Thermotropic Liquid Crystal Polymer and PBT Blend

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1. INTRODUCTION

Increasing demand for high modulus high strength polymeric materials have drawn considerable interest in industry. Thermotropic liquid crystal polymers (TLCP), differing from lyotropic liquid crystal polymers, have excellent melt processability and mechanical property resulting from the high degree of molecular orientation under a shear flow field in the molten state with relatively low viscosity[1,2]. From the advantages of LCP, the blends of rigid chain polymers forming LC phases with conventional thermoplastic polymers such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) could lead to the improvement of mechanical properties[3-8]. In general, the increment of physical properties is dependent on the influence of TLCPs upon the crystallization of thermoplastic polymer through a thermal process[9] and dispersity of the LCP in the matrix polymer. The crystallization rate of PET blending with LCP was higher than that of pure PET, which was attributed to nucleation of PET by LCP. The crystallinity also increased with the addition of the LCP[10,11]. TLC copolyesters commonly undergo chemical reactions with polyester such as PET or PBT in the melt. As interchange reaction proceeds, blends convert initially to block copolymers and finally to random copolymers, and it can lead to a more uniform polymer by minimizing molecular weight fluctuations in a melt, which enhances the miscibility between components leading a single phase blend[12].

In this research, the effects of LCP on crystallization and thermal behavior of matrix polymer were studied by thermal analysis. The nonisothermal crystallization behaviors of LCP and PBT blend, and the kinetic parameters were investigated on the influence of composition and cooling rate using differential scanning calorimetry (DSC). Also, the transesterification occurring between LCP copolyester and PBT during melt mixing with the different mixing time was investigated by nuclear magnetic resonance (NMR) spectra.

2. EXPERIMENTAL

The TLCP used in this research was a thermotropic copolyester LCP, RODRUN 3000 (Unitika Co., Japan) composed up 60 mol% of p-hydroxy-benzoic acid (PHB) and 40 mol% of poly(ethylene terephthalate) (PET), and designated as PHB60/PET40. Poly(butylene terephthalate) used as

thermoplastic matrix polymer was supplied from Samyang Co. in Korea.   Melt blending of
PHB60/PET40 and PBT was performed in a Minimax Molder model CS-183 MMX (CSI Co.) at 260°C.
All materials used in this study were dried in a vacuum oven at 110°C for 24 hours to minimize moisture
effects before use.   The blend ratios (PBT wt% / LCP wt%) were 100/0, 97/3, 95/5, 93/7, 90/10, 80/20,
70/30 and 50/50.   The samples for the NMR spectra were blended at 260°C in Haake Internal Mixer 600
with different mixing times.   Differential scanning calorimetric (DSC) measurements were carried out in
a Perkin-Elmer DSC 7 under N_2 atmosphere.   The sample weight was kept approximately 10 mg for the
accuracy, and scanning temperature range was from 30°C to 280°C with 10°C/min heating and cooling
rate.   Second heating and cooling thermograms were adopted after 1st heating and cooling scans.   The
tensile properties were measured using STM-10E(United Calibration Co.) tester are a constant crosshead
speed of 5mm/m and gauge length of 50mm.   The mechanical properties reported are based on
measurements made on at least seven samples.   Nonisothermal crystallization DSC study was carried
out at 2.5, 5, 10, 15, 20, 25, 30, 35, and 40°C/min cooling rates.   For eliminating anisotropy of LCP,
the sample was held in molten state at 280°C for 4 min.   The relative crystallinity was defined as the
fractional area confined between the rate-temperature curve and the measured DSC exotherms.   For the
NMR spectra, blends were dissolved in deuterated trifluoroacetic acid at a concentration of 10 wt.%.   [1]H-
NMR measurements were performed on a Jeol 300 MHz FT-NMR spectrometer.

3. RESULTS AND DISCUSSION

3.1 Thermal Behavior

Transition temperature and heat of fusion measured by DSC for PHB60/PET40, PBT and their
blends are listed in Table 1.   The crystal to nematic transition temperature (Tkn) of PHB60/PET40 was

Table 1. Thermal properties of PHB60/PET40 and PBT blends from heating or cooling scan of 10°C/min DSC.

PBT /LCP (wt%)	Tg (°C)	Tc_o[a] (°C)	Tc (°C)	Tm (°C)	ΔT[b] (°C)	ΔHc (J/g)	ΔHc PBT (J/g)	Xc[c] (%) (PBT/LCP)	Xc[d] (%) (PBT)
100/0	39.4	189.5	181.1	223.4	33.9	47.2	47.2	40.0	40.0
97/3	39.4	197.7	191.6	224.1	26.3	49.5	51.1	34.3	35.3
95/5	40.3	197.2	192.9	224.6	27.3	49.6	52.2	36.2	38.1
93/7	39.7	195.6	191.1	223.6	27.9	48.7	52.4	37.1	39.9
90/10	39.3	192.9	188.8	223.1	30.2	44.5	49.4	35.1	39.0
80/20	41.9	189.7	184.5	222.4	32.7	39.0	48.7	31.6	39.6
70/30	44.5	187.5	181.5	221.1	33.6	33.5	47.9	28.8	41.2
50/50	45.7	183.2	177.5	220.7	37.5	25.7	51.4	24.7	49.4

a: Crystallization onset temperature on the cooling scan
b: Degree of supercooling ($\Delta T = Tm - Tc_o$)
c: % Crystallinity of PBT/LCP blends
d: % Crystallinity of PBT

appeared at 197℃, and the melting temperature (Tm) of PBT was appeared at 225.4°℃ on the heating scans.   This narrow difference of the melting temperatures enables to do melt process.   The 3 or 5% additions of LCP to PBT matrix cause the slight ascend of melting temperature due to the increase of crystallinity or the transesterification between the two polymers.   Pure PBT exhibited a crystallization exotherm peak at 181.1℃, and LCP exhibited a nematic to crystallization temperature (Tnk) at 145℃ on the cooling scans.   Therefore, this wide difference between the crystallization temperature affects on the crystallization temperature of the blends.   The crystallization temperature and heat of crystallization tend to increased with LCP content from 3 up to 7 wt.%, followed by decrease thereafter.   One of the possible explanations for these inclinations is that a certain crystallization was induced by intermolecular reaction such as transesterification reaction during the heating scan.   The degree of supercooling required for initiating crystallization is much lowered at 3, 5 and 7% of LCP addition.

3.2 Mechanical properties

The tensile strength of injection molded dumbbell specimens for PBT/LCP blends at room temperature is shown in Figure 1.   From this figure, it can be seen that blends containing 5 and 7 wt% LCP exhibit higher tensile strength than pure PBT.   With increasing LCP content, the tensile strength drops gradually to 20 wt%.   As a result, flaw propagation due to stress content would go on doing the interface leading to complete failure.   Therefore, high tensile strengths could not obtain the synergistic effect when the LCP content was higher than 10 wt% content of LCP.   The mechanical properties of the *in situ* composites are greatly influenced by the resultant morphology.
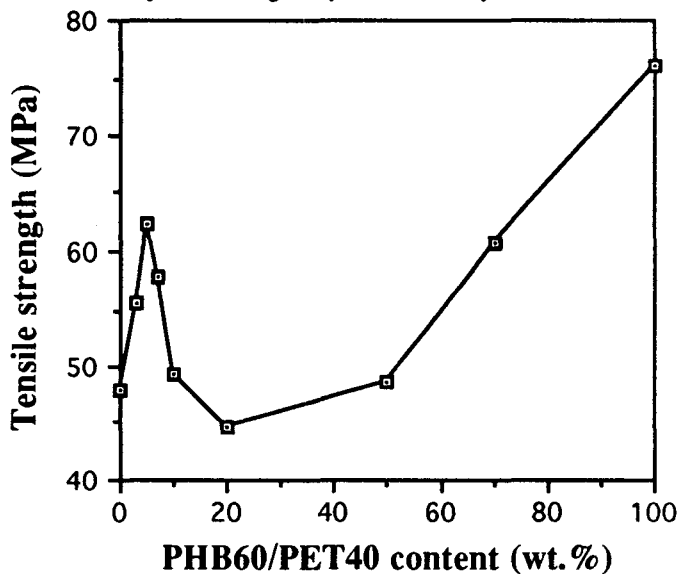

Figure 1. Tensile strength as a function of LCP content for PBT/LCP blends; Injection molded standard tensile bar at 260℃.

Thus, controlling the morphology is to obtain *in situ* composites products with desirable mechanical properties[13]. The morphology of polymer blends is decided by follow factors: first, LCP domains must be finely and uniformly disperse within the matrix during the mixing process. Second, the dispersed LCP domains must be effectively deformed during the find fabrication process to have aspect ratios large enough to play a rule of reinforcement. Third, good and ultimate adhesion between two incompatible phase is essential for enhanced mechanical properties. Among these, a good interfacial adhesion is a decisive factor in improving the mechanical properties.

3.3 Nonisothermal Crystallization Kinetics

Nonisothermal crystallization kinetics can be obtained by applying the nonisothermal data to the Ozawa equation[11], which is extended Avrami equation[12]. Accordingly, the relative crystallinity ($Xc(T)$) as a function of temperature T and cooling rate |a| is given by:

$$Xc\ (T) = 1 - \exp(\frac{-K(T)}{|a|^n}) \qquad (1)$$

Where, K(T) is the cooling crystallization function of nonisothermal crystallization at temperature T, and n is the Avrami exponent, which can assume a value between 1 and 4 depending on the type of nucleation and the growth dimensions. Taking the double logarithm of both sides of Eq. (1) at a constant temperature, it follows that

$$\ln\ [-\ln\ [1-Xc(T)]\ ] = K(T) - n\ \ln|a| \qquad (2)$$

Also, Avrami exponent (n) and crystallization function (K(T)) could be calculated from the slope and intercept of the straight line from Eq. (2), respectively. The values of the Avrami exponent

Table 2. Kinetic parameters of PBT/LCP blends at each temperature.

	Temperature (°C)	PBT	PBT/LCP (95/5)	PBT/LCP (90/10)	PBT/LCP (80/20)	PBT/LCP (50/50)
Avrami exponent (n)	196	3.0836	3.1815	3.4481	3.1700	-
	192	3.1435	3.3272	3.5442	3.0574	-
	188	2.8105	3.0391	3.3162	2.9863	3.1142
	184	2.4522	2.6433	2.9661	2.9465	3.0335
	180	-	-	-	2.8674	2.9984
	176	-	-	-	-	3.1248
	172	-	-	-	-	3.1880
Crystallization function	196	6.064	6.113	6.187	3.954	-
	192	8.251	9.656	8.736	6.139	-
	188	8.790	9.845	9.921	8.167	4.972
	184	8.953	9.895	10.242	9.681	6.871
	180	-	-	-	10.584	8.721
	176	-	-	-	-	10.278
	172	-	-	-	-	11.644

determined by this method are listed in Table 2. At a given temperature, the Avrami exponent ranging from 2.8 to 3.5 suggests predetermined nucleation and three-dimensional growth of the crystallites in thePBT and PBT/LCP blends. The values of X(t) show an increasing trend with decreasing temperature. The crystallization functions meaning the crystallization rates for 5% and 10% LCP/PBT blends are higher than that of pure PBT. The rate of crystallization increased at 5% and 10% LCP/PBT blends, which was attributed to nucleation of the PBT crystallization by the LCP.

3.4 Transesterification Reaction

The mol% of PHB units bonded to PET and PBT units shown from ^{1}H-NMR spectra of PBT/LCP blend in the region 7.73 and 7.85 ppm as a function of blending time for PBT/LCP blend is presented in Figure 2. As the blending time increased, the peak of PHB-PET plus PHB-PBT dyad relative to that of PHB-PHB dyad slightly increased from the initial ratio of 1.29 for the pure LCP. Owing to the stiffness of polymer backbone chain in the LCP, degree of transesterification between PHB-PHB and PHB-PET and PHB-PBT is not high. The initial transesterification reaction rates between 0 and 10 min are 0.5 ~ 1.7 x 10^{-1}. Also, the values of the slope at the period between 10 and 20 min are 2.3 ~ 3.9 x 10^{-1}, and these values are two times as high as those of initial transesterification reaction rate. The blend with 5 wt% LCP shows the largest ratio of PHB-PET plus PHB-PBT units to PHB-PHB units indicating the most frequent transesterification reaction between PBT and LCP phase. The unit in a LCP molecule certainly has more probability of interchange reaction with other molecules of PBT or LCP when LCP content is relatively small.
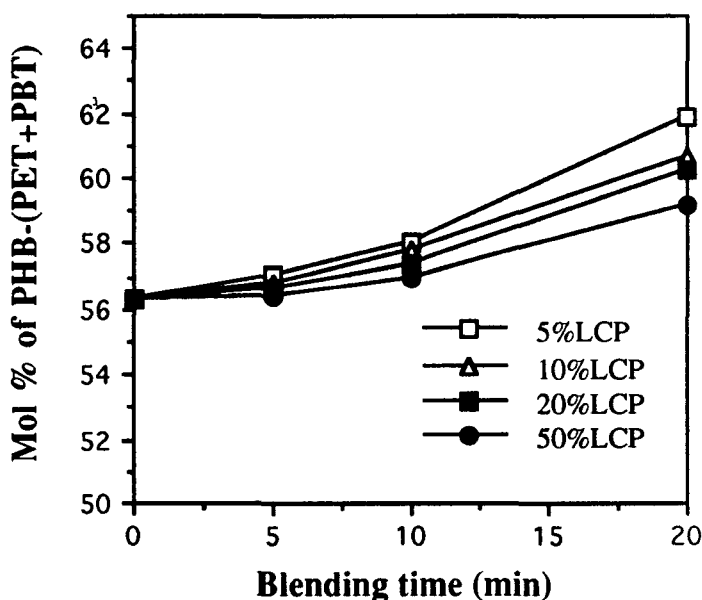

Figure 2. Mol % of PHB as PHB-(PET+PBT) with different blending time.

4. CONCLUSIONS

The thermal behaviors, nonisothermal crystallization kinetics and chemical interchange reaction of polymeric blends consisting of PHB60/PET40 and PBT have been studied as a function of LCP content during the reactive extrusion time. The blends compounded at 260°C showed the ascent of melting temperature, especially in 3 ~ 7% addition of LCP due to the increase of crystallinity or the transesterification between the two polymers. Also, transesterification reaction between LCP and PBT was happened to all composition ratios and slightly increased with increasing reactive extrusion time. Crystallization temperature and heat of crystallization were found to increase gradually in the range from 3 up to 7% LCP/PBT and begin to decrease on further addition of LCP to PBT matrix. According to nonisothermal crystallization kinetics using Ozawa equation, which is extended Avrami equation, the calculated Avrami exponent reveals predetermined nucleation and three-dimensional growth of the crystallites in the PBT and PBT/LCP blends. The rate of crystallization increased at 5% and 10% LCP/PBT blends, which was attributed to nucleation of the PBT crystallization by the LCP. The crystallization of PBT was affected by the addition of TLCP, which acts as a nucleating agent.

ACKNOWLEDGMENT

5. REFERENCES

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