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Physico-Mechanical Properties of Biodegradable Rubber Toughened Polymers

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Summary: In this study, blends of poly(lactic acid) (PLA) with poly(butylene adipate-co-terephthalate) (PBAT) were studied for their mechanical and thermal properties as a function of the PBAT content. Tensile testing, impact testing, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMTA) and scanning electron microscopy (SEM) were used to characterize the blends. It was observed that PLA/PBAT blends maintained quite high modulus and tensile strength compared to pure PLA. Small amounts of PBAT improved the elongation at break and the impact resistance showing a debonding effect typical of rubber toughened systems.

Keywords: biodegradable; biopolymers; blends; mechanical properties

Introduction

Biopolymers may be obtained from renewable resources, microbially synthetized, or from petroleum-based chemicals.[1] Through blends of two or more biopolymers new materials may be designed for specific requirements. One of the most common biopolymer is poly(lactic acid) (PLA), particularly utilized for both ecological and biomedical applications. PLA is produced by ring opening polymerization of lactides and the lactic acid monomer used is produced by sugar feedstocks.[2] PLA is easily biodegradable but its major defect is an extreme brittleness at room temperature. Extensive studies have been carried on PLA blends with other non biodegradable[3,4] or biodegradable polymers[5–15] or by modifying PLA with biocompatible plasticizers[16–19] to improve flexibility and impact resistance.

PLA/thermoplastic polyolefin elastomer (TPO) blends compatibilized with a TPO–PLA copolymer showed an increase in elongation at break and tensile toughness and a decrease in particle size dispersed in PLA matrix as the concentration of the compatibilizer increased.[3] A recent work focused on a blend of PLA/acrylonitrile-butadiene-styrene (ABS) showed an improved impact strength and elongation at break when a compatibilizer was added, otherwise uncompatibilized blends presented big phase size morphology and weak interface.[4]

Biodegradable blends of PLA with poly(3-hydroxybutyrate) (PHB),[5,6] poly(3-caprolactone) (PCL),[7] poly(butylene succinate) (PBS),[8] poly(vinyl alcohol) (PVA)[9] were also reported in literature. Some of these blends showed poor mechanical properties due to immiscibility of the two polymers whereas others demonstrated the utility of polymer blending in tuning material properties. Various studies focused on the use of thermoplastic starch (TPS) to obtain a biodegradable blend with PLA because it offers great advantages in terms of cost and sustainability.[10–13] The application of reactive agents during the extrusion process of PLA and thermoplastic starch led to significant improvements in tensile strength and elongation at break. Recent works also focused on binary blends of PLA/poly(butylene adipate-co-terephthalate) (PBAT)[14] and ternary blends with PLA, thermoplastic starch

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and poly(butylene adipate-co-terephthalate),[15] the resulting materials showed improvement in elongation at break with increasing PBAT content, and mechanical properties were improved also adding an anhydride functionalized polyester as compatibilizer.

Various types of chemicals have also been used as plasticizers for PLA like PEG,[16] PPG[17] and citrate esters.[18,19] The resulting PEG plasticized PLA showed an increase in modulus and a corresponding decrease in elongation at break for PEG contents above 50% while the modulus was found to decrease and the tensile strength was found to increase when the PEG content was 50% or lower. All of the citrate esters investigated were found to be effective in reducing the glass transition temperature and the results indicate that PLA can only incorporate a certain amount of plasticizer before becoming saturated and display phase separation.

The introduction of rubber is a well-established method of improving fracture toughness.[20] The mechanism for rubber toughening in non-crazing polymers has been modelled by Lazzeri and Bucknall.[21] They showed that the rubber particles can promote the formation of microvoids and activate dilatational yielding in the deformed zone close to the fracture surface.

The aim of this work is the physico-mechanical characterization of PLA/PBAT blends, in order to investigate the mechanism of toughness due to rubber introduction (in this work PBAT rubber particles with diameter of 2–5 μm). It was expected that the addition of PBAT should increase the impact strength with a little decrease of the modulus and the yield stress.

Experimental Part

Materials

The PLA used in this work is a commercial PLA (Nature Works). This PLA is a mix of L,D isomer (95% L), and exhibits a $M_W = 185650$ Da, a melting point of 140–152 °C, a glass transition temperature of 56.7–57.9 °C and a density of 1.24 g/cm^3. The PBAT used is Ecoflex® from BASF Corp. that exhibits a melting point of 110–120 °C, a density of 1.25–1.27 g/cm^3 and a $M_W = 131440$ Da. Both polymers were supplied in pellets and used as received.

Sample Preparation and Testing

PLA and PBAT were melt-blended using a single screw extruder in the ratios of 100/0, 95/5, 90/10, 85/15 and 80/20, where the first and second numbers represent PLA and PBAT by weight percentage, respectively. The blends were injection moulded into ASTM tensile bars and sheets for impact tests with a OIMA ECO 3080 injection moulding machine. All the mechanical property measurements were performed at room temperature, tensile tests were carried out using an Instron tensometer, model 4302, with a crosshead speed of 10 mm/min. Two extensometers were used to measure the longitudinal and the transverse strain. Young modulus, maximum tensile strength and volume strain were obtained. The volume strain $\Delta V/V_0$ was calculated according to the following formula:[20]

$$\Delta V/V_0 = (1+\varepsilon_1)(1+\varepsilon_2)^2-1 \qquad (1)$$

where ΔV is the volume change, V_0 is the original volume and ε_1 and ε_2 are the longitudinal and transverse nominal strain, respectively.

The stress intensity factor K_{IC} was determined using a CEAST impact pendulum, the notch was milled in, having a depth between 0.45 and 0.55 of the width of the specimen, according to the linear elastic fracture mechanic.[22] K_{IC} values was calculated on a basis of a minimum of five tests.

The critical strain energy release rate G_{IC} was calculated by:

$$G_{IC} = K_{IC}^2(1-\nu^2)/E \qquad (2)$$

where ν is Poisson ratio and E is Young modulus obtained from tensile tests.

A TA Instruments Q200 differential scanning was used to determine the thermal transition temperature of the polymer blends. The pure PLA and the PLA/PBAT blends were sealed in aluminium pans and heated at heating rate of 10 °C/min under a nitrogen flow. The samples (10–12 mg), in aluminum pans, were first heated from 30 to 100 °C (first heating run) and kept at this temperature for 5 min, then cooled to room temperature, and again heated above the melting of PLA (second heating run).

Dynamic mechanical analysis was carried out on a Gabo Instruments EPLEXOR® 100N. Test bars were cut from the tensile bar specimens (size: $30 \times 10 \times 3$ mm) and mounted on tensile geometry. The temperature used in the experiment ranged to −100 °C to 100°C, at a heating rate of 5 °C/min and frequency of 1 Hz. The viscoelastic properties were characterized versus temperature, namely the storage modulus, E', loss modulus, E'' and mechanical loss factor, $\tan \delta = E''/E'$.

Scanning electron microscope (SEM) was performed on fractured surfaces of PLA/PBAT specimens, after impact test, with a Jeol JSM-5600LV, prior to SEM examination all the surfaces were sputtered with gold.

Results and Discussion

Mechanical Properties

The main tensile properties such as Young modulus and yield stress, determined from the tensile stress-strain curves are presented in Figure 1.

The behaviour of these materials changed from neat PLA to PLA/PBAT blends. PLA was very stiff and brittle and showed pretty high tensile strength and Young modulus, but it broke at deformations of about 3%. PLA/PBAT blends maintained quite high modulus and tensile strength with an almost linear decrease increasing PBAT contents. Small amounts of PBAT improved dramatically the elongation at break as can be seen in Table 1.

Figure 2 presented the simultaneously measured tensile and dilatometric data of the typical PLA/PBAT blend. The stress and volume strain are presented as function of the longitudinal strain. The yield point was located at a longitudinal strain of ~2.3%. The samples presented stress whitening during tensile testing. The volume strain was calculated according to eq. (1), the initial increase in volume (zone I) was attributed to an elastic deformation with constant Poisson's ratio. After this response it was noted an increase in the slope of volume strain (zone II) due to microvoiding and debonding mechanisms, as reported in literature.[21] The volume strain is known to increase with increasing rubber particle content, which during deformation results in high amount of debonding.[23]

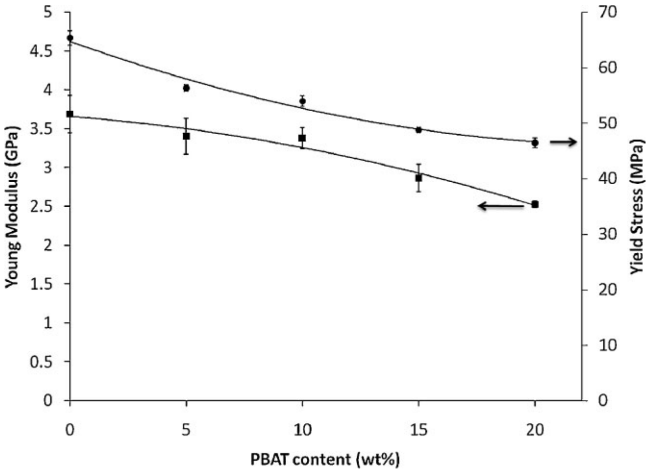

Figure 1.
Young modulus and yield stress curves for PLA/PBAT blend.

Table 1.
Mechanical properties of PLA/PBAT blend.

PLA/PBAT	Young's modulus (GPa)	At yield		At break		K_{IC} (MPa·m$^{1/2}$)	G_{IC} (KJ/m^2)
		Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)		
100/0	3.68 ± 0.24	65.36 ± 1.36	2.24 ± 0.05	60.57 ± 2.38	3.63 ± 1.27	6.41 ± 0.35	9.96 ± 1.07
95/5	3.40 ± 0.23	56.35 ± 0.53	2.10 ± 0.12	44.57 ± 5.80	21.22 ± 7.08	6.58 ± 0.33	12.10 ± 1.30
90/10	3.37 ± 0.13	53.96 ± 0.89	2.39 ± 0.35	35.91 ± 2.35	20.77 ± 6.27	6.47 ± 0.23	11.06 ± 0.81
85/15	2.86 ± 0.17	48.96 ± 0.49	2.08 ± 0.03	31.69 ± 2.38	37.56 ± 3.85	6.18 ± 0.41	11.94 ± 1.64
80/20	2.52 ± 0.04	46.45 ± 0.89	2.34 ± 0.04	30.18 ± 2.59	44.65 ± 5.62	6.26 ± 0.40	13.87 ± 1.72

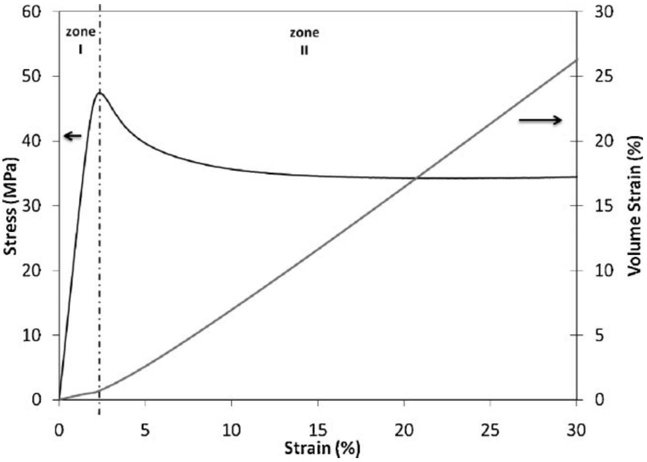

Figure 2.
Typical stress-strain and volume strain-strain curves for PLA/PBAT blend.

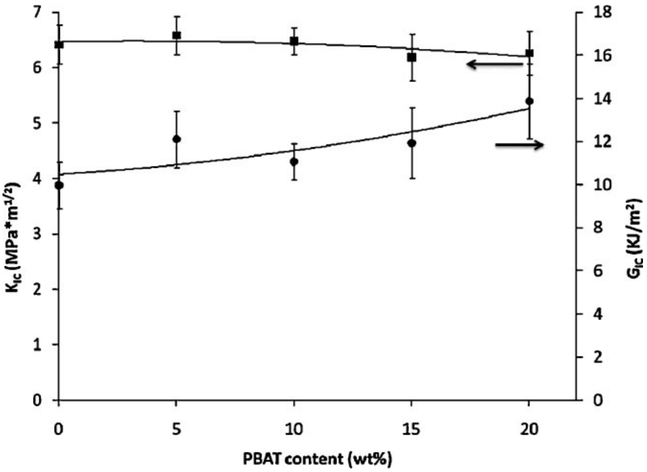

Figure 3.
K_{IC} and G_{IC} curves for PLA/PBAT blend.

The toughening effect of the rubber particles was determined by the impact analysis, in particular by examining the fracture toughness (K_{IC}) and the critical strain energy release rate (G_{IC}). Figure 3 illustrated the results of fracture toughness measurements and reported G_{IC} values for different blends and neat PLA. The figure presents the dependency of the fracture toughness on the rubber content for different blends. All modified blends exhibit an almost constant toughness with increasing mass fraction, but the increasing in the value of G_{IC}, at compositions ranging from neat PLA down to PLA mass fraction 0.8, shows a toughening effect of PBAT. It was also clear that exists an upper limit of the rubber content beyond which the toughness of the blend does not increase and may even decrease.

To improve toughness the internal phase morphology of the rubber particles should be studied together with particle size and distance between the particles and it will be object of future works.

Structural Characterization

The microscopic examination of the fractured surfaces of the impact samples of the blends was carried out using SEM analysis. Some SEM images of the neat PLA and PLA/PBAT blends were reported in Figure 4. Pure PLA showed typical brittle

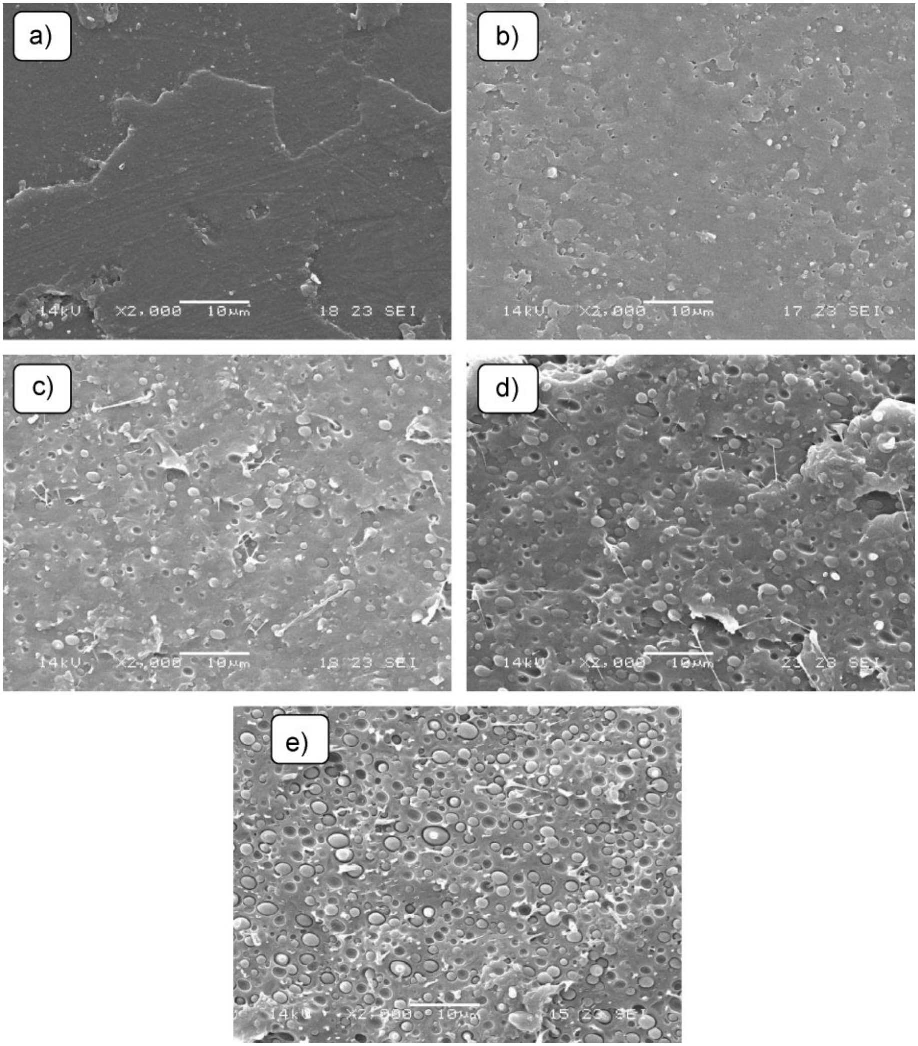

Figure 4.
SEM micrographs of the fracture zone of the PLA/PBAT blends: a) Neat PLA, b) 5% PBAT, c) 10% PBAT, d) 15% PBAT, e) 20% PBAT.

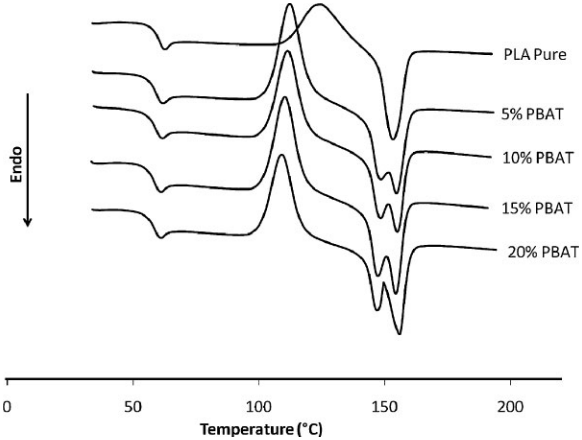

Figure 5.
DSC curves for PLA/PBAT blend.

fracture with a smooth surface. PLA/PBAT blend surfaces presented ductile fracture with several filaments coming out the surface. PLA/PBAT blend with 5% of PBAT presented small size rubber particles (less than 1 μm). This evidence could be explained by some effect of compatibilization, due to a possible transesterification reaction between PLA and PBAT.[24] By increasing the PBAT amounts above 5% wt. this effect progressively disappeared, because the two polymer are substantially immiscible. Moreover the PLA/PBAT blends showed the debonding effect typical of rubber toughened system.[20] The microstructure of PLA/PBAT blend with 20% PBAT was characterized by relatively small, spherical inclusions of PBAT in a PLA matrix. The particles had diameters ranging from 2 μm to 5 μm and appeared to be isolated from each other by the matrix. Debonding of the spherical inclusions of PBAT was clearly observed, suggesting there was very little adhesion between the two phases.

Second heating scans of PLA and PLA/PBAT blends are shown in Figure 5. The glass transition, cold crystallization and melting can be clearly observed in the curves. Pure PLA sample displayed a single melting peak at about 155 °C, whereas for the PLA/PBAT blends, a second melting peak was observed at lower temperatures (~147 °C), which suggests the occurrence of reorganization phenomena of the crystals during the heating run due to the nucleation effect promoted by the presence of the particles. The $T_{g,PLA}$ obtained by DSC ($T_{g,PLA} \approx 58\,^{\circ}C$) is lower than the value obtained by DMTA, which can be attributed to the different measuring mechanism for these two instruments.[25]

The similar amplitude of cold crystallization and melting peaks determined from DSC measurement showed that these blends were basically amorphous.

Figure 6 showed dynamic viscoelastic curves of pure PLA and a typical PLA/PBAT blend (all blends presented similar behaviour), respectively. The glass transition temperature corresponding to pure PLA ($T_{g,PLA} \approx 71\,^{\circ}C$), was not influenced by the presence of PBAT. The dispersed phase component was not miscible and its glass transition remained the same of the pure component ($T_{g,PBAT} \approx -23\,^{\circ}C$). Amorphous polymers usually have very high and sharp tan δ peak because the chains are free to move easily, like in pure PLA. The height of tan δ peak decreased as the PBAT concentration increased, this can be due both to some dilution effect and reorganization phenomena of the crystals as already observed by DSC analysis.

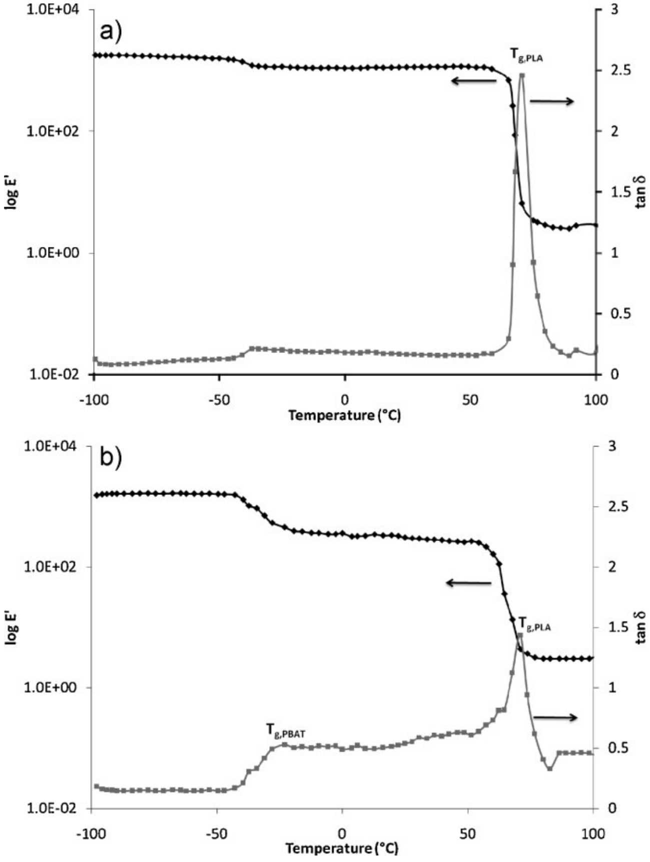

Figure 6.
Dynamic mechanical analysis of pure PLA (a) and a typical PLA/PBAT blend (b).

Conclusion

The mechanical properties of PLA/PBAT blends can be tuned through the blend composition. PLA/PBAT blends showed quite high modulus and tensile strength with a linear decrease increasing PBAT contents. Small amounts of PBAT improved dramatically the elongation at break. PLA/PBAT blends showed the debonding effect typical of some rubber toughened system in presence of a low interphase adhesion. The critical strain energy release rate G_{IC} increased as a function of composition, due to debonding between particles and matrix as supported by SEM data. From DMTA analysis it was clear that glass transition temperature corresponding to pure PLA was not influenced by the presence of PBAT. The PBAT phase was not miscible in PLA and its glass transition remains the same of the pure component. Concerning the DSC analysis, the presence of two melting peak in PLA/PBAT blends can be explained with reorganization phenomena of the crystals.

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