (AFM)

After the preparation of the surface by microtomy at room temperature, morphological observations of specimens PLA/PCL/TPS36 50/0/50 and 40/10/50 were carried out in tapping mode using a Multimode AFM from Veeco equipped with a Nanoscope IV controller. Silicon tips, from Pacific Nanotechnology, with spring constant of 42 N/m and resonant frequency of 320 kHz were used. Also, a binary blend of PLA/PCL was cryogenically cut, plasma-coated and then prepared using a focused ion beam (FIB) following the procedure developed by Virgilio et al. [20] to reveal the size of PCL domains in a PLA matrix.

2.5. Rheology

A dual-bore capillary rheometer (single barrel Rosand RH-7) was used to measure the viscosities of pure PLA and blends at high shear rates at 165 °C. For the rheological experiments, it should be mentioned that the pure PLA used was the original as-received. Using dies of the same diameter (1 mm, with an entrance angle of 180°), simultaneous measurements were carried out on both long and short dies (0.25 and 20 mm) to determine the inlet pressure drop at the die, and therefore the absolute viscosity, using the Bagley correction method. The Rabinowitch correction was also applied to calculate the true shear rate.

2.6. Thermal properties of blends by dynamic mechanical thermal analysis

DMTA experiments, performed on a 2980 DMA from TA Instruments, were conducted on Izod specimens for TPS/PLA, TPS/PLA + PCL blends and also on bars for PLA/PCL binary blends (molded by compression, 63 × 12.5 × 2 mm). The specimens were tested in the single cantilever bending mode at a frequency of 1 Hz with a target amplitude of 40 μm. The scanning rate was set at 2°/min in the range of −100 to 90 °C. The thermal transitions were determined from the maxima of the tan δ peaks, analyzed using the TA Instruments Universal Analysis 2000 software.

2.7. Mechanical properties

All the mechanical property measurements were performed at room temperature on injection molded blends. Tensile strength, elastic modulus and elongation at break were measured on a mechanical tensile tester (Instron 4400R) equipped with a 5kN cell, according to the ASTM D638 method. A crosshead speed of 5 mm/min was used. Ten specimens were used for each blend condition.

Izod impact tests were performed on notched samples on a Custom Scientific Instruments impact tester, equipped with a 5.42 J pendulum, according to ASTM D256 method. The units of energy are typically reported in J/m since the ASTM standard defines a constant thickness of samples. Ten specimens were used for each blend condition. Complete break and some hinge break modes were obtained. Only the complete breaks, as according to ASTM, are reported.

3. Results and discussion

3.1. Morphology and rheology

Fig. 1 presents the morphology of the native wheat starch granules and the typical morphology of the PLA/TPS blends. Wheat starch granules are characterized by a bimodal size distribution: large A-type, lenticular granules with a diameter of 10–35 μm as well as small B-type, spherical granules with a diameter of 1–10 μm are present [4,21]. Choi and Kerr [22] estimated the average diameters as 20.4 μm for the A-type and 2.3 μm for the B-type. In this study, the volume and number average diameters d_v and d_n for the starch granules are found to be 15.8 and 8.9 μm, respectively (Table 1). The morphology of the blends also reveals a bimodality for the size of dispersed TPS phase (Fig. 1b). Large deformed domains and small particles of plasticized starch coexist. It is known that the granule types can have significant differences in chemical composition and functional properties. The amylose/amylopectin ratio, for example, can have an

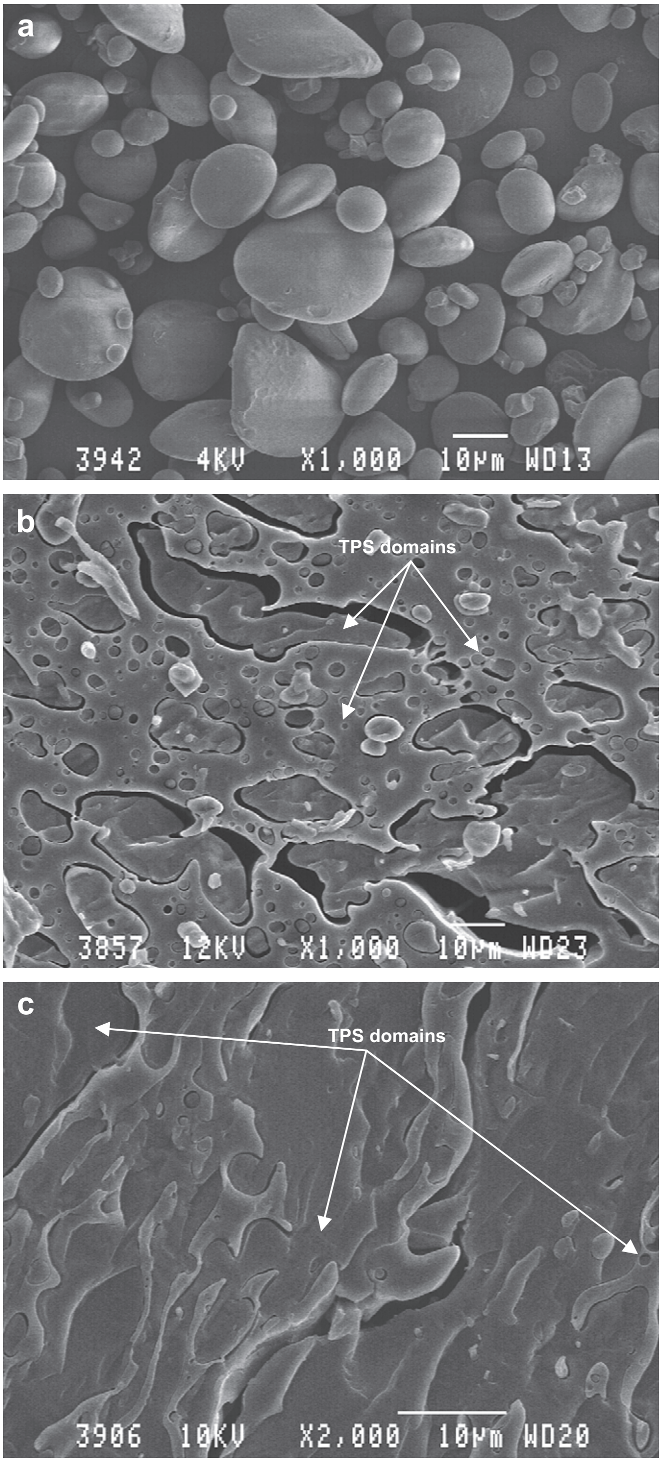

Fig. 1. Scanning electron micrographs of (a) pure wheat starch, (b) PLA/TPS36 50/50 blend and (c) PLA/TPS36 30/70 blend. The white bar indicates 10 µm.

Table 1
Native starch particle size and TPS phase sizes obtained by image analysis on SEM micrographs

Materials	d_n (µm)	d_v (µm)
Wheat starch	8.9	15.8
PLA/PCL/TPS36		
50/0/50 extruded	2.9	12.9
50/0/50 molded	3.9	16.3
40/10/50 extruded	1.4	12.1
40/10/50 molded	3.3	12.1

effect on gelatinization characteristics. Van Hung and Morita [23] measured the amylose content for the two types of granules: 30% for the A-type and 23% for the B-type. Large starch granules swell more easily than small granules and the more amylose that a starch contains, the more swelling it requires for gelatinization. Peng et al. [24] showed that A-type starch granules contain higher amylose concentrations and had higher gelatinization enthalpies than did B-type starch granules. Although A- and B-type starch granules start to gelatinize at a similar temperature, B-type starch granules had a higher gelatinization peak and completion temperatures than did A-type starch granules. Large TPS domain sizes, around 20 µm, can be found even at low TPS concentration, as shown in Fig. 2a and b. This indicates that some of the large starch granules have not fragmented. Eventually, the production of blends which separates out the two types of granules could be an approach to truly study the origin of the bimodal size distribution of the TPS phase in these blends. At 50% TPS, the TPS phase is not completely continuous while at 70% TPS, the blend appears to be virtually co-continuous (Figs. 1c and 2d).

Fig. 2c and e shows that 10% of PCL in the 50% TPS blends improves the dispersion of the well-plasticized TPS phase in the PLA matrix (the plasticization step is unchanged) and the number of the smaller TPS phase domains is visibly increased. The number average diameter of the TPS domains is halved after addition of 10% of PCL to a PLA/TPS blend, while the d_v remains the same (Table 1).

In order to further understand the morphology adopted by PCL in PLA, a FIB/AFM micrograph of the PCL/PLA blend was prepared and is shown in Fig. 3. The particle sizes are extremely small with a d_v of 510 nm and a d_n of 370 nm. Such small phase sizes in polymer blends are often an indication of some partial miscibility. However, DMTA experiments carried out on PLA/PCL binary blends (shown in Table 2) indicate no shifts in the T_g of PCL (-47.3 ± 1.0 °C) or PLA (about 63 °C) with PLA/PCL blend composition as measured using the tan δ peak. The PCL/PLA binary blend is clearly fully immiscible.

Polymer blends generally demonstrate a significant coarsening of the dispersed phase after injection molding. Fig. 2 indicates that the gross morphology for the blends in this study is preserved after the injection molding process. However, detailed image analysis in Table 1 demonstrates some low level coarsening of the dispersed phase for both binary PLA/TPS and PLA/PCL/TPS ternary blends. In the latter case the coarsening effect is more pronounced for the smaller particles in the system. For blends with TPS24, large phase domains are found (not shown here) and the addition of PCL does not influence the morphology. For this plasticizer level under the experimental conditions used, the TPS phase is formed from agglomerated starch granules, is partially plasticized, and cannot totally flow as a thermoplastic.

The viscosity of the binary PLA/TPS blends as a function of shear rate is shown in Fig. 4. In the typical range of

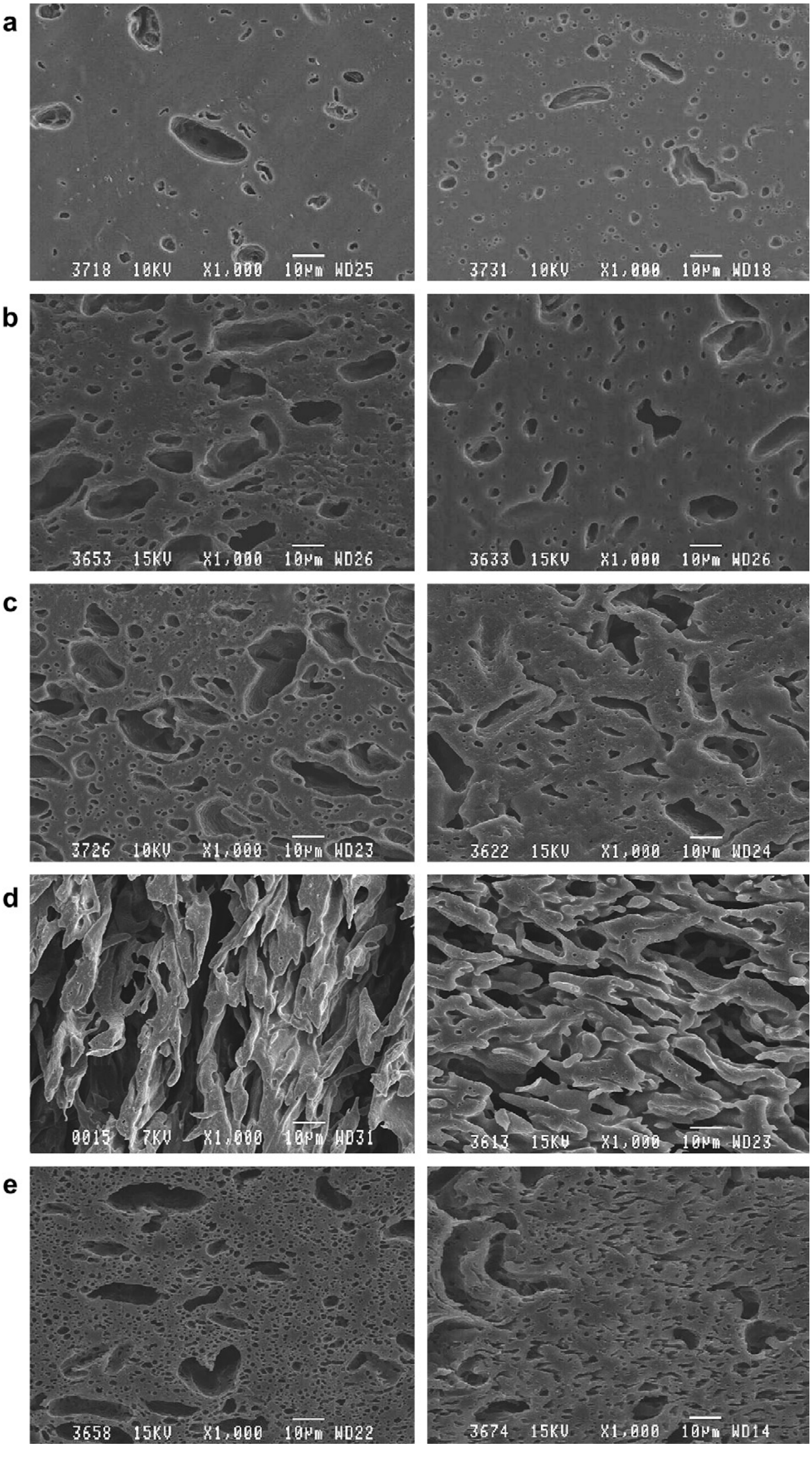

Fig. 2. SEM micrographs after TPS extraction for PLA/PCL/TPS36 blends in the transverse direction after one-step extrusion (first column) and injection molding (second column): (a) 90/0/10; (b) 70/0/30; (c) 50/0/50; (d) 30/0/70; (e) 40/10/50. The white bar indicates 10 μm.

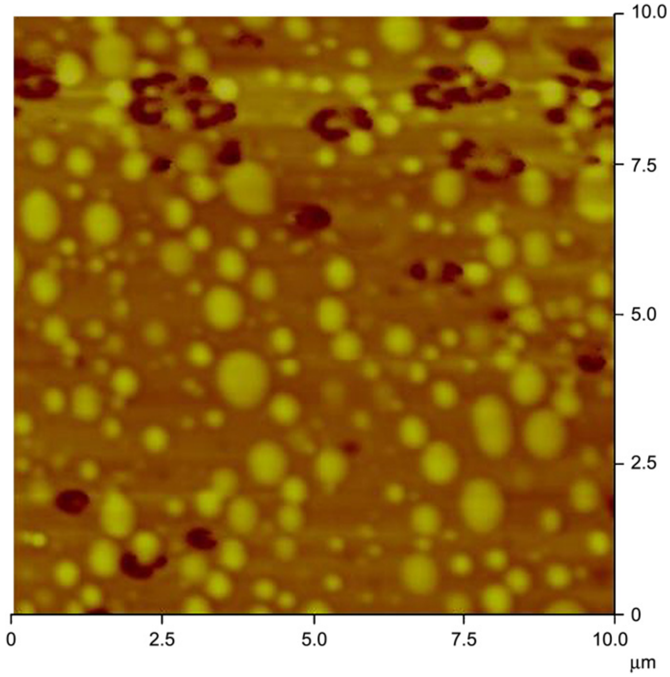

Fig. 3. Morphology obtained by FIB/AFM on PLA/PCL 75/25 blend.

processing shear rates (100–1000 s^{-1}), it can be clearly seen that the TPS containing 36% glycerol significantly reduces the blend viscosity as compared to pure PLA. This effect becomes more and more pronounced as TPS concentration increases. This viscosity reduction phenomenon is due to the presence of glycerol since TPS with 24% glycerol (Fig. 4b) shows much less of the effect. These results are important since they indicate that the optimal processing conditions for shaping operations of TPS blends could be quite different as compared to those for pure PLA. These results are also important since they indicate an increased benefit of TPS as a processing aid during melt processing. It should thus be possible to significantly reduce processing temperatures in shaping operations and hence lead to important energy reductions resulting from the use of TPS blends.

Table 2
Transition temperatures measured from tan δ (DMTA)

PLA/PCL	T_g PCL (°C)		T_g PLA (°C)
0/100	−47.2		–
25/75	−46.1		Not measured
50/50	−47.4		63.3
75/25	−48.5		63.9
100/0	–		62.8
PLA + PCL/TPS36	T_β (°C)	T_α (°C)	T_g PLA (°C)
70 + 0/30	−57.8	−5.9	62.8
50 + 0/50	−55.7	−8.6	63.1
30 + 0/70	−57.2	−7.6	62.1
47.5 + 2.5/50	−57.7	−8.6	61.9
40 + 10/50	−57.4	−9.2	62.5
PLA + PCL/TPS24	T_β (°C)	T_α (°C)	T_g PLA (°C)
70 + 0/30	−45.6	14.0	62.5
50 + 0/50	−46.7	24.5	61.2
30 + 0/70	−49.9	19.0	61.7
45 + 5/50	−46.3	20.6	62.7

3.2. Transition temperatures in the blends, measured by DMTA

The transition temperatures for TPS/PLA and TPS/PLA + PCL blends were measured by DMTA. Fig. 5a indicates that at temperatures lower than approximately −57 °C, the TPS36 phase has the higher storage modulus. At higher temperatures, the PLA phase becomes the more rigid component. The evolution of tan δ versus temperature shows three transitions (Fig. 5b and c). The higher temperature, at about 62–63 °C, corresponds to the glass transition for PLA (Table 2). The T_g of PLA measured here does not depend on the TPS composition in the blend and this finding contradicts previous results in the literature [13]. For the ternary blends, this temperature also remains unchanged. The two other transitions at lower temperature in Fig. 5 are due to the TPS phase. For glycerol contents higher than 10–15%, as described by Lourdin et al. [11,25], a relaxation peak can be found at low temperature, close to the glass transition of glycerol, suggesting that a phase separation

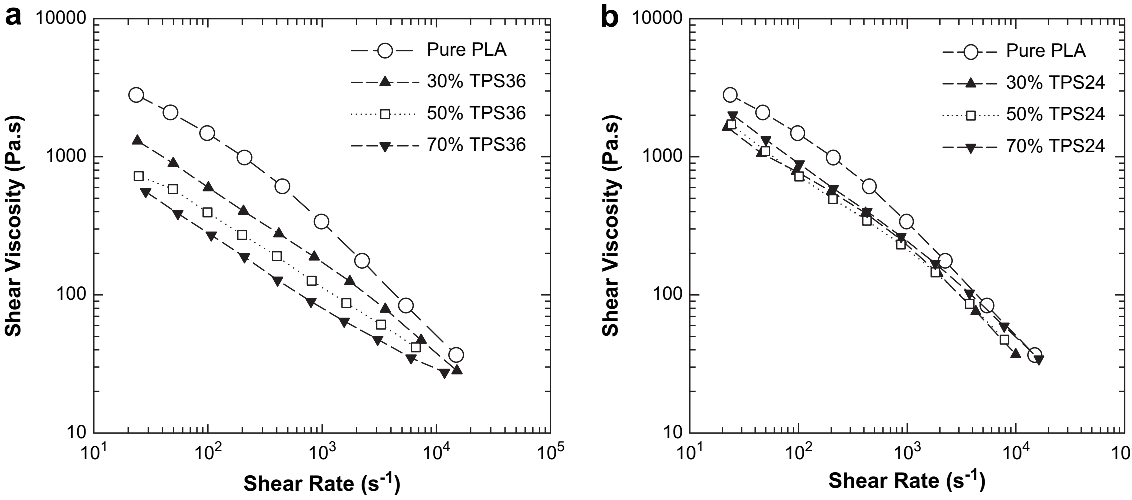

Fig. 4. Melt viscosity for pure PLA and PLA/TPS as a function of the shear rate, at 165 °C: (a) PLA/TPS36; (b) PLA/TPS24.

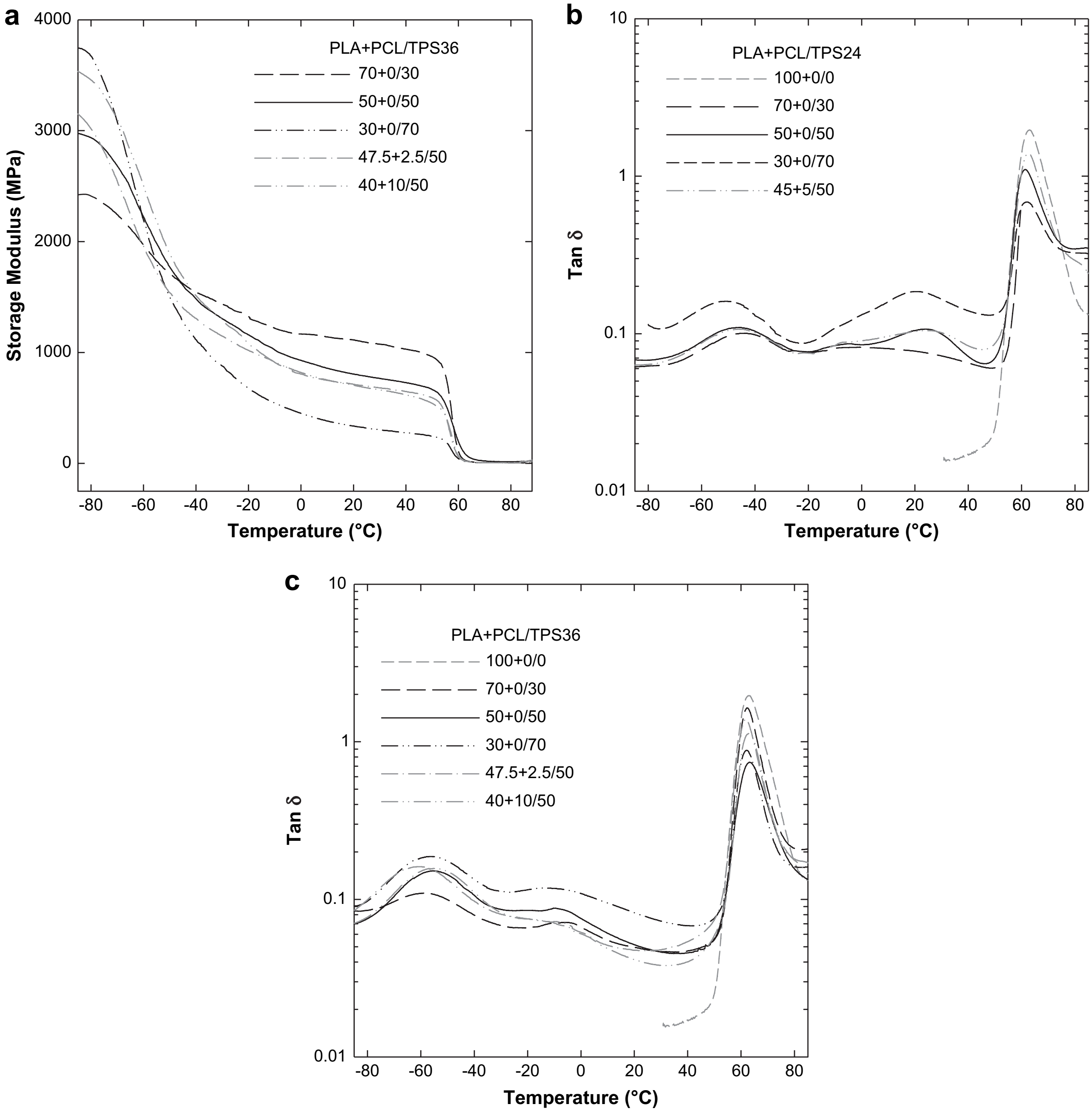

Fig. 5. (a) Storage modulus for PLA/TPS36 and tan δ as a function of the temperature for (b) PLA/TPS24 blends and for (c) PLA/TPS36 blends.

(glycerol demixing) occurs in thermoplastic starch. This peak corresponds to a glycerol rich phase transition, β [11].

For all the TPS36 blends, a tan δ peak located around −57 °C is observed (Table 2, Fig. 5c). For the terblends, this peak represents the overlapping of two transitions, relaxation β for the plasticized starch and the glass transition for PCL. Lourdin et al. [26] and Avérous et al. [27] observed that the magnitude of the tan δ peak for the β transition was strongly dependent on the glycerol content. Those results are confirmed here and TPS36 blends have a lower Tβ than TPS24 blends (more than 10 °C less) indicating that the glycerol content in these blends is superior as expected.

The other transition, α relaxation, can be related to the glass transition of the starch rich phase and the T_g shift between TPS36 and TPS24 blends (Table 2) can be attributed clearly to various amounts of plasticizer. T_α values are found to be around −8 and 20 °C, for TPS36 and TPS24, respectively. Thus the starch is, as expected, more plasticized when the concentration of glycerol in the blend increases. The TPS concentration in the blend and the presence of PCL have no effect on the starch plasticization. At room temperature, the TPS phase in the blends should demonstrate a rubbery behavior for TPS36 blends in a glass PLA matrix and a more glassy behavior for TPS24 blends due to the α relaxation of the starch rich-phase.

3.3. Mechanical properties

For TPS36 blends, increasing the concentration of TPS in PLA results in a continuously increasing strain at break as

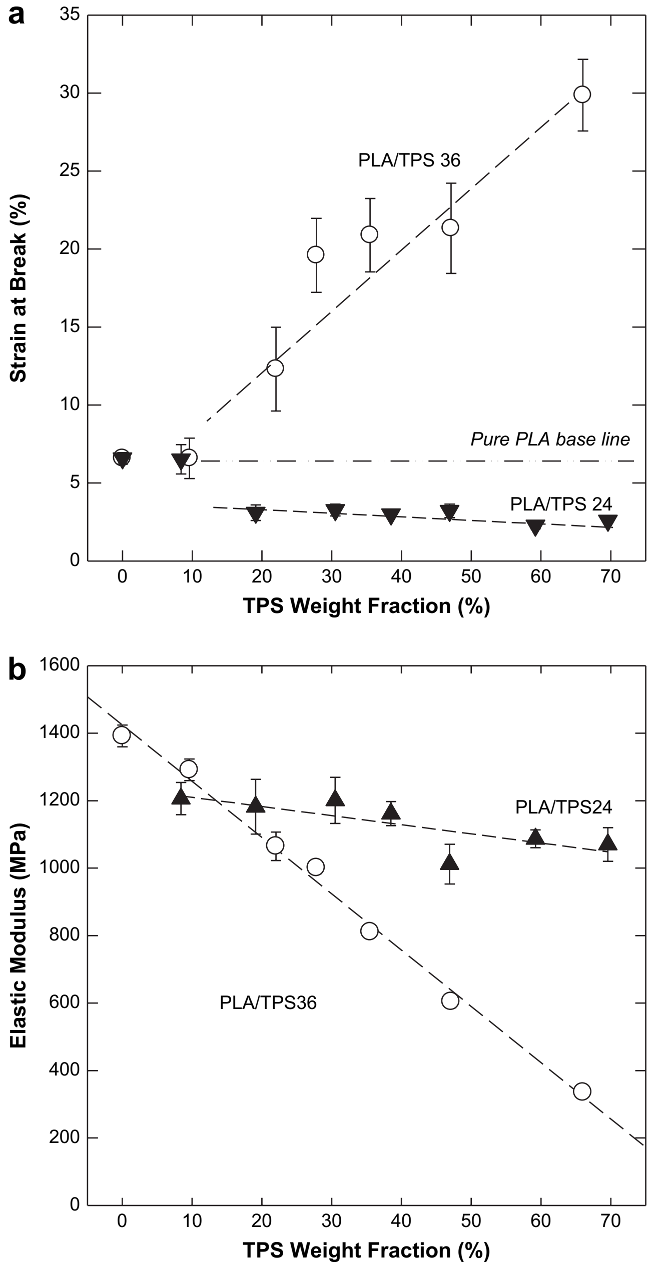

Fig. 6. (a) Strain at break and (b) elastic modulus for PLA/TPS blends, as a function of TPS weight fraction and glycerol content.

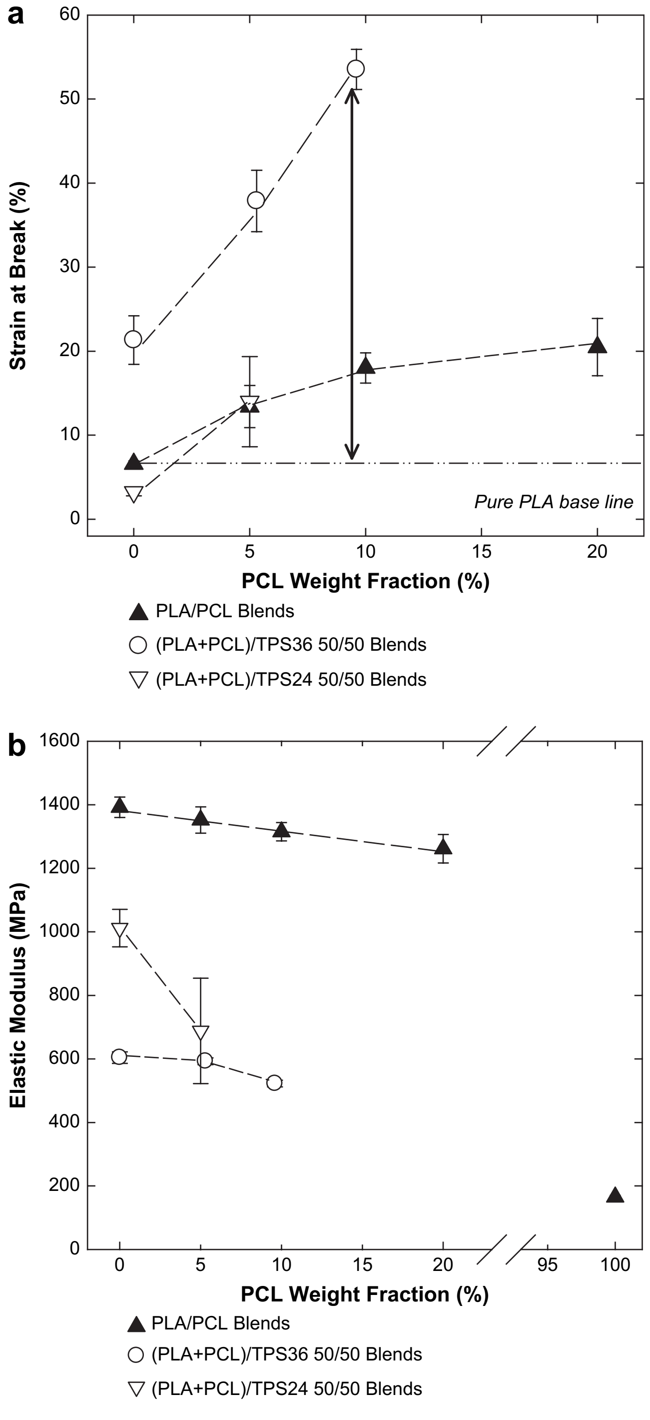

Fig. 7. (a) Strain at break and (b) elastic modulus for PLA/PCL and (PLA + PCL)/TPS 50/50 blends, as a function of PCL weight fraction.

shown in Fig. 6a. This increased strain at break of the blends is accompanied by a decrease in the elastic modulus (Fig. 6b) and maximum strength (not shown here) with TPS weight fraction. The TPS24 blends present a more brittle behavior than pure PLA, with a somewhat lower elastic modulus. Table 2 shows that TPS24 has an α relaxation temperature that is close to room temperature, while TPS36 is well below. Since PLA also has a glass transition temperature above room temperature, TPS24/PLA represents a totally glassy material.

The addition of 5% PCL in the PLA/TPS24 blends results in an increase in the strain at break, higher than for pure PLA, and is accompanied by a large decrease in the modulus (Fig. 7). The addition of 10% PCL to the PLA/TPS36 blend results in a much more evident and significant increase in the strain at break as shown in Fig. 7a with an elongation at break of 55% as compared to 5% for pure PLA. It is also accompanied by a small reduction of the elastic modulus (Fig. 7b). This increase in ductility also results in a substantial increase in the notched Izod impact energy as shown in Fig. 8. The impact energy for the ternary blends significantly exceeds that obtained for the binary PLA/TPS36 or PLA/TPS24 blends. Under these test conditions, the results indicate that

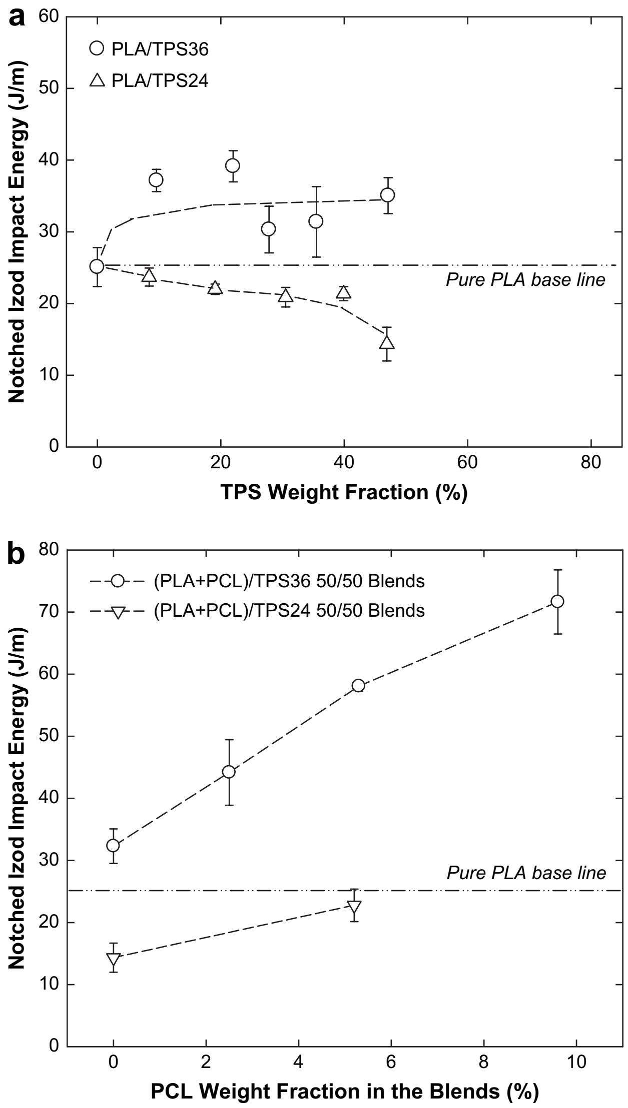

Fig. 8. (a) Impact energy as a function of TPS weight fraction; (b) impact energy as a function of the PCL fraction in (PLA + PCL)/TPS 50/50.

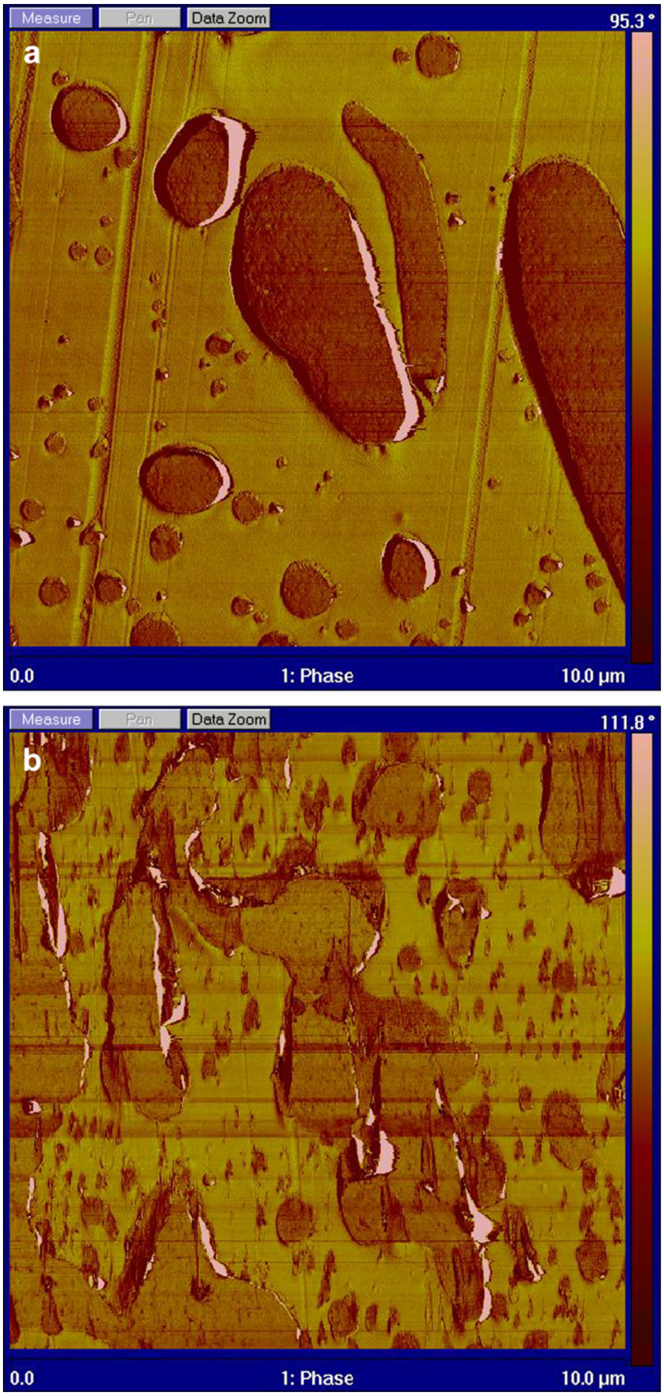

Fig. 9. Morphologies obtained by AFM after microtoming at room temperature; (a) PLA/TPS36 50/50; (b) PLA/PCL/TPS36 40/10/50.

a PLA/PCL/TPS36 40/10/50 blend possesses an impact energy that is three times greater than that for pure PLA. These results are highly dependent on the glycerol content in the starch and blends with TPS24 do not demonstrate the higher impact strength of the TPS36 samples (Fig. 8a).

The significantly improved elongation and impact strength properties observed after addition of TPS to PLA and then also after addition of PCL into a PLA/TPS blend are important. Since PLA is a fragile material, any efforts to improve its ductility are highly relevant. In a previous work from this laboratory [15], we showed that at high glycerol contents in the TPS, it was possible to prepare high loadings of hydrophilic TPS in hydrophobic polyethylene that demonstrated elongations at break very similar to the virgin PE. These results were obtained without the addition of interfacial modifier. The most important property improvements were obtained at the same high glycerol contents in the TPS as used in this work. We postulate in that paper, based on Harkins spreading coefficient theory, that a glycerol rich layer forms at the surface of the thermoplastic starch. The same highly optimal processing conditions are used here and hence it is not surprising to observe an improved ductility of PLA with addition of TPS. However, in this study the ability of TPS to improve the ductility of PLA is limited by the fragile nature of the PLA itself. In Fig. 7a we clearly show that the PCL improves the ductility of the PLA. The improved ductility obtained by the addition of PCL to PLA then allows for the additional synergistic interactions with the ductile TPS (TPS36) to come into play. In our study, none of the SEM or AFM micrographs show any evidence of the PCL being located at the PLA/TPS interface.

In order to visualize this increased ductility, AFM micrographs of PLA/TPS36 and PLA/PCL/TPS36 specimens microtomed at room temperature are shown in Fig. 9. In Fig. 9a for the PLA/TPS blend, the effect of the microtome knife is barely evident (apart from some minor plowing). However, in Fig. 9b, 10% PCL in the blend leads to the presence of massive deformation and tearing at the interfaces between PCL and PLA. The results shown here strongly support the notion that a minimum level of ductility is necessary in the matrix phase in order to obtain significantly improved properties. When high glycerol contents are present in the TPS phase and PCL is added to modify the ductility of the PLA, synergies come into play which allow the ternary PLA/PCL/TPS blend properties to exceed that observed with any of the binary pairs.

Overall, the mechanical properties indicate that the ternary blend approach with PCL is a useful technique to expand the property range of PLA materials.

4. Conclusion

This paper reports on significant improvements in the impact and elongation at break properties of PLA through the addition of thermoplastic starch as well as PCL. A fragile to ductile transition is achieved for PLA. The work demonstrates that ternary blend preparation of polylactide, polycaprolactone and thermoplastic starch is a viable technique to expand the property range of PLA materials. Although DMA results indicate that the three components are mutually immiscible, it is shown that small quantities of a very finely dispersed PCL phase ($d_n = 370$ nm) dispersed in PLA can significantly improve the ductility of PLA/TPS blends. An elongation at break for PLA/PCL/TPS 40/10/50 of 55% was achieved, as compared to 5% for the pure PLA. A substantial increase in the notched Izod impact energy is also observed with some blends demonstrating three times the impact energy of pure PLA. The results shown here strongly support the notion that a minimum level of ductility is necessary in both the TPS and PLA phases in order to obtain significantly improved properties. When high glycerol contents are present in the TPS phase and PCL is added to modify the ductility of the PLA, synergies come into play which allow the ternary PLA/PCL/TPS blend properties to exceed that observed with any of the binary pairs.

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