

Reactive Extrusion and Characterization of *Pseudo* Liquid Crystalline PEN

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1. Introduction

Increasing demands for high modulus and high strength polyesters have drawn considerable interest in various applications, such as fiber, film and packaging. Thermotropic liquid crystal polymers (TCLP), differing from lyotropic LCPs, have excellent melt processability and mechanical property resulting from the high degree of molecular orientation under shear flow or elongational flow in the molten state with low viscosity. The potential to apply the advantages of LCP such as high strength, high modulus, high thermal stability, excellent dimensional stability, low dielectric constant and low coefficient of thermal expansion. From the advantages of LCP, blends of strong and rigid type LCP with conventional polyesters such as poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT) can provide improvement of mechanical properties.(1,2)

Our research group has mainly concerned with LCP reinforced polyester *in situ* composites, and p-hydroxybenzoic acid 60 mol % / polyethylene terephthalate 40 mol % (PHB60/PET40) copolyester with PBT shown synergic mechanical property improvement even add 5-10 % of the PHB60/PET40 LCP.(3) The key factor to obtain synergic mechanical property improvement with adding small amount of expensive LCP is formation of long LCP fibril and well dispersed LCP fibril domain in the polyester matrix. Analysis of distribution and dimension of LCP is performed and applied to establish theoretical equations, which shows relationship between LCP fibril dimension and distribution and mechanical property of the blended filaments.

In recent years, poly(ethylene 2,6-naphthalate) (PEN) may be the most attractive materials for industry, because it possesses high thermal transition temperature and better mechanical properties than them of PET. Synthesized PHB/PET/PEN ternary copolyester can have LC phase, which containing 30 mol % PHB is partially LC phase and containing over 50 mol % is completely LC phase.(4) Our research group concerned obtaining *pseudo* LC phase with reactive extrusion, without performing expensive and time consuming polymerization process.(5) Mechanical, chemical and morphological properties of the PHB/PET/PEN *pseudo* LC polyester will be presented.

PHB80/PET20 LC copolyester reinforced PEN *in situ* composite also prepared by reactive extrusion. The effect of the third component or a compatibilizer on physical property of the partially miscible blend system was investigated. The key factors to improve properties are good interfacial adhesion, appropriate phase separation to form LCP fibril in the PEN matrix, and uniform LCP distribution. In particular, our interest is to expand application area of the LCP reinforced PEN featuring better mechanical property, which can be obtained through transesterification between LCP and polyesters.(6,7)

2. Experimental

PHB/PET/PEN ternary copolyester

LCP used in this research was a Rodrun 5000 by Unitika Co., Japan, supposed to be prepared from 80 mol % PHB and 20 mol % PET (PHB80/PET20). The PEN with an intrinsic viscosity of 0.51 dL/g was supplied by courtesy of Kolon Co. in Korea. The PET with an intrinsic viscosity of 0.64 dL/g was prepared by courtesy of Samyang Co. in Korea. The blends were made by melt blending in a Haake Rheomix 600. Blending composition of PHB/PEN/PET blends in weight ratios were 0/0/100, 0/100/0, 10/45/45, 20/40/40, 30/35/35, 40/30/30, 50/25/25, 60/20/20, 70/15/15 and 80/0/20.

(PHB80/PET20) / PEN with reactive catalyst used copolyester

PHB80/PET20 LCP also used for this work, and PEN was supported by Mitsubishi Co. The PEN had reported T_m of 270°C and i.v. of 0.61 dL/g in phenol/tetrachloroethane 60/40 mixture. Dibutyltindilaurate (DBTDL) used as a reactive catalyst. The contents of LCP in the PEN blends were varied as 1.5, 3, 5, 10, and 25 wt%. The amount of DBTDL added was 500 and 1000 ppm to the total weight of PEN and LCP. Blending was performed using Brabender twin screw extruder, and mono-filament was spun using Rosand Capillary rheometer (Model RH7-2).

3. Results and Discussion

Rheological and mechanical properties of PHB/PET/PEN ternary copolyester

Torque value versus PHB content for the PHB/PEN/PET ternary copolyester is shown in Fig. 1. Pure PEN (0.65 Nm) needs the highest torque versus pure PET (0.38 Nm) and all the blends due to its high melt viscosity. Torque values of blends show similar levels below 30 wt% PHB content. Torque values are greatly decreased with increasing PHB content over 40 wt% PHB; we suppose that the high content of PHB

provides *pseudo* LC phase to the ternary blend, as is confirmed by the morphology study.

Tensile strength and modulus of the PHB/PEN/PET ternary blends are shown in Figure 2. Mono filaments are melt spun using Haake single screw extruder with different winding speed to apply different elongational flow field. Winding speeds were 500 m/min. and 1000 m/min. Tensile strength was increased with increasing PHB contents. PHB 40 mol % added PET and PEN shows the highest tensile strength, and the higher winding speed 1000 m/min provides higher tensile strength of the PHB/PEN/PET blended filament fibers. Fibril formation of LCP may be induced by stronger elongational flow with higher winding speed.

Mechanical property of (PHB80/PET20) / PEN with reactive catalyst used copolyester

Figure 4 describes the effect of DBTDL as a reactive catalyst on the tensile strength for the 75/25 PEN/LCP blends at draw ratios 10 and 20. Addition of DBTDL slightly enhances mechanical properties of the blends at the particular content. The optimum amount seems to be 500 ppm at the draw ratio 20. However, mechanical properties deteriorate when the amount of catalyst exceeds the optimum level. Interfacial adhesion and compatibility between two phases of PEN and LCP are enhanced. Therefore, DBTDL can be used as a catalyst to produce reactive compatibilizer in this blend system. This suggests the possibility of improving the interfacial adhesion between immiscible polymer blends containing LCP by reactive extrusion processing at a very short residence time.

4. Conclusions

Mechanical property improvement of LCP reinforced polyester *in situ* composite can be obtained by controlled LCP distribution and appropriate miscibility between LCP and matrix polyesters. PHB 40 mol % added PEN and PET ternary blend shows *pseudo* LC phase with high mechanical property and low melt viscosity. LCP and PEN with DBTDL reactive catalyst added blend shows better compatibility between them and improved mechanical properties.

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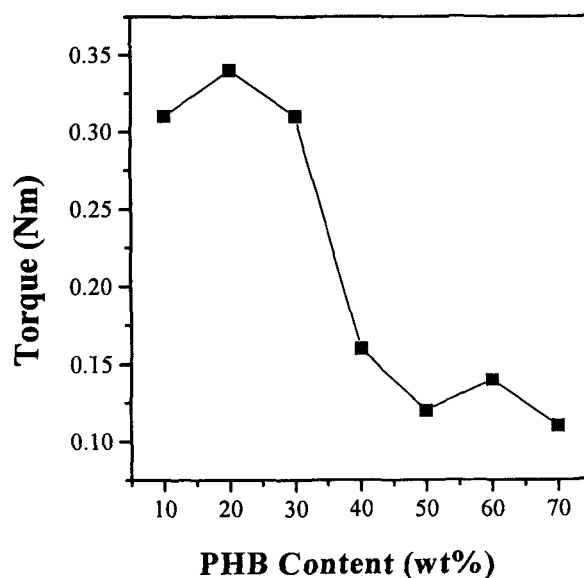


Figure 1. Torque value as a function of PHB content for PHB/PEN/PET ternary blends measured at 285°C 60 rpm in Haake Rheometer.

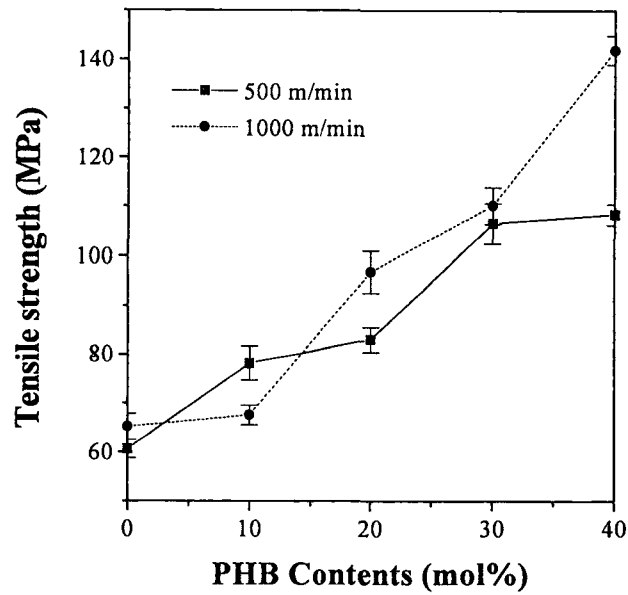
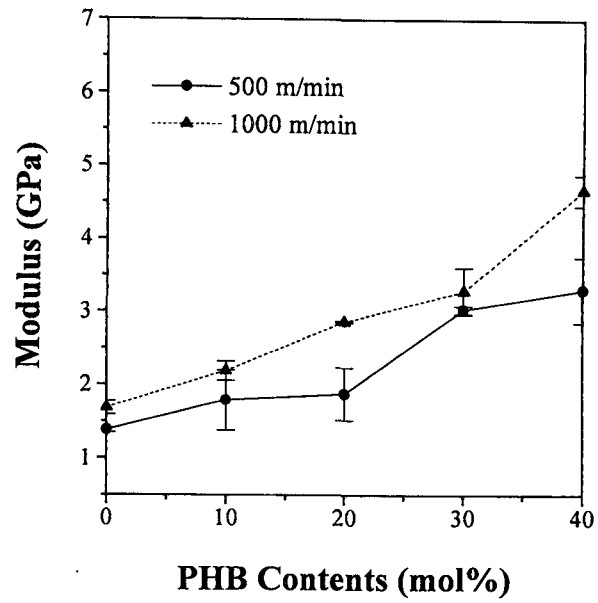


Figure 2. Tensile strength and tensile modulus of PHB/PEN/PET fiber with increase of PHB content (mol%)

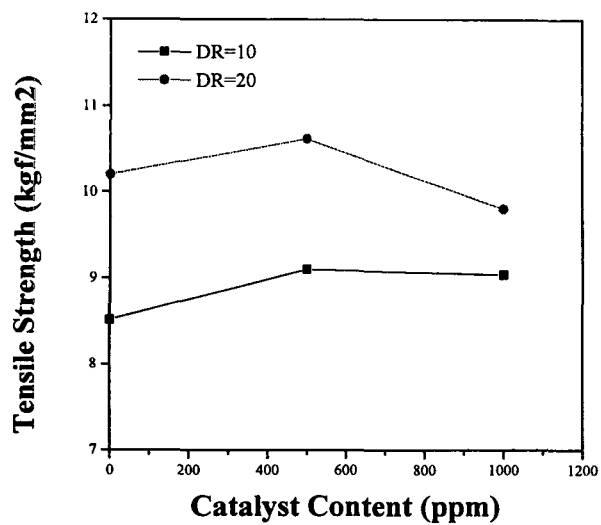


Figure 3. Tensile strength of 75/25 PEN/LCP blends as a function of catalyst content at draw ratio of 10 and 20