

STUDY OF RHEOLOGICAL AND MECHANICAL PROPERTIES OF BIODEGRADABLE POLYLACTIDE AND POLYCAPROLACTONE BLENDS

R Umamaheswara Rao*,

Department of Mechanical Engineering, GMR Institute of Technology, Rajam-532127,
Srikakulam District, Andhra Pradesh, INDIA
email: umr_r@yahoo.co.in, Fax: +91 8941-251591

KNS SUMAN and VVS KESAVA RAO,

Department of Mechanical Engineering, Andhra university, Visakhapatnam-530003,
Andhra Pradesh, INDIA
email: sumankoka@yahoo.com

K BHANUKIRAN

Department of Mechanical Engineering, GITAM University, Visakhapatnam-530045,
Andhra Pradesh, INDIA
email: bk_1381@yahoo.co.in

Abstract:

In this study, blends of biodegradable Poly (lactic acid) (PLA) and Polycaprolactone (PCL), were prepared using Hakee Rheomix and characterized for rheological and mechanical 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, and decrease in strength, 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. 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.

Keywords: poly laciacid; poly Caprolactone; biodegradable polymers; mechanical properties; reheological properties

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, Sriroth, and Tokiwa, 2006). PLA is a linear aliphatic thermoplastic polyester made from the ring opening polymerization of lactide and the cyclic dimer of lactic acid (γ -hydroxy acid) (Drumright, Gruber, and Henton, 2000 ; Lunt 1998). Although Carothers et al. (Holten, 1971) first polymerized the lactic acid in 1932; it was Cargill who advanced in the pilot production of PLA (Bhardwaj and Mohanty, 2007). 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 has 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. Biodegradable polymer such as with poly (butylenes succinated adipate) (PBSA) (Lee and Lee, 2005), poly (butylene adipate-co-terephthalate) (PBAT) (Jiang, Wolcott, and Zhang, 2006), poly (ϵ -caprolactone) (PCL) (Todo et al., 2007) and poly (ethylene succinate) (PES) (Lu, Qiu, and Yang, 2007), etc are among the better alternatives for blending with PLA.

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. Long Jiang et al. (2007) investigated the rheological, morphological and mechanical properties of PLA and PBAT blends. Rheological results revealed that PBAT had higher melt elasticity and viscosity than PLA, and the melt elasticity and viscosity of blends increased with concentration of PBAT. SEM micrographs show that PBAT was evenly dispersed in the PLA matrix.. Apart from the above mentioned polymers Poly (ϵ - 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 SEM images. In this investigation, PLA and PCL blends of different compositions were prepared by a Hakee Rheomix. All the properties of the blends were compared with that of the neat or virgin PLA.

2 Experimentation:

2.1 Materials Procured:

Poly lactide (PLA) with 4320-grade, pellet form with Density 1.25g/cm³ and melt index (MI) =15g/10min) has been procured from Green Chemical Co. Ltd., South Korea. PLA has negligible solubility in water and has a melting point of 170°C. Biodegradable PCL Polymer with G4460-grade, having Density 1.3gm/cm³, melt index (MI) =10 gm/10 min) by Pestrup, U.K was used to blend with PLA. PCL has a melting point of 80°C.

2.2 Blends and Specimen Preparation

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 and 130°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.

2.3 Tensile Testing

Tensile properties (strength, toughness, elongation-at-break) were measured at room temperature (~25 °C) as well as atmospheric conditions (relative humidity of ~50± 5%) with a 10KN load cell on an Instron Model 3389 tensile tester. The cross-head speed was set at 5mm/min. All tests were carried out according to the ASTM D638 (Type I). Five specimens of each sample were tested and the average results were reported.

2.4 Scanning Electron Microscopy (SEM)

Fractured surfaces from the tensile tests were examined using Zeiss EVO MA scanning electron microscopy (SEM) operated at 10 KV. All specimens were sputter-coated with a thin layer of gold (~20 nm) prior to examination.

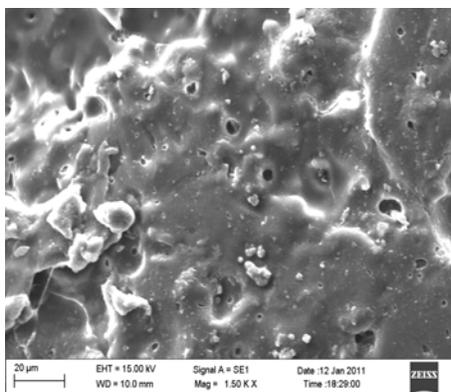
2.5 Rheology

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

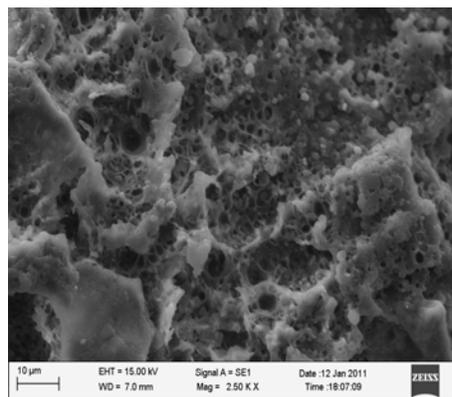
3 Results and discussion

3.1 Scanning Electron Microscopy

To investigate the morphology of PLA/PCL blends, tensile fractured surfaces of the blends were observed through SEM after being gold coated. As shown in Fig. 1, oval cavities and enclosed round PCL particles were visible on the fractured surfaces of all the three blend compositions considered. The blend is a kind of immiscible, two-phase system with PCL dispersing in PLA matrix. SEM of PLA/PCL blend of 90/10wt% show relatively smooth surfaces corresponding to low fracture absorbed energy shown in Fig.1 (a) the voids observed in PLA/PCL blend of 90/10wt% are considered to be created by debonding at interfaces between PCL spherulites and matrix.. The surrounding matrix appears to be mainly brittle PLA, and the voids cause local stress concentration; therefore, initiation of local failure such as matrix micro cracking is faster than PLA/PCL blend of 80/20wt%, resulting the less fracture absorbed energy than PLA/PCL blend of 80/20%. The other two blends exhibit relatively ductile fracture surfaces compared to PLA/PCL blend of 90/10 wt%. It is clearly seen that the ductility of fracture surface is the most excessive in PLA/PCL blend of 80/20wt%. PCL spherulites were observed in PLA/PCL blend of 80/20 and 70/30wt %. The ductile deformation of the matrix implies that the matrix consists of PLA and PCL. The matrix of PLA/PCL blend of 90/10wt% may also contain PCL; however, the amount is too little to create such ductile deformation. Larger PCL spherulites are observed in PLA/PCL blend of 70/30wt%, and therefore, larger voids are created. These large voids result in local stress concentration in broader region than the other blends, causing faster fracture progress, and therefore the fracture absorbed energy suddenly becomes much lower than PLA/PCL blend of 80/20wt% as shown in Fig.1(c).



(a)



(b)

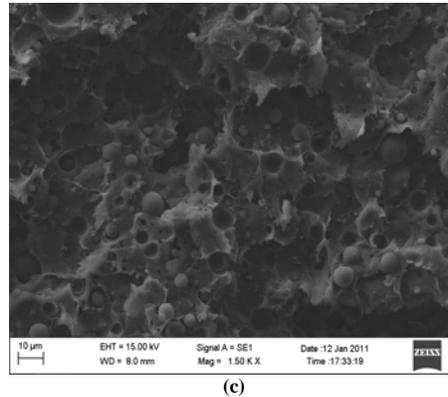


Fig. 1. Phase morphologies of the PLA/PCL blends with (a) 10, (b) 20, and (c) 30% PCL

3.2 Rheological Properties:

Shear rheological properties of each blend and neat polymers were measured using Parallel plate rehometer. Tests were performed at 200°C under nitrogen atmosphere to avoid degradation. Dependence of steady shear viscosity on shear rate at 200°C for neat polymers and their blends is shown in Fig.3. The shear viscosity of the blend system decreased with increase in shear rate, exhibiting shear thinning behaviour. Similar behavior was observed for biodegradable polymers like PBS (Ramkumar and M Bhattacharya, (1998), and biodegradable aliphatic polyester (BAP) (Shin et al., 2000). PCL showed higher steady shear viscosities than PLA (Figure 3). 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 2. In Figure 2, 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.

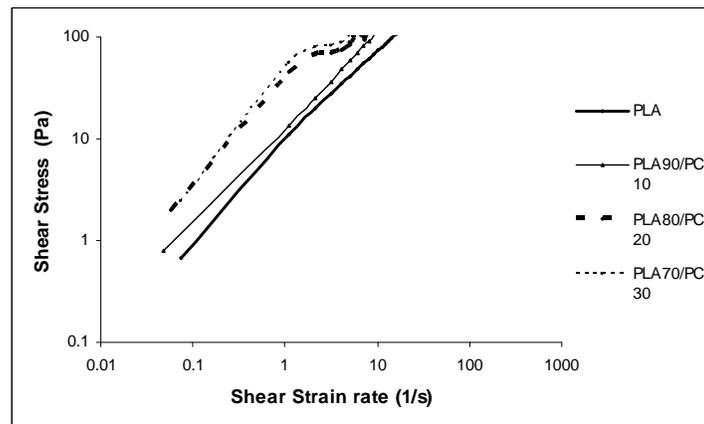


Fig.2. Shear Stress Vs Strain rate at 200°C of PLA/PCL blends

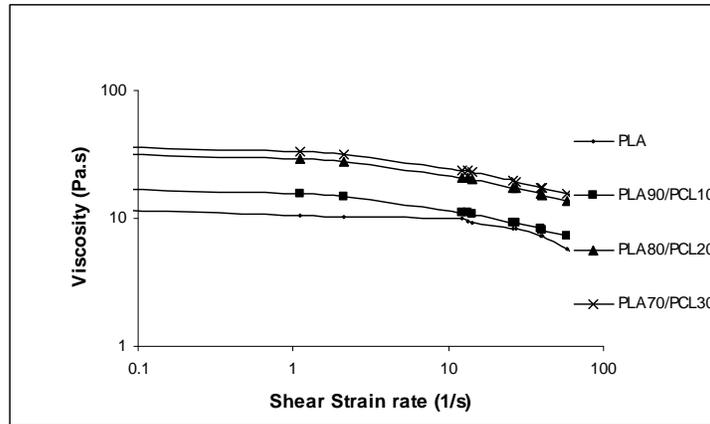


Fig.3. Shear viscosities Vs strain rate at 200°C of PLA/PCL blends

3.3 Mechanical Properties and Toughening

During tensile testing it is observed that fracture behavior of the specimen changed from brittle fracture of neat PLA to ductile fracture of the blends. This is demonstrated in the tensile stress- extension curves as shown in Figure 4. Neat PLA showed failure by neck instability, and its strain at break was only about 4.7%. On the contrary, all the blends showed stable neck growth through cold drawing. It was noticed that even at 10% of PCL the elongation of the blend was tremendously increased to (19 %), and the elongation continuously increased with the increase in PCL content till 20% wt of PCL there after it got reduced. Tensile strength of the PLA/PCL blends decreased with increasing PCL content (Figure. 4). Tensile strength decreased by 35% for neat PLA with that of 20%PCL blend. This was expected since PCL has a lower tensile strength than PLA. With the addition PCL flexural strength decreased gradually as shown Figure 5. Impact strength of the PLA/PCL blends was also measured for various PCL contents, as shown in figure 6. An increase in PCL content resulted gradual increase in toughness up to 20% wt of PCL and there after it decreased.

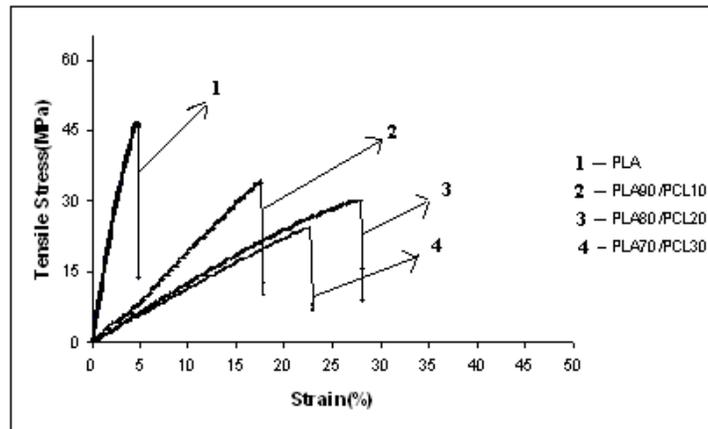


Fig.4. Tensile stress- strain curves of the blends with different PCL contents

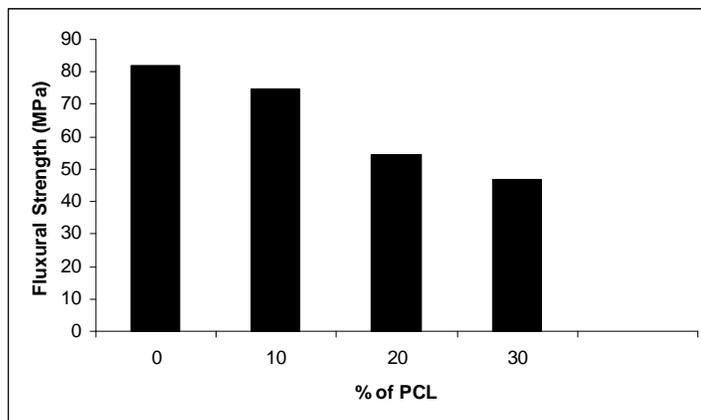


Fig.5. Flexure strength of the blends with different PCL contents

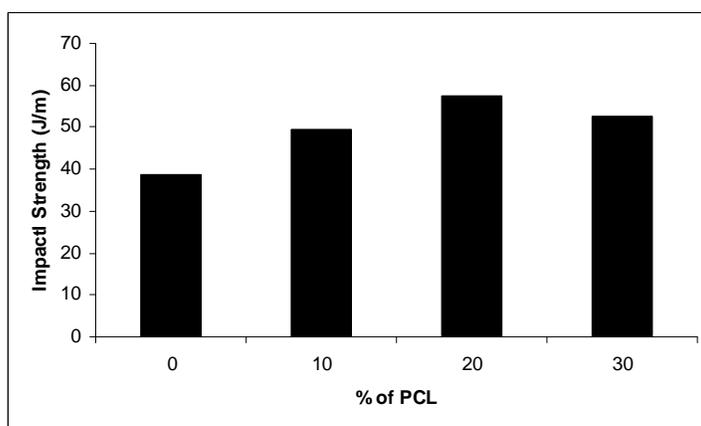


Fig.6. Effect of PCL concentration in the blends on impact strength

4 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.. Even with 10% PCL, the tensile toughness of the PLA blend was greatly increased without severe loss in tensile strength and modulus. The impact strength of the blend was also significantly improved at 10% or higher percentage of PCL addition.

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