Miscibility study of solution cast blends of poly(lactic acid) and poly(vinyl butyral)

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ABSTRACT
Poly(lactic acid) (PLA) was blended with poly(viny1 butyral) (PVB) through solution casting method using chloroform as the common solvent. The films obtained were characterized for miscibility using Differential Scanning Calorimetry (DSC), tensile testing and FTIR spectroscopy. The DSC results showed that the glass-transition temperature (T_g) of the PLA and PVB remained more or less constant with the composition of the blend. The existence of two T_g's in the blends indicated that PLA and PVB were immiscible over the composition range investigated. percentage crystallinity (χ_c), of PLA phase remained constant with increasing PVB content in the blend. FTIR measurements showed that there was no appreciable change in the spectra with respect to blend composition, implying the immiscibility of the two polymers. Mechanical analysis showed that the tensile strength and elongation decreased on blending.
Keywords: *Poly(lactic acid), Poly(vinyl butyral), blends, miscibility, tensile strength.*

1 INTRODUCTION

Lactic acid is a natural chemical that is widely employed in foods as a preservative and as flavouring agent. Although lactic acid can be synthesized chemically, it is produced naturally by microbial fermentation of sugars. The sugar feed stocks can be derived from potato peelings, corn and dairy wastes. The presence of a hydroxyl and carboxylic functional group in lactic acid (Figure 1) allows it to be easily converted into poly(lactic acid).

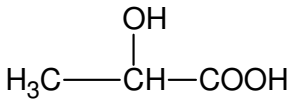

Figure 1. Molecular structure of lactic acid.

PLA has some commercial potential advantages such as high strength, thermoplastic behaviour, environmental degradability, biocompatibility and availability from renewable sources. Due to its high cost, PLA has been used mainly for specific purposes (Donald 2002). However, through the introduction of modern technologies, the production cost of PLA has decreased and as a result the use of PLA to make biodegradable films and containers for packaging and medical devices is increasing (Martin and Averous 2001). In the medical industry, there has been extensive research on the *in vivo* and *in vitro* degradation of PLA and surgical sutures, drug delivery systems and internal bone fixation etc have been prepared (Drumright *et al*. 2000).

Several approaches have been used to improve the properties of PLA, including blending with other polymers and copolymerization. However, blending is the most widely employed method as it is relatively simple and cost-effective in comparison with copolymer synthesis. Through an appropriate choice and composition of the second polymer, a material with specific properties can be obtained. In recent years interest has grown in blending of PLA with other polymers and its blends with several polymers such as poly(ε-caprolactone) [PCL] (Tamura *et al.* 2004) (Sivalingam *et al.* 2004), starch (Zhang and Sun 2004), poly(vinyl pyrollidone) [PVP] (Zhang *et al.* 2003), chitosan (Suyatma *et al.* 2003), poly(3-hydroxybutyrate) [PHB] (Zhang *et al.* 1996), poly(ethylene oxide) [PEO] (Nijenhuis *et al.* 1996), poly(ethylene glycol) [PEG], (Sheth e*t al.* 1997) and poly(viny acetate-*co*-vinyl alcohol) (Park and Im 2003) have been reported.

PVB is an industrially important polymer widely used in laminated safety glasses and interface treatments. It is prepared by reacting poly(vinyl alcohol) with butyral aldehyde in acidic medium. Substantial number of unreacted vinyl alcohol and vinyl acetate groups remain in the chain and as a result PVB is best considered as a terpolymer of vinyl alcohol, vinyl acetate and vinyl butyral. Random copolymers are able to form miscible blends with other homopolymers because of interchain attraction and repulsion between the different units in the chain. PVB have been found to form miscible blends with other polymers such as PVC (Nadia and Magdy 1999) and PHB.

In this paper we report the miscibility study of PLA/PVB blends prepared by solution casting method and characterized using DSC, FTIR spectroscopy and tensile studies.

2 EXPERIMENTAL

2.1 MATERIALS

PLA was purchased from the Polysciences Inc. and PVB (Mw 50-80 x 10^3) was purchased from Aldrich Chemicals. Both polymers were used without further purification. Chloroform (AR grade) was distilled twice and stored in amber bottles.

2.2 PREPARATION OF POLYMER BLENDS

Blends of PLA and PVB were prepared by the solution casting technique using chloroform as the common solvent. PLA and PVB were dissolved separately in chloroform to obtain 1.5% (wt/vol) solutions. The solutions were mixed in predetermined ratios to obtain blend solutions with varying PLA/PVB mass ratios of 100/0, 90/10, 70/30, 50/50, 30/70, 10/90 and 0/100. The resulting blend solutions were left overnight before casting onto clean glass plates. The solvent was allowed to

evaporate at room temperature. The dried samples in the form of films were peeled off from the glass and further dried in the vacuum oven at 45°C for several days to completely remove the residual solvent.

2.3 METHODS OF MEARSUREMENTS

2.3.1 DIFFERENTAIL SCANNING CALORIMETRY

DSC measurements were performed using Perkin-Elmer DSC- 6. Sample weight ranged between 1-5 mg. Samples were scanned twice from 0°C to 220°C at a heating rate of 10°C per minute under nitrogen flow. One minute holding time was allowed at 0°C in each scan for isothermal scanning of the blend films. All results were obtained from the second scan to eliminate different thermal history effects. The percentage crystallinity, X_c, of PLA in the blends was estimated according to the following equation (Jian-Feng and Xiuzhi 2004).

$$X_c = \frac{\Delta H_m / \Phi_{PLA}}{\Delta H^O_m} \times 100\% \quad (1)$$

where ΔH_m and ΔH^o_m are the enthalpies (J/g) of fusion of blend and PLA crystal of infinite size with a value of 93.6 J/g, respectively and ϕ_{PLA} is the PLA fraction in the blend.

2.3.2 FT-IR SPECTROSCOPY

The thin films were scanned on a Perkin Elemer Infra-Red Spectrometer Spectrum 1000. 32 scans at a resolution of 2 cm^{-1} were obtained and stored.

2.3.3 MECHANICAL PROPERTIES

Mechanical properties of the films were studied using Shimazdu Photometer following the ASTM D882-90. The sample dimensions were 50 x 10 mm in length and width and was measured using a verneir caliper. The thickness ranged from 0.202 to 0.078 mm and was measured using a micrometer with an accuracy of ± 0.001 mm. The crosshead speed was maintained at 5 mm/min. Five samples were tested for each blend and the average value for each blend is reported. Elongation and maximum tensile strength were calculated using the instrument's software.

3 RESULTS AND DISCUSSION

3.1 THERMAL ANALYSIS

The second DSC scans of the films of PLA and their blends are shown in Figure 2 and the analysis is summarized in Table 1.

Pure PLA and PVB films showed a single T_g around 63°C and 76°C respectively. The blends showed two T_g's indicating that the PLA/PVB system is immiscible over the entire composition range. It is evident from the scans that all the blends have crystallinity in them indicating the blends to be in a heterogeneous state. The percentage crystallinity. X_c is given in Table 2. It was found that the X_c remained constant throughout the blend composition range indicating that the addition of PVB had no contribution in decreasing the crystallinity in PLA. This indicates that PVB has no interaction with PLA. During the cooling scan an exothermic peak at around 110°C was observed and is assigned to the crystallization of PLA. It was observed that the crystallization temperature of the blends increased as the concentration of PVB in the blends increased. This temperature reached its highest point of 126°C in PLA50. and then decreased to 120°C in PLA10. However, this peak was found to become broad.

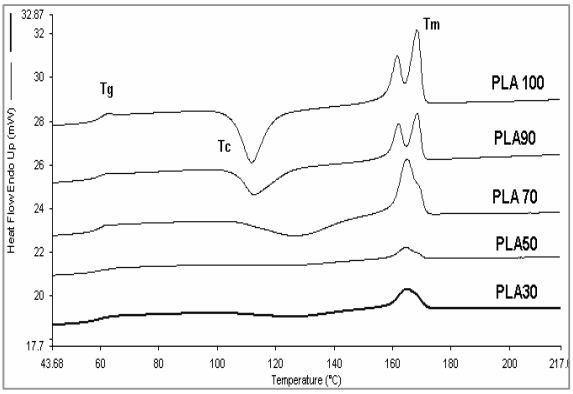

Figure 2. Second-heating-scan DSC thermograms.

The melting curve of PLA in the second heating scan was found to be different from that of the first heating scan. A double melting peak appeared around 162 and 168°C for pure PLA and blends containing more than 50 wt% PLA. The thermograms are shown in Figure 2. These double peaks indicate two populations of crystals with different lamellar thickness that arises when the sample is cooled from the molten state. The lower temperature peak, 164°C, is due to the melting of thin lamellar crystals while the one at higher temperature, 168°C is that of thick crystals.

Table 1. Thermal results of Melting Temperature (T_m), Glass Transition Temperature (T_g), and Re-crystallization Temperature (T_c) of PLA/PVB blends from the second heating.

Blends	T_m(°C)	T_c (°C)	T_g (°C)
PVB			71
PLA10	163	120	62, 72
PLA30	164	123	61, 72
PLA50	164	125	63, 72
PLA70	165, 169	124	63, 71
PLA90	162 , 168	113	63
PLA	162, 168	111	63

Table 2. % Crystallinity of PLA/PVB blends

Blends	Enthalpy of fusion (J/g)	% crystallinity
PVB	0	0
PLA10	3.7	39.5
PLA30	10.0	35.6
PLA50	18.0	38.5
PLA70	26.5	40.4
PLA90	34.0	40.3
PLA	38.1	40.7

Figure 2 shows that with increasing PVB concentration in the blends, the melting peak at 164°C increases and the peak at 168°C gradually diminishes indicating that the presence of PVB restricts the formation of thick crystals of PLA. Similar DSC and Infrared results were observed by (Zhang *et al.* 2003) in the PLA/PVP system.

3.2 MECHANICAL PROPERTIES

Tensile testing was carried out on the film samples to determine the mechanical properties. Figures 3 and 4 summarize the results for tensile strength and percent elongation, respectively for all the blend compositions. The effect of PVB content on mechanical properties of PLA/PVB blends reveal that maximum % elongation was observed in pure PVB and it decreased with increasing amount of PLA in the blends. This is due to the increasing amount of crystallinity in the blends brought about by PLA. Blend containing 10% PLA showed similar strength as in pure PVB. But on further addition of PLA, the tensile strength decreased significantly. The minimum was observed for PLA 50%.

3.3 FT-IR SPECTROSCOPY

FTIR spectra of pure PLA, PVB and blends are shown in Figures 5 and 6 respectively. In many miscible blend systems polymers containing the carbonyl group usually undergo some interaction such as hydrogen bonding etc. and a shift in this peak is observed. In PLA the peak centred at 1760 cm^{-1} is attributed to the carbonyl group and is of interest because any interaction would shift the peak positioning. However, no shift in this peak or any other peaks were observed in the blends. This indicated that the two polymers are immiscible.

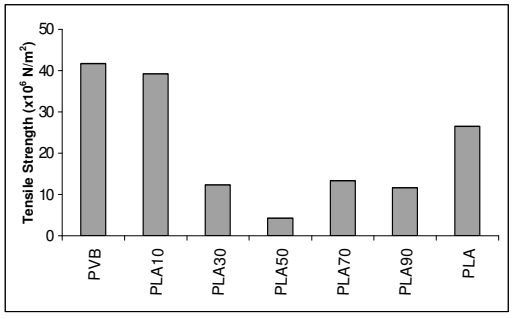

Figure 3. Tensile strength of the blends.

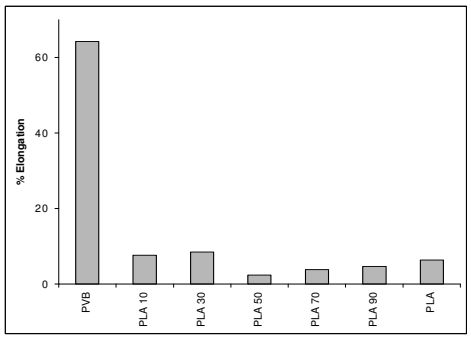

Figure 4. % Elongation of the blends.

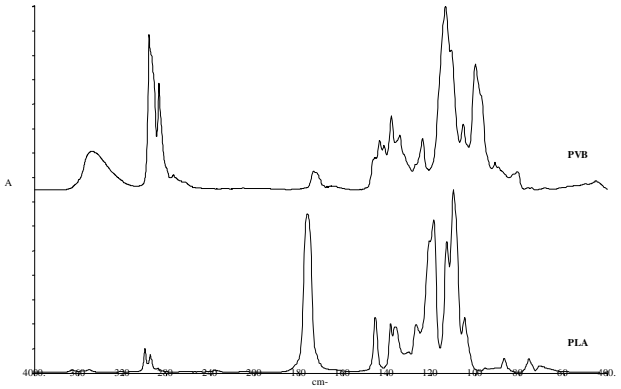

Figure 5. FTIR spectra of pure PLA and PVB.

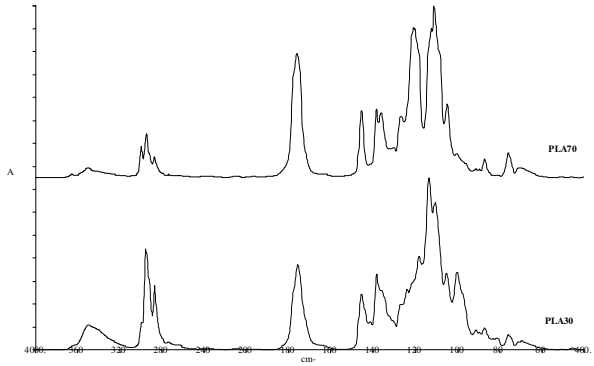

Figure 6. FTIR spectra of PLA30 and PLA70 blends.

4 CONCLUSION

Binary blends of PLA/PVB were prepared by casting films from polymer solutions in chloroform. The miscibility of these blends was studied by DSC, FTIR spectroscopy and tensile testing. DSC measurements revealed that the T_g of PLA and PVB in the blends were almost constant over the entire composition range indicating immiscibility of the polymers. The percentage crystallinity of PLA in the blends remained constant over the entire composition range and the crystallization process of PLA was not significantly affected by the addition of PVB. FTIR measurements indicated that no intermolecular interactions existed between the two polymers as no shift in the absorption peaks of the PLA or PVB in the blends was observed which again suggests that PLA and PVB are immiscible. Tensile strength of the blend films decreased up to 50 wt% PVB but increased as the percentage of PVB increased.

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