Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) blends for packaging application

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Abstract

Biodegradable polymeric blends are expected to be widely used by industry due to their environmental friendliness and comparable mechanical and thermal properties. Poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) are such biodegradable polymers which aim to replace commodity polymers in future applications. Since cost and brittleness of PLA is quite high, it is not economically feasible to use it alone for day to day use as a packaging material without blending. In this study, blends of PLA and PBS with various compositions were prepared by using a laboratory-scale twin-screw extruder at 180°C. Morphological, thermal, rheological and mechanical properties were investigated on the samples obtained by compression molding to explore suitability of these compositions for packaging applications. Morphology of the blends was investigated by scanning electron microscopy (SEM). Morphology showed a clear phase difference trend depending on blend composition. Modulated differential scanning calorimetry (MDSC) thermograms of the blends indicated that the glass transition temperature (T_{e}) of PLA did not change much with the addition of PBS, but analysis showed that for PLA/PBS blend of up to 80/20 composition there is partial miscibility between the two polymers. The tensile strength and modulus were measured by the Instron Universal Testing Machine. Tensile strength, modulus and percentage (%) elongation at break of the blends decreased with PBS content. However, tensile strength and modulus values of PLA/PBS blend for up to 80/20 composition nearly follow the mixing rule. Rheological results also show miscibility between the two polymers for PBS composition less than 20% by weight. PBS reduced the brittleness of PLA, thus making it a contender to replace plastics for packaging applications. This work found a partial miscibility between PBS and PLA by investigating thermal, mechanical and morphological properties.

Keywords : poly (lactic acid) (PLA); poly (butylene succinate) (PBS); biodegradable polymers; miscibility; mechanical properties; rheological property; blends; morphology

1. Introduction

In recent years, environmental pollution has become a great concern due to the high impact of plastic waste in daily use. One of the possible solutions to this problem is to replace the commodity synthetic polymers with the biodegradable polymers which are readily susceptible to microbial action. PLA and PBS are such biodegradable polymers which aim to replace commodity synthetic polymers. High brittleness and cost of PLA is the major issue for their commercialization and many applications such as packaging. Therefore, to improve the various properties and lower the production cost, various studies on PLA blends with other biodegradable polymers were carried out.

In the binary system of PLA and PEO, Nijienhuis et al. (1996) reported that up to 50 wt% of PEO, all blends showed single (T_{α}) . In their study, the equilibrium melting points of PLA in the blends decreased with increasing PEO wt%, which suggests that PLA and PEO are compatible in the amorphous phase. A single T_g for all the blend compositions for PLA/PVA system was also observed by Gajria et al. (1996), indicating blends as miscible. Sheth et al. (1997) concluded from differential scanning calorimetry analysis results that the miscibility of the PLA/PEG blends depends on the concentration of PEG. For higher concentrations of PEG, T_g could not be observed by DSC while at lower concentrations of PEG (30 wt%), a decrease in T_g of PLA was noticed from 57°C to 37°C. Zhang et al. (1995) studied the various blends including PLA and Poly (e-caprolactone) (PCL). Their DSC results concluded PLA /PCL blends as immiscible because blends showed a very

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slight shift in melting endotherm. SEM for PLA/PCL also gave a two phase separation system agreeing to the results of DSC.

According to Huang *et al.* (1990), the first generation of biodegradable materials consisted of blends of polymers with natural food sources such as starch. The second generation concentrated on the insertion of functional groups such as ester linkages on the polymeric backbone. The third stage is the development of materials such as poly (lactic acid) (PLA) that are naturally synthesized by bacteria grown by fermentation which can be considered as truly biodegradable and eco-friendly after their composting (Huang *et al.*, 1990).

In this study the polymers used for blending having comparatively good properties to obtain the biodegradable material are PLA and PBS due to the following properties.

PLA, a linear aliphatic polyester, produced from renewable resources has attracted much attention in recent years due to its biodegradability and could be a possible solution for solid waste (Ray and Bousmina, 2005). PLA has good mechanical, thermal and biodegradable properties and therefore is a good polymer for various end-use applications (Qi and Hanna, 1999). However, other properties like flexural properties, heat distortion temperature (HDT), gas permeability, impact strength, melt viscosity for processing, etc. are not good enough in applications like packaging (Ogata et al., 1997). Also high price and brittleness of PLA lowers the possibility of its commercialisation. Therefore, blending PLA with other suitable biodegradable polymer which has comparably better flexural properties, excellent impact strength, melt processibility will modify various properties and also contribute towards low overall material cost. PLA was reported to be miscible with other stereo isomers such as poly (DL-lactic acid) (Tsuji and Ikada, 1996 and Perego et al., 1996), and some other polymers like poly (ethylene oxide) (PEO) (Nijienhuis et al., 1996), poly (vinyl acetate) (PVA) (Gajria et al., 1996), and poly (ethylene glycol) (PEG) (Sheth et al., 1997). The blends had varying properties of the blended polymers according to their ratio of mixing.

PBS, trade name 'BIONOLLE' is biodegradable aliphatic polyester produced by the polycondensation reaction of 1,4-butanediol with succinic acid (Bhari *et al.*, 1998; Doi *et al.*, 1996). It has high flexibility, excellent impact strength, and thermal and chemical resistance (Doi and Fukuda, 1994). It can be processed easily and is the best choice to blend with PLA. Many studies on PBS, in the form of films and moulded objects, have exhibited significant biodegradation within several months in soil, water with activated sludge, and sea water (Nishioka *et al.*, 1994).

The objective of this research is to produce a blend from PLA and PBS and investigate the mechanical and rheological properties of the blends. Miscibility of the two biodegradable polymers was also studied by MDSC experiments and SEM images of these blends.

In this investigation, PLA and PBS blends of different compositions were prepared by a twin-screw extruder. Various properties were examined and studied by different characterization techniques. Miscibility of the polymers in the blends was examined by SEM images and MDSC thermograms, while standard stress-strain analyses were used to assess mechanical properties. In addition, rheological properties were studied by the Advanced Rheometric Expansion System (ARES). All the properties of the blends were compared with that of the neat or virgin polymers. This study further aimed to obtain an extensive understanding of the environmental hazardous issues caused by solid waste of the commodity plastics by considering replacement with biodegradable PLA and PBS polymer blends.

2. Experimental methods

2.1. Materials

PLA polymer (4032D-grade, biaxially oriented films) from NatureWorks produced by Cargill Dow LLC was used in this study. PLA has negligible solubility in water and has a melting point of 170°C.

Biodegradable Polyester, PBS Polymer (G4460-grade, MI=1.8 g/10 min), trade name 'EnPol' by Ire Chem. Co., Korea was used to blend with PLA. PBS has a melting point of 95°C.

2.2. Blend Preparation

The pellets of both PLA and PBS were initially dried in a vacuum oven at a temperature of 50°C and pressure -80 KPag for 2 days to remove water before processing through the extruder. Drying is necessary to minimize the hydrolytic degradation of the polymers during melt processing in the extruder. Blends of PLA and PBS with various compositions were extruded by melt blending at 180°C. Blends of various compositions were prepared as shown in Table 1.

Measured quantities of each polymer were first mixed in a container before blending in a Brabender twin-screw extruder. The extruder was operated at 180°C and 60 rpm screw speed for the compounding of all the blends. To mix the polymers well, three passes were carried out through the extruder. All the blends were given the same processing treatment to maintain the overall consistency. Prepared blends were again dried at 50°C in vacuum oven for 12

Table 1. Compositions of PLA/PBS blends

| PLA % by wt | 100 | 90 | 80 | 50 | 20 | 10 | 0 |
|-------------|-----|----|----|----|----|----|-----|
| PBS % by wt | 0 | 10 | 20 | 50 | 80 | 90 | 100 |

Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) blends

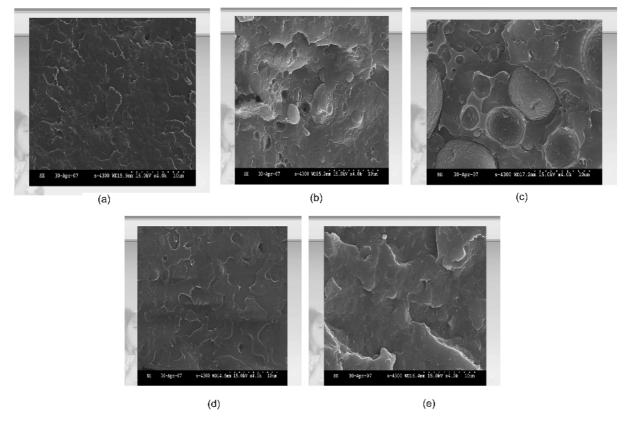


Fig. 1. SEM images of different PLA/PBS blend compositions: (a) 90/10 (b) 80/20 (c) 50/50 (d) 20/80 (e) 10/90.

hours before compression. The molding temperatures for neat PLA, neat PBS and their blends were 200°C, 130°C and 190°C, respectively. Molded specimens were then cooled to 50°C before removal from the mold. Dog bone shaped samples (ASTM D638) were compressed for 8 minutes under pressure for mechanical testing. Thermal characterization was carried out by obtaining film samples of 0.2 mm thickness.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

The morphology of the blends was investigated with high-resolution scanning electron microscopy (SEM), operated at an acceleration voltage of 15 kV. The blends were fractured in liquid nitrogen. SEM images of the blends are shown in Fig. 1.

SEM images (Fig. 1) of fractured surfaces show the morphology of the various blends of PLA/PBS. From Figs. 1(a) and (b), it is clear that the dispersed phase PBS have relatively small mean diameter as compared to the other blends (Figs. 1(c), (d) and (e)). As the PBS wt% increases, the phase separation is quite evident in these blends. Moreover, due to the increase in the PBS content, the particle size (*i.e.* mean diameter) increases (Fig. 1(c)). Above 50/50 wt% (PLA/PBS) blend, the morphology is reversed *i.e.*

when PLA concentration is less than 50 wt%; PLA becomes the dispersed phase in PBS. Beyond 80/20 (PLA/ PBS) blends *i.e.* for high PLA content, the traditional morphology of immiscible blends can be seen. The same immiscible morphology trend was reported for blends of PLA with co-polyester Poly (butylene succinate adipate) (PBSA) by Lee and Lee (2005).

3.2. Modulated differential scanning calorimetry (MDSC)

Thermal property characterization of the blends was performed with a modulated DSC (TA Instrument Model 2920). Sealed aluminium pans containing 5-10 mg of the blend samples were used in all the experiments. To eliminate the thermal history, all the samples were heated up to 200° C and held for 5 minutes and then rapidly cooled to -50° C. The actual measurements reported here were performed during a second heating cycle from -50 to 200° C at a heating rate of 2° C/min.

Fig. 2 shows the MDSC thermograms of neat PLA, neat PBS and their blends. For neat PLA, a broad crystallization peak is observed between 95 and 105°C. It is followed by a sharp melting peak at around 170°C. For neat PBS, the thermogram shows a melting peak at 93°C. It also shows that the glass transition temperatures (T_g) of the neat PLA and the neat PBS is about 58 and -34°C, respectively. A

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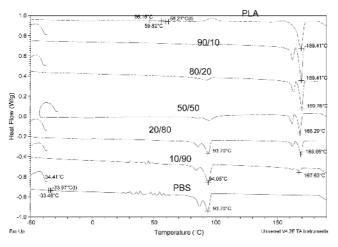


Fig. 2. MDSC thermograms of PLA/PBS blends (heating rate: 2°C/min).

direct proof of polymer miscibility can be obtained by observing the change in T_g and T_m of both the polymers in the blend. Up to 10 wt% of PBS in PLA, T_g and T_m of PLA have not changed, while as the composition of the PBS content increases (>10 wt%) the thermogram starts showing a small exothermal peak shift towards lower temperature and continues for other blends. The increase in the PLA content in PLA/PBS blends also shows exothermal peak shift of PBS towards higher temperature. But the shifts in the blends are not so noticeable, which indicates immiscibility. In the entire composition range investigated, two distinct melting peaks were also observed, indicating that each component crystallized individually. This demonstrates that for up to 20 wt% of PBS in PLA, miscibility is possible and beyond that they become immiscible. It was reported by Sweet and Bell (1972) and Roberts (1970) that blends of PLA and PBSA also show double endothermic peaks in the differential scanning calorimetry (DSC) thermogram for the second heating. They reported that these peaks are attributed to re-melting of newly formed crystallite during heating. It was concluded by these researchers that PLA/PBSA blends are immiscible. Lee and Lee (2005) provided reason for the appearance of double endothermic peaks in the second heating scan. They concluded that the appearances of double endothermic peaks are due to quenching after the first heating cycle. It does not give sufficient time for high melting crystallite to form. Therefore, more low crystallites are produced.

3.3. Rheological properties

Shear rheological properties of each blend and neat polymers were measured using an Advanced Rheometric Expansion System (ARES) using 50 mm parallel plate geometry. Tests were performed at 200°C under a nitrogen atmosphere to avoid any degradation. All samples were dried in a vacuum oven prior to the test. The following rheological

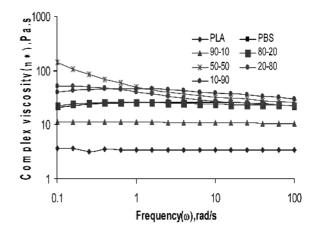


Fig. 3. Complex viscosity (η^*) versus frequency at 200°C of PLA/PBS blends.

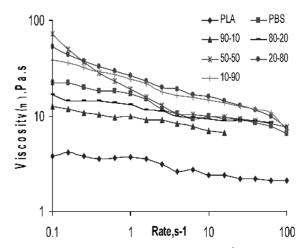


Fig. 4. Viscosity (η) versus shear rate at 200°C of PLA/PBS blends.

measurements were carried out.

a) dynamic strain sweep tests to confirm the linearity of viscoelastic region up to 100% strain@10 rad/s frequency

b) dynamic frequency sweep tests over a frequency range of $0.1-100 \text{ rad}^{-1}$

c) steady shear rate sweeps tests over a shear rate range of $0.1-100 \text{ s}^{-1}$.

The linear viscoelastic response of blends was determined by measuring their storage (G') and loss (G") moduli at 200°C to confirm that the dynamic properties were conducted in the linear viscoelastic region. PLA, PBS and their blends were found to be within the linear viscoelastic range for up to 10 wt% strain.

The dynamic complex viscosities of the neat polymers and their blends as a function of frequency at 200°C are shown in Fig. 3. Both the polymers, PLA and PBS exhibited almost Newtonian behavior in the investigated frequency range. PLA/PBS blend of 50/50 wt% showed a strong shear thinning behavior at low frequencies, while all other blends showed nearly similar behavior as neat poly-

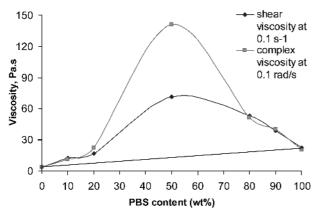


Fig. 5. Viscosity versus PBS wt% content at 200°C at 0.1 rad/s.

mers *i.e.* shear thinning was not observed. The viscosity of PLA was much lower than that of PBS as well as of the blends at all frequencies.

Dependence of steady shear viscosity on shear rate at 200°C for neat polymers and their blends is shown in Fig. 4. The shear viscosity of the blend system decreases with increase in shear rate, exhibiting shear thinning behaviour. Similar behavior was observed for biodegradable polymers like PCL (Ramkumar and Bhattacharya, 1998), and biodegradable aliphatic polyester (BAP) (Shin et al., 2000). Both the neat polymers showed a plateau at low shear rate indicating zero-shear viscosity. Viscosities of the blends increased as PBS content increased above 50 wt% while, 10 and 20 wt% PBS content blend composition showed viscosities in between the neat polymers which indicates that below 20 wt% of PBS, blends show miscibility and beyond that they become immiscible. Similar observation is evident with complex viscosity from Fig. 3 regarding miscibility of 80/20 wt% and 90/10 wt% (PLA/PBS) blends.

From rheological point of view, positive deviation in blends (PDB) indicates compatibility between two or more polymer matrix. If the interphase interactions between the polymers are due to compatibilization then the blend system will show positive deviation from the log-additivity rule for both viscosity and the normal stress (Utracki, 1983). In this case 50/50 blend of PLA/PBS showed a higher value of complex viscosity at a fixed frequency of 0.1 rad/s than that predicted by the additive rule (Fig. 5). Shear viscosity also showed higher value at fixed shear rate of 0.1 s⁻¹ for 50/50 wt% blend composition. Prest and Porter, (1972) concluded that Poly (phenylene oxide) (PPO)/polystyrene (PS) blends belong to PDB type. The data on miscible systems on polypropylene (PP)/polybutene-1 (PB-I) by Genillon and May (1978), and high density polyethylene (HDPE)/ethylene-vinyl acetate copolymer (EVA) by Fujimura and Iwakura (1970 and 1974), also give positive deviation blends. Viscosity values of PLA/PBS blends up to 20 wt% of PBS content show

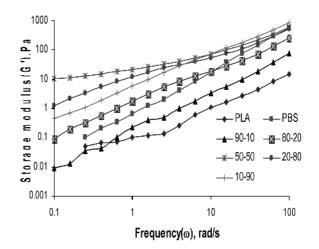


Fig. 6. Storage modulus (G') versus frequency at 200°C of PLA/ PBS blends.

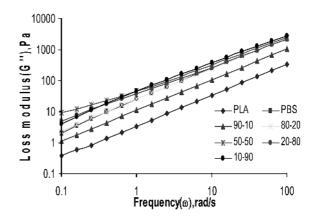


Fig. 7. Loss modulus (G") versus frequency at 200°C of PLA/ PBS blends.

approximate log-additivity rule, indicating a limited miscibility only within a range of low concentrations.

Figs. 6 and 7 demonstrate that both moduli of PLA and PBS blends increase monotonically as compared to neat PLA and PBS over the frequency range investigated (0.1-100 rad/s). At high frequencies (>20 rad/s), the qualitative viscoelastic behavior *i.e.* G' (storage modulus) and G'' (loss modulus) of all the blends particularly high PBS content is same. A systematic increase in G' and G'' was noticed at low frequencies with the increase of PBS content. Blends with 90/10 wt% and 80/20 wt% (PLA/PBS) concentration falls between the neat polymers. Moduli of the blends having PBS content less than 20 wt% are showing same analogy as demonstrated by SEM images and the thermogram of MDSC.

3.4. Tensile properties

Tensile testing to study tensile strength, tensile modulus and % elongation at break were performed using Instron 4467 Universal testing machine at 25°C (room temperature). All tests were done according to ASTM D638 stan-

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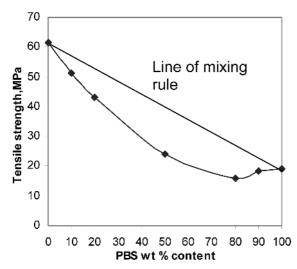


Fig. 8. Tensile strength of PLA/PBS blends.

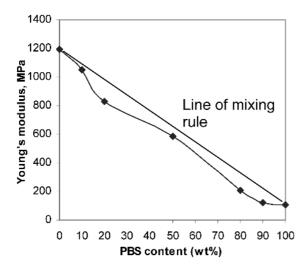


Fig. 9. Modulus of PLA/PBS blends.

dard. Tests for neat PLA and blends were carried out with a crosshead speed of 5 mm/min and 50 mm/min for neat PBS. Property values reported here represent an average of the results for tests run on five specimens.

Fig. 8 shows tensile strength of various PLA-PBS compositions. It is clear from this figure that tensile strength decreased up to 80 wt% contents of PBS and then slightly increased at more than 80 wt% PBS contents. The same type of behavior is seen in Young's modulus as shown in Fig. 9. The trend of decreasing modulus and tensile strength very well matched with McCarthy *et al.* (1999) findings. They reported a decrease in Young's modulus and tensile strength with the increase of PBS content in the blends is an example of outstanding strain hardening blends. However, it can be seen from Figs. 5 and 6 that up to 80/20 (PLA/PBS) blend compositions, tensile strength and modulus are near to the mixing rule line. This means that compatibility between PLA and PBS is possible whilst

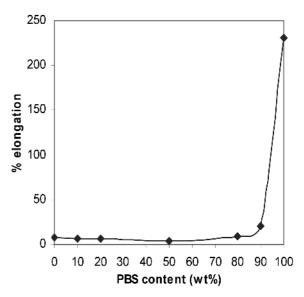


Fig. 10. % elongation at break of PLA/PBS blends.

PBS concentration is lower. A slow decline of both tensile strength and Young's modulus in 50/50 wt% PLA/PBS blends proved that each polymer showed their individual properties.

Results for percentage elongation at break are shown in Fig. 10. The percentage elongation at break of the blends is quite similar to that of neat PLA for compositions up to 80 wt% PBS and then increased for 10/90, PLA/PBS composition and neat PBS. This may be attributed to the more elastic characteristic of the neat PBS matrix. The elongation at break of PBS is superior to that of PLA. Similar type of behavior was found by Lee and Lee (2005), where they characterized co-polyester poly (butylene succinate adipate) (PBSA) and fibre grade PLA blends. They noted that PLA and PBSA are completely immiscible as the tensile strength values were far below the line of rule of mixing where as in this case up to 20 wt% of PBS in PLA values are comparatively nearer to the line of rule of mixing.

Specimens for neat PBS broke after necking and stress increased with the strain above the yield stress. However, for all the blends and neat PLA no yield phenomenon existed and samples broke rapidly after yielding (brittle fracture). Hence, these blends are showing almost constant percentage elongation at break at all compositions. From the above results it can be concluded that up to 20 wt% of PBS in PLA miscibility is possible and beyond that they become immiscible in agreement with the results of MDSC thermograms and SEM images.

4. Conclusions

Blends of PLA with PBS were studied. The morphological investigation by SEM revealed that both the polymers are immiscible beyond 20 wt% of PBS in PLA. Tensile strength and modulus of the blends decreased with PBS content but followed approximately the mixing rule for 90/10 and 80/20 (PLA/PBS) blends. It is concluded that percentage elongation at break remains almost constant for all the blends. Modulated DSC showed that the composition beyond 20 wt% PBS has two distinct melting peaks indicating immiscibility of the two polymers. However, compositions 90/10, 80/20 (PLA/PBS) seem to be miscible.

Rheological study concluded that both the neat PBS and PLA polymers exhibited Newtonian behavior. 50/50 wt% (PLA/PBS) blend showed strong shear thinning behavior at low frequencies, while other blends showed similar behavior as that of neat polymers. The shear viscosity of the blend system exhibited shear thinning behavior similar to biodegradable polymers. Viscosities of blends increased as PBS content increases from 50 wt% while 10 wt% and 20 wt% PBS content has viscosities in between the neat polymers which indicate that below 20 wt% of PBS, blends are miscible and above that they become immiscible. Also, values of the blends below 20 wt% of PBS are quite near to the predicted values from the log-additivity rule for viscosity, thus can be considered as miscible.

Blends of up to 20 wt% PBS content in PLA is also expected to overcome the deficiencies of polylactic acid such as brittleness, flexural properties, heat distortion temperature and impact strength for applications in food packaging, compost bags, and other biodegradable disposable bags.

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