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Preparation and Characterization of Biodegradable PLA/PCL Polymeric Blends

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Abstract

In this study, blends of biodegradable Poly (lactic acid) (PLA) and Polycaprolactone (PCL), were prepared using Hakee Rheomix and characterized for rheological , thermal, mechanical and viscoelastic properties. Morphology of tensile fractured surfaces was examined through scanning electron microscopy (SEM). The blends of PLA/PCL exhibited an increase in percentage of elongation, impact toughness, loss factor and decrease in strength and modulus, when compared to that of neat PLA. Among the various blend proportions considered in this work, 80/20% PLA/PCL blend exhibited the highest elongation and impact strength. Differential scanning calorimetry (DSC) showed the influence of PCL content on glass transition temperature (T_g), melting temperature and degree of crystallinity of PLA/PCL blends.

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. Of the many biobased and biodegradable polymers, polylactic acid (PLA) has been attracting much attention due to its mechanical properties resembling that of present day commodity plastics such as PE, PP and PS, Sudesh and Iwata (2008). PLA, though discovered in the 1890s, is finding an edge in this new era of science, due to increasing environmental consciousness as it is produced from corn, starch and sugars Fukushima et al. (2004) Timbuktu et al. (2006). PLA is a linear aliphatic thermoplastic polyester made from the ring opening polymerization of lactide and the cyclic dimer of lactic acid (v-hydroxy acid) Drumright et al. (2000) Pure PLA is usually colorless and glossy thermoplastic polymer with similar properties as that of polystyrene. It can be processed using injection-molding, compression-molding, extrusion, thermoforming etc. Garlotta (2002). PLA has high modulus, reasonable strength, excellent flavor and aroma barrier capability, good heat sealability and can be readily fabricated, thereby making it one of the most promising biopolymers for varied applications Fang and Hanna (1999). As such, PLA can become one of the most preferred commodity plastics in the future. Despite these desirable features, several drawbacks tend to limit its widespread applicability such as high cost, brittleness, and narrow processing windows. Thus in order to broaden the applications of PLA, material properties and processability have to be improved. Polymer blends are the one of the convenient approaches to tailor

the material cost and for improve the material properties. Polymer blending is a method for obtaining properties that the individual do not possess and has been widely used for various kinds polymers. Blending of PLA with other polymers offers the possibility of improving the degradation rate, permeability characteristics, drug release profiles, thermal and mechanical properties.

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In the binary system of PLA and PBS, Amita Bhatia (2007) reported that tensile strength and modulus of the blends decreased with PBS content but percentage elongation at break remains almost constant for all the blends. Rheological study concluded that both the neat PBS and PLA polymers exhibited Newtonian behavior and 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. Yongjin and Shimizu (2007) investigated thermal, static and dynamic mechanical properties of PLA/ Poly (ether) urethane (PU). They demonstrated that the addition of PU elastomer not only accelerates the crystallization rate of PLA, but also decreases the PLA crystallinity. The PLA/PU blends show significantly increased elongation at break as well as impact strength, compared with neat PLA. Apart from the above mentioned polymers Poly (€ - caprolactone) (PCL) is another polymer which seems to be promising due to its encouraging properties and its compatibility with many types of polymers Hung and Edelman (1995).

The objective of this research is to produce different blends of PLA and PCL and investigate the mechanical and rheological properties of the blends. Miscibility of the two biodegradable polymers was also studied through DSC and SEM images. In this investigation, PLA and PCL blends of different compositions were prepared by a Hakee Rheomix. 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 PLA.

Nomenclature	
T_g	glass transition temperature
T_m	melting temperature
w_1, w_2	weight fractions of blend components
ΔH	Crystallization enthalpy
X_C	Crystallinity
C	Shear Modulus
Greek symbols	
α	heat flux
tanδ	loss factor
Subscripts	
g	glass transition
m	melting
c	Cold crystallization

2. Blends, Specimen Preparation And Characterization

The pellets of both PLA and PCL were initially dried in vacuum oven at a temperature of 50°C for 2 days to remove the absorbed moisture, before processing through Rheomex. Blends of PLA and PCL with 90/10, 80/20, 70/30 % were extruded by melt blending at 170°C. Measured quantities of each polymer were first mixed in a container before blending in a Hakee Rheomix. Rheomix was operated at 170°C, 160°C, 150°C, 140°C and130°C at zones 5, 4, 3, 2 and 1 respectively and 60 rpm screw speed for compounding of all the blends. All blends were given the same processing treatment to maintain overall consistency. Prepared blends were again dried at 50°C in vacuum oven for 12 hours before further processing. Specimens were prepared by compression moulding process. Process parameters such as molding temperature, pressure, soak time and cooling rate for pure PLA and their blends were set at optimal conditions obtained through Taguchi design of experiments. Molded specimens were cooled to

50°C before removal from the mold. Specimens were cut as per ASTM standards for characterization. Characterization has been done to analyze various properties such as Dynamic Mechanical properties, Rheological Properties and Thermal properties

3. Scanning Electron Microscopy

Tensile fractured surfaces were examined by using Zeiss EVO MA scanning electron microscope (SEM) with an acceleration voltage of 10kV; SEM images were shown in Fig .1 (a), (b), (c) . In all the samples, spherical shaped PCL droplet-matrix morphology can be observed in continuous PLA matrix. PCL spherulites formed in the continuous PLA matrix, acts as stress concentrators and thereby results in decrease of tensile strength and tensile modulus. Diameter of the PCL spherulites increase with increase in weight fractions of the PCL content. Moreover at 20wt. % PCL, PCL spherulites are uniformly dispersed in PLA matrix. Larger PCL spherulites observed in PLA/PCL blend of 70/30wt. % causes local stress concentration in broader region than the other blends, resulting in faster fracture progress, and therefore the toughness and percentage elongation suddenly becomes much lower than PLA/PCL blend of 80/20wt. %
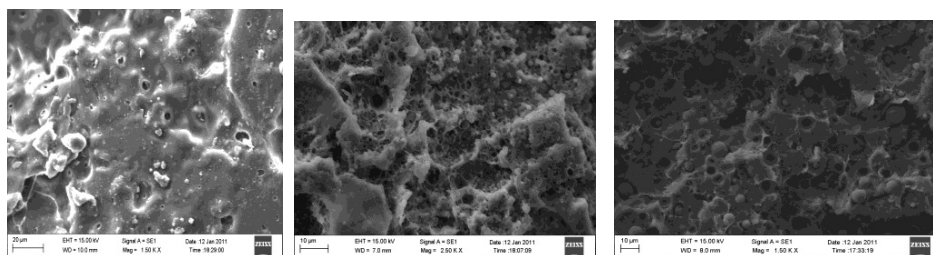

Fig. 1. (a) (b) (c) SEM images of tensile fractured surfaces of the PLA/PCL blends with 10% PCL; 20% PCL; 30% PCL.

4. Differential Scanning Calorimetry

Thermal properties of neat PLA and PLA/PCL blends were obtained from their DSC thermographs shown in fig 2. The variation of glass transition temperature, cold crystallization temperature, melting temperature, crystallization enthalpy and melting enthalpy with PCL content for PLA/PCL blends is presented in table 1. Fox equation (equation 1) was   used to estimate the glass transition temperature of the blend.

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \qquad \text{------ (1)}$$

Where Tg is the glass transition temperature of the blend, and T_{g_1} and T_{g_2} are those of the blend components. w_1 and w_2 are the weight fractions of the blend components. For PLA/PCL blends measured transition temperature are not consistent with Fox equation, indicating the immiscibility of blend components. Cold crystallization temperature remains constant with PCL content, whereas melting temperature decreased with PCL content.

The degree of crystallinity of PLA and PLA/PCL blends was computed using equation (2) Garlotta et al. (2002)

$$X_c \left(\% \text{ Crystallinity}\right) = \frac{\Delta H_m - \Delta H_c}{w \times \Delta H_{m0}} \times 100 \qquad \text{------ (2)}$$

Where ΔH_{mo} = 93.7 J/gm and w is the weight fraction of PLA in the sample. Crystallization enthalpy and Degree of crystallanity of quench cooled virgin PLA are 23.17J/gm and 31.99J/gm respectively. Crystallization enthalpy and degree of crystallanity decreased with increase in PCL content.
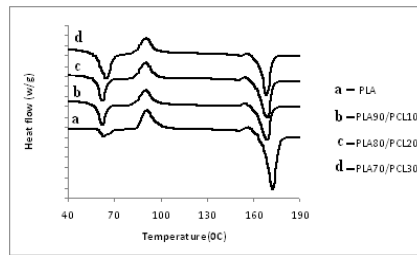
Fig. 2. DSC curves of PLA/PCL blends.

Table 1. Thermal characteristics of PLA and its blends.

Sample	Tg ^{0}C	Tcc ^{0}C	ΔHc (J/gm)	Tm ^{0}C	ΔHc (J/gm)	Xc (%)
PLA	62.5	90.97	23.17	172.49	53.15	31.99
10% PCL	61.24	90.52	19.13	171.81	40.66	25.53
20% PCL	60.90	90.09	18.57	169.07	35.83	23.02
30% PCL	60.62	90.39	17.14	168.40	30.93	21.02

5. Dynamic Mechanical Analysis

The viscoelastic properties of PLA and the PLA/PCL blends were studied using DMA. A declining trend was observed for storage modulus of all the specimens with respect to temperature, rapid reduction occurring at the glass transition region Fig.3a. In the glassy region, storage modulus of the specimen decreased with increasing (PCL). In the glass transition region, no cross-over was observed in any of the samples, and the same trend continued. Above the glass transition region (temperatures above 69 °C), no significant difference was observed in the storage modulus. Variation of Tan-δ with temperature for neat PLA and PLA/PCL blends is presented in fig.3b. As shown in fig.3b, tan-δ increased with the addition of PCL. Thus, the damping ability, that is, the energy absorption and dissipation capacity of PLA, improved with addition of PCL, which may be due to higher molecular mobility of low melting point PCL phase, dispersed in PLA matrix.

Fig. 3 (a) Viscoelastic properties of PLA and PCL blends with storage modulus as a function of temperature; (b) loss factor (Tan-δ) as a function of temperature.

6. Rheological Properties

Shear rheological properties of each blend and neat polymers were measured using Parallel plate rehometer. Tests were performed at 200^{0}C under nitrogen atmosphere to avoid degradation. Dependence of steady shear viscosity on shear rate at 200^{0}C for neat polymers and their blends is shown in Fig.4(b). The shear viscosity of the blend system decreased with increase in shear rate, exhibiting shear thinning behaviour. PCL showed higher steady shear viscosities than PLA Fig.4(b). The addition of PCL resulted in the gradual increase in the viscosity of the blends and showed viscosities in between that of the neat polymers. It also appeared that PLA had a longer Newtonian region than PCL, and the addition of PCL reduced the Newtonian region of the blends. Although rheology data indicated higher viscosity of PCL than PLA at 200 °C, the addition of PCL was found to increase the

processability of PLA in extrusion. Shear stress vs. shear rate plot of the neat polymers and their blends is presented in figure 4(a). In Fig.4(a), higher Shear stress of PCL indicates higher elasticity of PCL than that of PLA. The Shear stress of the blends increased with increase in PCL content. This means that the elasticity of the melt blend increased with PCL.
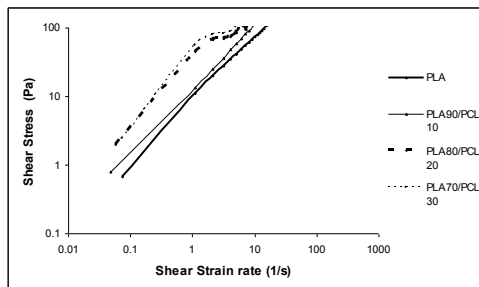

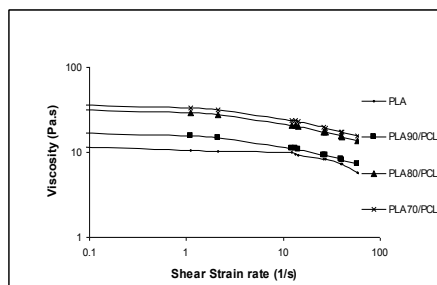Fig. 4(a) Shear Stress Vs Strain rate at 200°C of PLA/PCL blends

Fig.4(b) Shear viscosities Vs strain rate at 200°C

Conclusion

PLA and PCL were melt blended using a Hakee Rheomix and palletized for compression molding. Rheological results revealed that PCL had higher melt elasticity and viscosity than PLA, and the melt elasticity and viscosity of the blends increased with the concentration of PCL. SEM micrographs show that PCL was evenly dispersed in the PLA matrix. DMA and DSC results indicated that the blend is an immiscible two phase system. The addition of PCL was found to accelerate the crystallization rate of PLA but had little effect on its final degree of crystallinity. Like in other blend systems, the semi crystalline PLA experienced extensive cold crystallization and the PLA was almost totally amorphous in the molded products at the normal processing condition.

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