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Effect of PCL and compatibility contents on the morphology, crystallization and mechanical properties of PLA/PCL blends

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Abstract

This study focused on the effect of PCL on crystalline morphology, isothermally crystallization of PLA in PLA/PCL blends using POM on investigation. The blend with Pluronic used as a plasticizer was also studied. The blends were prepared by melt blending in an internal mixer. The contents of PCL incorporated were varied from 0-30 % by weight. The content of Pluronic used in this study was at 2.5, 5 and 7.5 phr. The blends were characterized for their morphology, crystallization and mechanical properties. Melt strength of the blends was also investigated. The morphology of the blends confirmed immiscibility of two polymer phases. Scanning electron microscope (SEM) of PLA/PCL blends indicated larger particle size of PCL dispersed in PLA with the increase of PCL contents. T_g of PLA in the blend could not be observed on Differential Scanning Calorimetry (DSC) traces. This was due to the overlapping with T_m of PCL. The presence of Pluronic in PLA/PCL blends resulted in T_ms shifting to slightly lower temperatures. The crystallinity of PLA was also decreased. The spherulitic growth of PLA in blends was followed by polarized optical microscope using isothermal condition at 141 °C. The spherulite structure was found affected by the presence of Pluronic hence effect on crystallization of PLA. Tensile properties of PLA/PCL blend were suffered with PCL content except for elongation at break which seems to be enhanced. It was found that the presence of pluronic in PLA/PCL blend increased ductility of the blends. At Plurunic of 2.5 phr and PCL content of 10-20 % by weight, tensile strength of these blends was increased. This was explained by the fine dispersed PCL particles facilitated orientation of PLA chain after proportional limit and hence increased tensile strength. With higher content both PCL and Pluronic, large PCL particle size was disadvantaged for tensile properties.

*Keywords:*Poly (lactic acid); Polycaprolactone; Crystallization; Polarized optical microscopy

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1. Introduction

Nowadays replacement petrochemical based polymers with bio-based polymers are interesting for packaging application. Many research efforts have been focused on aliphatic polyesters including polylactic acid and poly (ε-caprolactone) as the most important biodegradable materials. [1] Poly (lactic acid) (PLA) is one of the most popular biodegradable polymers which can be produced from renewable resources, known as linear aliphatic thermoplastic polyester. PLA is rigid and brittle below its glass transition temperature (T_g) which is in the range of 50-60 °C [2]. PLA has high tensile strength, rigidity and stiffness. [1-3]. Its high strength and biodegradability makes it an ideal candidate for packaging application. On the other hand, its brittleness limited their uses in many applications. The improvement for the brittle PLA to be better was studied in many researches. Huda M. S. et al. [4] reported that mechanical properties of the wood-fiber-reinforced PLA composites are suitable to be used in automotive and packaging industries. Also, few studies have used flexible polymers with PLA. PLA can be blended with flexible polymers such as poly (ε-caprolactone) (PCL), poly (buthylene succinate) (PBS), and poly (butylene succinate adipate) (PBSA) to achieve the flexibility and high elongation the brittleness of PLA and improves strain at break [1-6].It is well known that blending of polymer is the most cost-effective way to obtain material with required properties. The miscibility of two polymers can be determined by the Gibbs free energy of mixing by using the solubility parameter value of the two polymers [2]. Polycaprolactone (PCL) is semicrystallinealphatic polyester, flexible polymer and biodegradable but this one is obtained through petrochemical processes [3]. PCL has low glass transition and melting temperature (T_g = -50 ^oC, T_m = 60 ^oC) [5]. Blending of PCL with PLA can reduce brittle behavior of PLA.PLA blends with PCL have been report as phase-separate blend system [2-7]. Jen-Taut Yeh et al. [6] blended PLA with PCL by melt blending. They found that PLA and PCL form a partial miscible blend. Takeshi et al. [7] showed an increase of ultimate tensile strain of PLA when PCL was added to this blend system. Kamolrat et al. [8] used a block copolymer of poly (ethylene glycol) and poly (propylene glycol) as compatibilizer in PLA/PCL blends. SEM micrographs revealed that the PCL phase was better distributed and more miscible in the PLA matrix. The presence of compatibilizer increased strain at break.

The aim of this research is to improve the strength and ductility by incorporation PCL to PLA. The crystallinity of the blends is also aimed to be studied. The addition of PEG-PPG-PPE block copolymer is also added to investigat whether it to be a compatibilizer or plasticizer in the blends.

2. Materials and Methods

2.1. Materials

Poly (lactic acid) (PLA) grade 2003D, with melt flow index (MFI) of 6 g/10min (temperature 210^{o}C, pressing mass 2.16 kg), was purchased from Nature Works LLC. Poly (ε-caprolactone) (PCL) (CAPA^{TM} 6506 technology) with number-average molecular weight of 50,000 g/mol was purchased from Perstorp. The MFI, measured at 160 $^{\circ}$C, same pressing mass as for PLA, is in the range from 5.2 to 11.3 g/10min. Poly (ethylene glycol)-Poly (propylene glycol)–Poly (ethylene glycol) block copolymer (PEG-PPG-PEG), trade name Pluronic® L-81, was purchased from Sigma Aldrich with the number-average molecular weight of 2,800 g/mol.

2.2. Preparation of the PLA/PCL blends

PLA pellets and PCL powder were dried in hot air oven at 60 ^{o}C and 30 $^{\circ}$C respectively, for 12 hours before melt blending. The ration of PLA/PCL formulated for melt blending was 100/0, 90/10, 85/15, 80/20, 75/25 and 70/30by weight percentage. The blending was carried out by melt mixing using an internal mixer at 180 $^{\circ}$C with rotor speed of 50 rpm for 15 min.The PLA/PCL with Pluronic loading at 2.5, 5 and 5 phr was also processed under the same conditions.

After the melt mixing, PLA/PCL blends and PLA/PCL filled with Pluronic was compressed, using compression molding machine, at 160 $^{\circ}$C and 800 psi to obtain blend sheet with dimension of 15 mm x 18 mm x 0.7 mm.The blend sheet was cut into dumbbell shape (dog-bone), according to the ASTM D638 type 4A standard for tension testing, using laser cutter.