Preparation and Properties of Polycaprolactone/Poly (Butylene Terephthalate) Blend

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ABSTRACT: *Polycaprolactone (PCL) and poly(butylene terephthalate) (PBT) blend was prepared by melt processing. The PCL/PBT blend showed similar morphology with that of pure PCL. The crystallization temperature of PCL was increased by the incorporation of PBT. It was also observed that the peak height in the DSC thermograms decreased and then disappeared by adding 40 % or more PBT which might be due to the transestrification between – OH end groups of PCL and ester groups of PBT. The size of PCL spherulites was about 13 µm which decreased highly in the case of blends due to the nucleation effect. The thermal stability of the PCL/PBT blend was higher than pure PCL.*

KEY WORDS: *Polycaprolactone, Blend, Morphology, Thermal properties.*

INTRODUCTION

Polymer blending is simple versatile and inexpensive technique for producing new types of polymeric materials having tailored properties without a need to synthesize entirely new materials [1-5]. The blend components are usually immiscible, which yield multiphase systems by mixing two polymers. The corresponding performance depends upon the phase morphology of the blend as well as the composition, rheological and physical characteristics of the components, relative compatibility, and nature and intensity of mixing. Hence, control of phase morphology (blend performance), can be achieved by controlling the mixing parameters and/or by compatibilization [6].

PCL, aliphatic polyester made from the ring opening polymerization of ε-caprolactone, is known to be a biodegradable polymer. The specific characteristics of PCL such as low melting point and mechanical properties, and solubility in a wide range of solvents, are disadvantages in many practical applications. To expand its applicability, PCL is blended with polymers [7] or other reinforcing materials [8]. Many research groups have been trying to enhance the properties of PCL by incorporation of a wide variety of other polymers, which give blends (both compatible and incompatible), and make PCL a preferred material for theoretical and

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fundamental blend studies [9]. *Nojima et al.* [10] prepared PCL–PS blends and studied their morphological as well as the crystallization behavior at various crystallization temperatures using X-ray scattering method. It was also reported that PCL–PS blends have good mechanical properties, although the blend was incompatible [11]. *Zhang et al.* studied orientation of PCL crystals in miscible PCL / Poly Vinyl Chlorid (PVC) blends, by Wide Angle X-ray Diffraction (WAXD), [12]. *Lorenzo et al* [13] analyzed the miscibility, and thermal and mechanical properties of PBT blends with PCL as a function of the molecular mass of PCL. It was found that the PCL (oligomeric) is miscible when blended with PBT, due to the favorable interactions between – OH end groups of PCL and ester groups of PBT. While in the case of high molar mass PCL, the resultant blend was partially miscible, which was due to the lower concentration of hydroxyl end groups. It was also found that the resulting blends display good mechanical properties. In the case of Poly Ethylene Terephthalate (PET)/PCL blend, the crystalline structure of the blend components changes and the morphology is also converted into a homogeneous phase. The biodegradability of PET/PCL copolyesters increases with a decrease in the sequence length of ethylene terephthalate and caprolactone blocks. It was suggested that the biodegradable copolyesters with desired biodegradability behaviors might be prepared by the melt blending of polymers [14].

In the present study we prepared PCL/PBT blend, because PBT is a semi-crystalline polymer with high commercial value and due to its good chemical resistance, high melting temperature and good dimensional stability, it is a material of major interest for numerous applications [15]. While PCL is known for its unique biocompatibility, degradability [16], and its applications in degradable packing and drug delivery systems in medical supplies, its low melting point has been a disadvantage in many applications. In this work we studied the morphologies, thermal properties and crystallization behavior of the PCL/PBT blend and compared with that of pure PCL.

EXPERIMENHTAL SECTION

Material

PCL (average molecular weight 90,000) was prepared by the same method as reported elsewhere [17]. PBT were kindly supplied by Korean company.

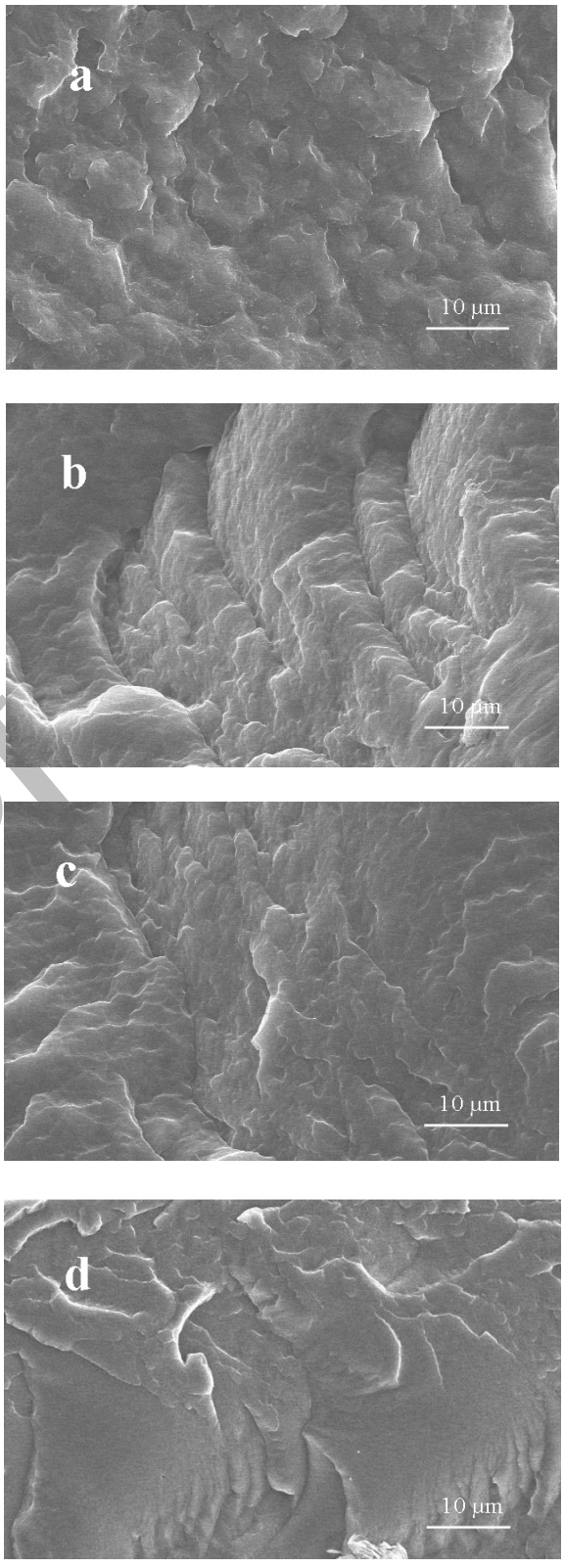

Fig. 1: SEM images of PCL and PCL/PBT blend, with different wt % of PBT (a) 0, (b) 20, (c) 30 and (d) 40.

Blend Preparation

Both PCL and PBT polymers were dried in a vacuum oven at room temperature for 12 h. PCL/PBT blends were then prepared by melt mixing at 270 °C for 1h under nitrogen atmosphere. Binary blends with a constant PCL/PBT 80/20, 70/30 and 60/40 wt/wt composition were prepared.

The films of PCL and PCL/PBT blend were made by hot pressing the blend samples between two aluminum plates and then quenching them in icy water.

Measurement

The micrographs of the gold-coated fractured surfaces (broken in the liquid nitrogen) were analyzed using a JEOL JSM-5910 scanning electron microscope (SEM). The thermal properties of the PCL and the PCL/PBT blend were studied by DSC and TGA. The DSC analyses were carried out on a Dupont 2000 Thermal Analyzer. A specific amount of sample was sealed in aluminum sample pans and prepared by compression molding. DSC thermograms were obtained at heating and cooling rates of 10 °C /min under a nitrogen atmosphere in order to diminish oxidation. The TGA of PCL and PCL/PBT blend were obtained in a nitrogen atmosphere, at a heating rate of 20 °C/min from room temperature to 900 °C using a Diamond TG/DTA (Perkin Elmer). Polarized optical microscopic photographs were obtained using a Moram JI-213 Polarized Optical Microscope (POM). The sample was melted on a heater and squeezed between two glass slides at 250 °C for 10 min in the presence of nitrogen, quickly transferred to hot stage, and annealed at 50 °C for 2 h.

RESULTS AND DISCUSSION

The phase morphology of the PCL/PBT blend system is shown in Fig. 1, which was broken in liquid nitrogen. The SEM micrographs of the fractured surface of PCL/PBT blend samples revealed that the blends systems showed more similarity with that of pure PCL. It presented that no obvious phase separation occurred and the PCL and PBT seemed to be miscible over the entire composition range. The miscibility of the components might be due to favorable interactions between – OH end groups of PCL and ester groups of PBT [13].

The DSC thermograms of PCL and PCL/PBT blend with various compositions are shown in Fig. 2.

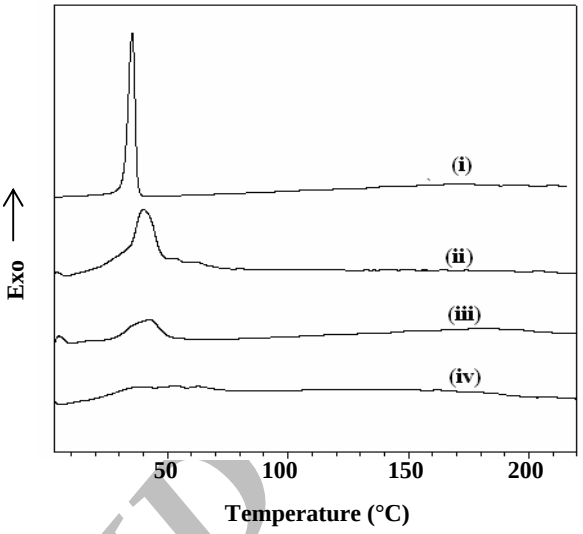

Fig. 2: DSC cooling curves of PCL and PCL/PBT blend, with different wt % of PBT 0, 20, 30 and 40.

The crystallization temperature (T_c) of pure PCL was 36.4 °C. The T_c of the blend was increased by about 3-5 °C as compared to the T_c of pure PCL (Fig. 1). It might be due the more crystallizable PBT molecules, which helps to promote the crystallizability of the blends [18] or the nucleating effect of PBT on the primary nucleation of PCL in the PCL/PBT blend [19]. It was also observed that the peaks height in the blend decreased and then disappeared when 40 % of PBT were incorporated into PCL, which shows that the crystallization is hindered. The increase and disappearance of the T_c peak in the blend system might be due to the tranestrification between the PBT and PCL chains. *Hameed et al.* [20] have also reported that the T_c peak in the DSC thermogram increased in phenoxy/PCL-b-P2VP blends and then disappeared in the blend containing 40 wt % or more phenoxy contents. They suggested that the increase in crystallization peak temperature upon the addition of phenoxy might be due to the relaxation of PCL blocks of the block copolymer caused by the formation of strong hydrogen bonds between poly(2-vinyl pyridine) and phenoxy in lower phenoxy content blends.

Fig. 3 shows the POM of PCL, and PCL /PBT blend, which were prepared by cooling from the melt state and annealed at 50 °C for 2 h under cross polarizing filters. The polarized optical micrograph of PCL showed a Maltese cross pattern with a size of 13 μm as shown in Fig. 3a (as also shown in our previous reported article [8]).

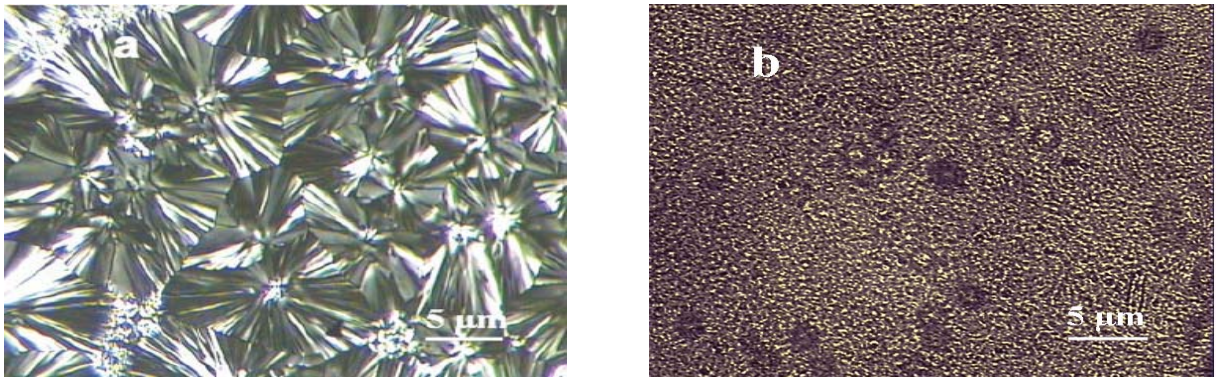

Fig. 3: Polarized optical micrographs of (a) PCL and (b) PCL (30 wt %)/PBT(40 wt %) blend.

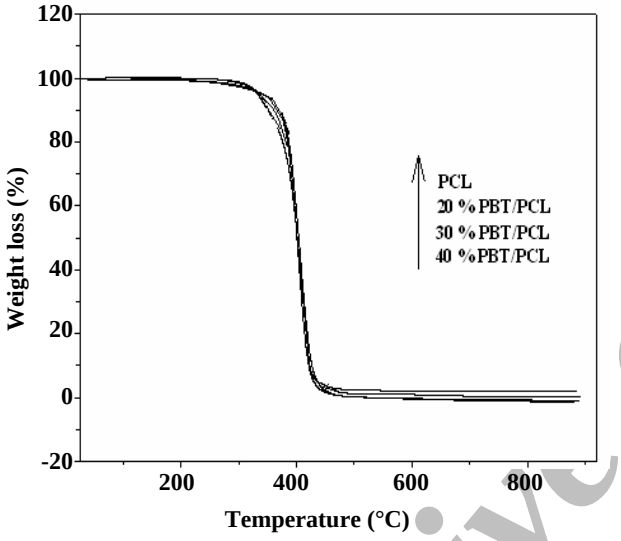

Fig. 4: TGA thermograms of PCL and PCL/PBT blend.

The spherulites observed in PCL are similar to the reported pattern [21]. A large number of very small spherulites could be observed in the background of the spherulitic morphology for the PCL/PBT blend samples (Fig. 3b). It suggested that the PBT has a nucleation role in the blend system, which might result in small granular spherulites.

Fig. 4 shows the TGA curves of the PCL and PCL/PBT blend samples. The TG curves presented that initially the mass of the PCL and blend samples remained constant up to 310 and 340 ^{o}C, respectively and then reduced abruptly. The pure PCL started weight loss at about 320 °C and completely decomposed at about 450 ^{o}C. The thermograms of the PCL/PBT show that the weight loss of the blends started at about 350 °C and decomposed at about 450 °C, which is about 30 ^{o}C higher than the pure PCL. The increase of the degradation temperature indicates that the incorporation of PBT into the PCL exerts a thermal stabilizing effect.

CONCLUSIONS

It is concluded from the present study that the crystallization temperatures of PCL/PBT blends increased but the peak height in the thermograms decreased and disappeared completely when 40 wt% PBT was added. The typical Maltese-cross spherulites of PCL were converted into small granular spherulites by the addition of PBT. The decreased in size of the spherulites presented that PBT might act as a nucleation effect. Also blend system showed morphological similarities with pure PCL.

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