

Deformation Behavior and Nucleation Activity of a Thermotropic Liquid-Crystalline Polymer in Poly(butylene terephthalate)-Based Composites

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Abstract: Polymer composites based on a thermotropic liquid-crystalline polymer (TLCP) and poly(butylene terephthalate) (PBT) were prepared using a melt blending process. Polymer composites consisting of bulk cheap polyester with a small quantity of expensive TLCP are of interest from a commercial perspective. The interactions between the PBT chains and the flexible poly(ethylene terephthalate) (PET) units in the TLCP phase resulted in an improvement in the compatibility of PBT/TLCP composites. TLCP droplets deformed and fragmented into smaller droplets in the PBT/TLCP composites, which resulted in TLCP fibrillation through the effective deformation of the TLCP droplets. The nucleation activities of the PBT/TLCP composites increased by adding even a small amount of the TLCP component.

Keywords: composites, deformation, liquid-crystalline polymers (LCP), miscibility, nucleation, poly(butylene terephthalate) (PBT).

Introduction

Thermotropic liquid-crystalline polymers (TLCPs) that are a class of the materials producing anisotropic melts of relatively low viscosity have been used for high performance engineering plastics due to their high mechanical properties and excellent thermal stability.¹⁻⁴ Due to rigid rod-like molecules of TLCPs, they exhibit high strength and stiffness, which develop into highly ordered structures and result in the self-reinforcing characteristics.^{5,6} The behaviors of TLCP play an important role in determining the properties of polymer composites based on conventional thermoplastics and TLCP. Poly(butylene terephthalate) (PBT) is a semi-crystalline polymer, and has been used as structural materials in the automotive, electrical, and electronic industries due to its high mechanical strength and good processability.⁷⁻⁹ Recently, polymer composites based on TLCP and

conventional thermoplastics have been extensively investigated because they exhibited high mechanical properties, excellent thermal stability, and good processability, resulting in the application for high performance polymers.¹⁰⁻²⁶ The research topic that has attracted great attention is the development of the reinforcement of polymer composites by the incorporation of the dispersed TLCP phase. The major advantage of these systems is that TLCP can act as a reinforcing agent and processing aids simultaneously. For this reason, polymer composites containing TLCP have been investigated intensively not only for the scientific interest but also from the industrial point of view because of their potentials to generate *in situ* composites with high performance.¹⁰⁻²³ As high performance polymers usually involve high costs and are difficult to process, it is very important to reduce their processing costs without any deterioration of mechanical properties. It is known that the incorporation of TLCP, because of its low melt viscosity, can reduce effectively the melt viscosity of polymer composites, thereby improving the processability.²⁷⁻²⁹ In general, the morphology

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of polymer composites affects the characteristic features of the resulting polymer composites. To achieve high performance polymer composites, LCP fibrillar structures with fine fibrils having high aspect ratio should be formed in the polymer composites to transfer effectively between the reinforcement and polymer matrix.³⁰ That is, the formation of the well-dispersed and highly oriented TLCP fibrils with high aspect ratio can be required for achieving the excellent mechanical properties and good processability. The TLCP fibrillation in polymer composites can be influenced by various factors, such as the thermal behaviors of component polymers, the TLCP concentration, the viscosities of component polymers and their viscosity ratio, the characteristics of component polymers and their compatibility, the flow mode, the interfacial tension, and the processing conditions.³⁰⁻³³ Among these factors, the viscosity ratio of dispersed phase to matrix phase is an important factor in controlling the morphology of polymer composites. La Mantia *et al.*³⁴ investigated the morphology of polymer blends containing LCP that were determined by particular viscosity ratios, and they proposed that the fibrillation could occur only when the viscosity of polymer matrix was higher than that of LCP phase. Therefore, the viscosity ratio of LCP phase to matrix phase should be lower than unity to improve the dispersion and fibrillation in polymer composites containing LCP. In addition, the processing of polymer composites involves complex deformation behaviors, which may affect the nucleation and crystallization behaviors of polymer composites. Thus, it is important to characterize the nucleation and crystallization behavior of polymer composites for optimizing the process conditions of polymer composites.

In this research, polymer composites consisting of PBT and TLCP were prepared by a process of melt blending. The effects of TLCP component on physical properties and crystallization behavior of PBT/TLCP composites were investigated. The deformation behavior and nucleation activity of TLCP droplets in polymer composites were also discussed.

Experimental

Materials and Preparation. Conventional thermoplastic polymer used was the PBT with an intrinsic viscosity of 0.87 dL/g, supplied by SamYang Co., Korea. The TLCP used was a thermotropic liquid crystal copolyester synthesized from poly(*p*-hydroxybenzoate) (PHB) and poly(ethylene terephthalate) (PET) with a molar ratio of 60:40, purchased from Unitika Co., Japan. According to the supplier, TLCP has an intrinsic viscosity of 0.58 dL/g, determined at 30°C in a phenol/tetrachloroethane (50:50, v/v) mixture. All the materials were dried at 100°C *in vacuo* for 24 h before use, to minimize the effect of moisture. The PBT/TLCP composites were prepared by a melt blending process in a Haake Rheocord 600 Internal Mixer at 260°C and the fixed rotor

speed of 60 rpm. The predetermined blend compositions of PBT/TLCP composites were 100/0, 97/3, 95/5, 90/10, 80/20, 50/50, 30/70, and 0/100 by weight ratio, respectively.

Characterization. Rheological properties of PBT/TLCP composites were measured at 260°C with a Haake Rheometer that has a twin-screw extruder (RX252, L/D=25) and a capillary die (L/D=10). Tensile test and impact test specimens were prepared at 260°C with a Minimax Molder model CS-183 MMX (CSI Co.). Tensile tests were performed with a UTM 10E (United Calibration Co.) according to the ASTM D 638 standard. The gauge length and crosshead speed were set to 50 mm and 5 mm/min, respectively. Unnotched Izod impact strength tests were performed with an Impact Tester model 6545 (Cease Co., Italy) according to the ASTM D 256 standard. Morphologies of the fracture surface for PBT/TLCP composites were observed with a Topcon model SX-30 scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was performed with a TA Instrument 2010 TGA in the temperature range of 30 to 800°C with a heating rate of 20°C/min under a nitrogen atmosphere. Thermal behaviors of PBT/TLCP composites were investigated with a Perkin-Elmer DSC7. The samples were first heated from room temperature to 280°C at a scanning rate of 10°C/min under the nitrogen and kept at this temperature for 5 min to eliminate the influence of their previous thermal history. Each sample holder was loaded with a single disc weighting approximately 10 ± 0.3 mg to minimize the thermal lag between samples and DSC sensor. For the non-isothermal crystallization measurement, samples were heated and kept at 280°C for 5 min and then cooled at different cooling rates of 2.5, 5, 10, 15, 20, 30, and 40°C/min, respectively.

Results and Discussion

Thermal Behavior. Thermal properties of PBT/TLCP composites were investigated with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in a nitrogen atmosphere, and the results were shown in Table I. The glass transition temperature (T_g) of PBT/TLCP com-

Table I. Thermal Behavior of PBT/TLCP Composites

TLCP Content (wt%)	T_g^a (°C)	T_d^b (°C)	Char Yield ^c (%)
0	39.4	378	0.6
5	40.3	381	2.9
10	39.3	381	7.5
20	39.7	382	9.7
50	41.9	384	15.3
100	-	428	26.3

^aFrom the second heating trace of DSC measurements conducted with a heating rate of 10°C/min under a nitrogen atmosphere.

^b5% weight loss temperature in TGA at 20°C/min heating rate.

^cResidual yield in TGA at 800°C under a nitrogen atmosphere.

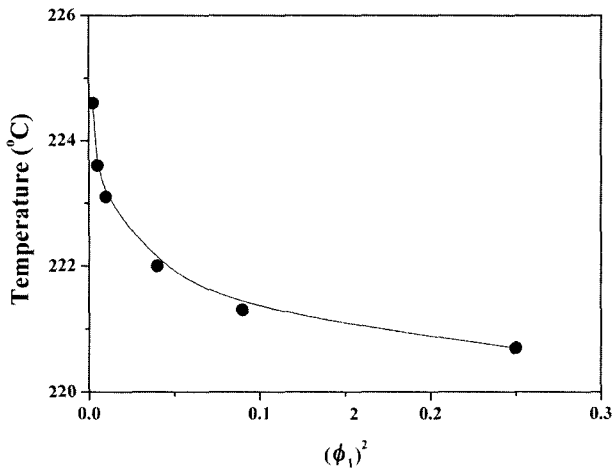


Figure 1. The variation of the melting temperature with the volume fraction of TLCP phase in PBT/TLCP composites.

posites was not significantly affected by the presence of TLCP phase. The thermal degradation temperature (T_d) of PBT/TLCP composites was higher than that of pure PBT, and it was increased as TLCP content was increased. The residual yield in the TGA at 800 °C was increased with increasing TLCP content, which was attributed to high heat resistance exerted by TLCP component. Thus, it can be deduced that the introduction of TLCP component can improve the thermal stability of PBT/TLCP composites, suggesting that TLCP may act effectively as the thermal stabilizer. The variation of the melting temperature (T_m) with the square of the volume fraction of TLCP phase in PBT/TLCP composites is shown in Figure 1. The T_m was decreased with increasing the volume fraction of TLCP phase, and two linear lines with different slopes could be observed. The thermodynamic mixing of two polymers was treated by Scott³⁵ using the Flory-Huggins theory,³⁶ and the Flory-Huggins interaction parameter (χ_{12}) could be determined by using the theory of the melting point depression suggested by Nishi and Wang.³⁷

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{-RV_2}{\Delta H_2 V_1} \left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1} \right) (1 - \phi_2) + \chi_{12} (1 - \phi_2)^2 \right] \quad (1)$$

where T_m and T_m^0 are the melting temperature of the blends and pure PBT, respectively; V_1 and V_2 are the molar volumes of the repeating units of TLCP and PBT, respectively; ϕ_1 and ϕ_2 are the volume fractions of TLCP and PBT, respectively; m_1 and m_2 are essentially the degree of polymerization;³⁶ ΔH_2 is the heat of fusion of 100% crystalline PBT; R is the gas constant; T is the absolute temperature, and χ_{12} is the polymer-polymer interaction parameter. If both m_1 and m_2 are large enough compared with 1, the eq. (1) can be simplified into the eq. (2), and thus, the χ_{12} can be

determined by calculating the melting point depression.³⁷

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{-RV_2}{\Delta H_2 V_1} \chi_{12} (1 - \phi_2)^2 \quad (2)$$

If the effects of the entropy and V_2 are neglected,³⁸⁻⁴⁰ the χ_{12} can be assumed as the eq. (3):

$$\chi_{12} = \frac{BV_1}{RT} \quad (3)$$

where B is the interaction energy density characteristics of polymer pairs. Substitution of the eq. (3) into the eq. (2) yields the following relationship:

$$T_m = T_m^0 + T_m^0 \left(\frac{V_2}{\Delta H_2} \right) B (\phi_1)^2 \quad (4)$$

Therefore, the χ_{12} and B can be calculated from the eqs. (1)-(4). In accordance with the Flory-Huggins theory, the χ_{12} value can be used to analyze the compatibility between the component polymers of the blends. It is known that the miscibility of component polymers depended on the χ_{12} value, and that the more negative the χ_{12} value is, the more miscible or compatible the component polymers of the blends are.³⁸ The values of χ_{12} and B calculated from the plots of $(1/T_m - 1/T_m^0)$ versus ϕ_1^2 for PBT/TLCP composites according to the eqs. (1)-(4) are shown in Table II. The negative values of the χ_{12} and B in PBT/TLCP composites suggested that TLCP was partially compatible with PBT in the melt state due to the physical entanglement and interaction between PBT and TLCP.³⁹ In addition, it can be deduced that the improvement of the compatibility for PBT/TLCP composites with lower TLCP content was attributed to the interaction between PBT chains and flexible PET units in TLCP phase. However, as TLCP content was increased above 10 wt%, the number of TLCP molecules in PBT/TLCP composites was increased, and the TLCP have a tendency to link themselves because of the interaction between TLCP molecules, resulting in the less interaction between TLCP and PBT molecules.⁴⁰ As a result, the compatibility for PBT/TLCP composites with higher TLCP content became poorer than that of PBT/TLCP composites with lower TLCP content.

Rheological Properties. The shear viscosities of PBT and TLCP measured at 260 °C as a function of shear rate are shown in Figure 2. It could be seen that PBT and TLCP

Table II. The Interaction Parameters and Interaction Energy Densities of PBT/TLCP Composites

TLCP Content	χ_{12}	B (J/cm ³)
≤ 10 wt%	-8.0044×10^{-4}	-0.3107
> 10 wt%	-2.9552×10^{-4}	-0.0115

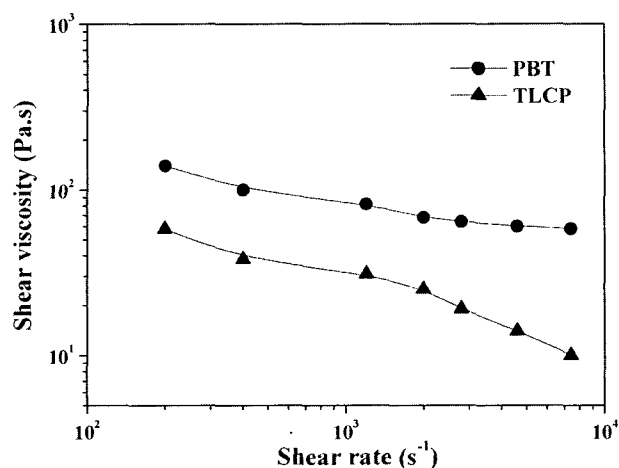


Figure 2. The shear viscosities of PBT and TLCP at 260°C as a function of shear rate.

exhibited non-Newtonian and shear thinning behaviors at all shear rates, and TLCP exhibited a stronger shear thinning behavior than PBT. The shear viscosity of PBT was always higher than that of TLCP at all shear rates studied, indicating that the viscosity ratio (P) of the dispersed phase to the matrix phase was less than a unity. It was expected that the low viscosity ratio resulted in the effective transfer of shear stress from the matrix phase to the dispersed phase for the deformation of TLCP droplets. The power law index (n) of PBT and TLCP can be determined by the following power-law:⁴¹

$$\log \eta = \log K - (1 - n) \log \gamma \quad (5)$$

where η is the viscosity; γ is the shear rate; n is the power law index to define the extent of shear dependence of the viscosity, and K is the consistency index. For Newtonian fluids, $n = 1$; for dilatant fluids, $n > 1$; for pseudo plastic fluids, $n < 1$. The power law indices (n) of PBT and TLCP were 0.76 and 0.55, respectively. This result indicated that TLCP was more pseudo-plastic than PBT over the shear rate range measured due to the easier alignment of TLCP domains. The variations of the shear viscosity with TLCP content are shown in Figure 3. The PBT/TLCP composites reached the apparent maximum at lower TLCP content, and thereafter, they tend to decrease significantly with further increasing TLCP content. La Mantia *et al.*^{42,43} reported that the maximum in the viscosity-concentration curve for LCP/polyamide 6 blends was observed at about 1% concentration of LCP, and they proposed that the viscosity maximum was attributed to the interfacial slip and the usual slip is replaced by some specific reactions, resulting in the increase in the viscosity. The shear viscosities of PBT/TLCP composites were decreased with increasing shear rates as shown in Figure 3. Generally, polymer chains in

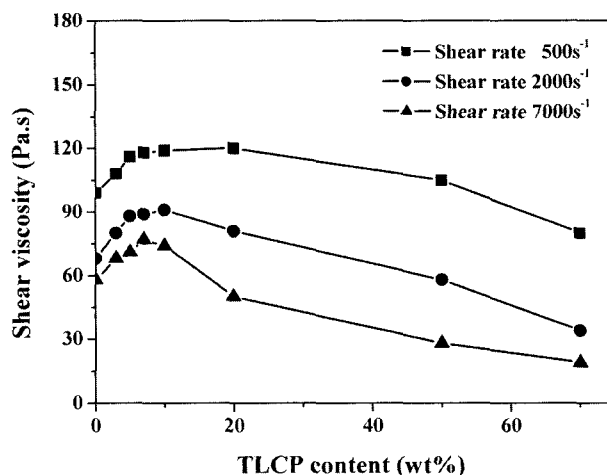


Figure 3. The shear viscosities of PBT/TLCP composites with different shear rates at 260°C as a function of TLCP content.

TLCP phase tended to be more oriented in the melt state by shearing force which made it easier to slide past each other and reduce the viscosity with shear rates.⁴⁰ The TLCP domains in PBT/TLCP composites could be oriented and aligned themselves in the flow direction with higher shear rate and they could be deformed due to their high relaxation, resulting in the decrease in the viscosity with shear rates.

Droplet Deformation. For polymer composites based on thermoplastic polymers and TLCP, it is very important to form long and well dispersed TLCP chains to reinforce polymer matrix. Generally, deformation behavior of TLCP phase in polymer blends can be characterized by using the Taylor's theory.⁴⁴⁻⁴⁶ Taylor reported that droplets were deformed into the spheroidal form under shearing, and the deformation of droplets depended on the dimensionless parameters such as the capillary number and the viscosity ratio. In case of the steady shear flow, the capillary number, Ca , that is the ratio of the hydrodynamic stress to the interfacial stress and the viscosity ratio, P , can be expressed as follows:

$$Ca = \frac{\gamma \eta_m a}{\sigma} \quad \text{and} \quad P = \frac{\eta_d}{\eta_m} \quad (6)$$

where η_d and η_m are the viscosities of the dispersed and matrix phases, respectively; γ is the shear rate; a is the radius of the droplet, and σ is the interfacial tension. As presented in Table III, the viscosity ratio of TLCP to PBT was lower

Table III. Viscosity Ratios and Capillary Numbers of PBT/TLCP Composites Obtained from Capillary Rheometer

Shear Rate (s ⁻¹)	P	Ca	Ca_c	Ca^*
500	0.38	2.57	0.70	3.67
2,000	0.36	7.17	0.69	1.45

than a unity over the shear rates studied, and they have a tendency to decrease with increasing shear rates. It was expected to the effective deformation of TLCP droplets in PBT/TLCP composites. Taylor⁴⁵ reported that LCP domains could be deformed into fibrils when their viscosity was lower than that of polymer matrix, and thus LCP fibrillation occurred when the viscosity ratio of LCP to polymer matrix was smaller or closer to a unity. Heino and Seppala⁴⁷ reported that for PET/Vectra A950 blends the viscosity of PET was always higher than that of Vectra A950 between 60 and 10,000 s⁻¹, and they suggested that this behavior was found to be responsible for the good dispersion of Vectra A950 in PET.

In general, the capillary number, Ca , has a critical value beyond which droplets can no longer sustain further deformation, and it breaks up into a number of smaller droplets.⁴⁴⁻⁴⁶ The critical capillary number, Ca_c , also depended on the viscosity ratio, and for the viscosity ratios of unity, the shape of the droplets in steady shear flow became unstable for the critical capillary number of the order of unity.⁴⁴⁻⁴⁶ Below the critical capillary number, the droplets deformed slightly. If Ca was slightly higher than Ca_c , droplets broke up into smaller droplets. If Ca was much higher than Ca_c , the interfacial stress became negligibly small compared with the hydrodynamic stress, and droplets deformed finely with the applied macroscopic deformation.⁴⁸ Huneault *et al.*⁴⁹ reported that the deformation and breakup of droplets depend on the reduced capillary number, Ca^* , which was defined as the ratio of the capillary number to the critical capillary number as following:

$$Ca^* = \frac{Ca}{Ca_c} \quad (7)$$

The droplets will be either deformed or broken in both shear and elongation as follows: for $Ca^* < 0.1$, droplets do not deform; for $0.1 < Ca^* < 1$, droplets deform but they do not breakup; for $1 < Ca^* < 4$, droplets deform but they break conditionally, and for $Ca^* > 4$, droplets deform into stable fibrils.

For the dependence of the critical capillary number, Ca_c , on the viscosity ratio, P , De Bruijn⁵⁰ suggested that in a simple shear flow, droplets break most easily for $0.1 < P < 1$ and droplets do not break up for $P > 4$, and he proposed that the critical capillary number as a function of the viscosity ratio can be expressed as following:

$$\log\left(\frac{Ca_c}{2}\right) = C_1 + C_2 \log P + C_3 (\log P)^2 + \frac{C_4}{\log P + C_5} \quad (8)$$

where $C_1 = -0.5060$, $C_2 = -0.0994$, $C_3 = 0.1240$, $C_4 = -0.1150$, and $C_5 = -0.6110$. The values of the P , Ca , Ca_c , and Ca^* calculated from the eqs. (6)-(8) are shown in Table III. As shown in Figure 2, the P was far below unity over the shear

rate range studied. The Ca was higher than the Ca_c , and the Ca_c^* was in the range of 1 to 4 in Table III. Therefore, it was expected that TLCP droplets deformed and broke up into smaller droplets in PBT/TLCP composites, resulting in TLCP fibrillation by the effective deformation of TLCP droplets. Karam *et al.*⁵¹ reported that droplets could only be broken when the viscosity ratio was in the range of 0.005 to 4, and Torza *et al.*⁵² also reported that the breakup of droplets occurred for $0.003 < P < 3$, and droplets did not break for $P > 3$.

Mechanical Properties. The mechanical properties of PBT/TLCP composites with TLCP content are presented in Figures 4 and 5. On the addition of 5 wt% TLCP the impact strength, tensile strength and tensile modulus of PBT/TLCP composites were increased significantly. This result may be attributed to the effective transfer of the applied stress between TLCP and PBT due to the formation of elongated TLCP domains. The mechanical properties of PBT/TLCP

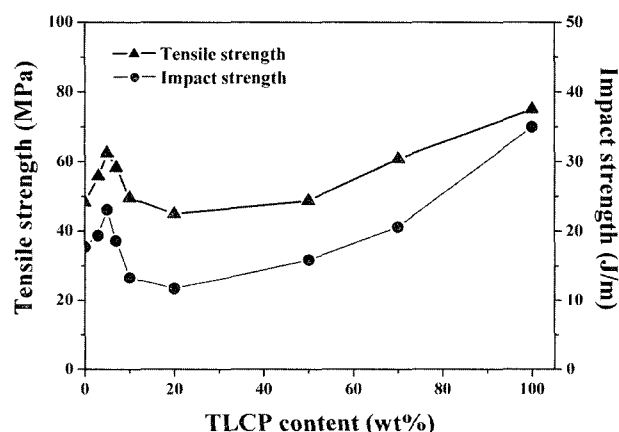


Figure 4. Tensile strength and impact strength of PBT/TLCP composites with TLCP content.

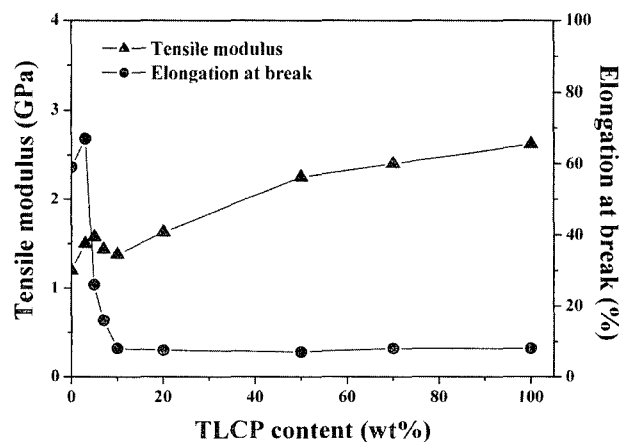
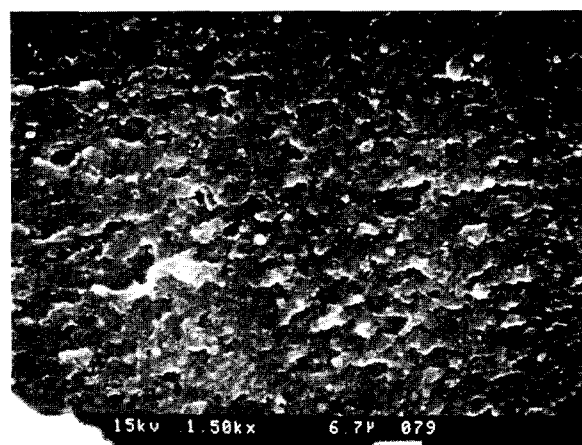


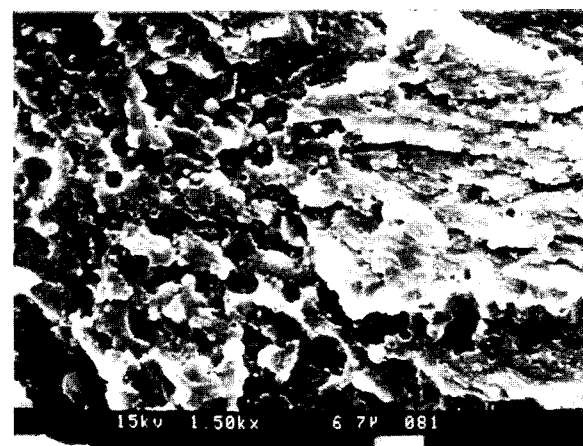
Figure 5. Tensile modulus and elongation at break of PBT/TLCP composites with TLCP content. (a) PBT/TLCP (95/5), (b) PBT/TLCP (80/20), and (c) PBT/TLCP (30/70).

composites were decreased slightly above 5 wt% TLCP content, and thereafter tended to increase with further increasing TLCP content. A synergistic increment of mechanical properties for PBT/TLCP composites with lower TLCP content may be attributed both to the smaller size of TLCP droplets distributed in polymer matrix and to the reinforcement effect of polymer matrix by TLCP. Therefore, it can be deduced that the addition of small amount of TLCP may enhance the compatibility and interfacial adhesion between PBT and TLCP phases, thereby enhancing mechanical properties of PBT/TLCP composites. The elongation at break for PBT/TLCP composites was decreased drastically with increasing TLCP content and approached a steady-state condition when TLCP content reached 20 wt% and such a behavior was a typical characteristic of polymer composites.⁵³ The improvement of mechanical properties of PBT/TLCP composites may also be related to the development of spherulites in polymer matrix. It was expected that during the melt processing, PBT would interact with oriented TLCP phase and TLCP domains might provide the nucleating sites for crystallization. The mechanical properties of polymer composites can be influenced by crystallization behavior,⁵⁴ which will be discussed in the following section of the non-isothermal crystallization behaviors.

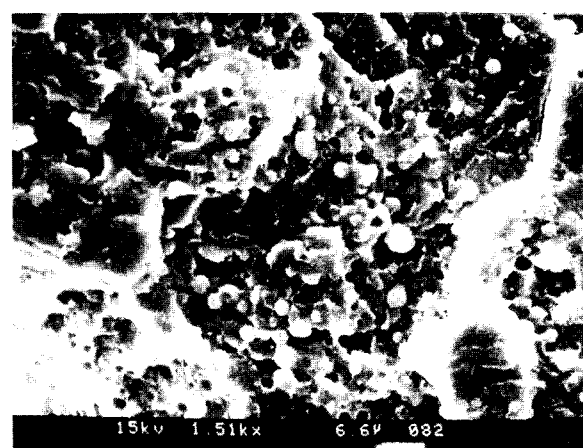
Morphology. SEM microphotographs of PBT/TLCP composites extruded at 260 °C are shown in Figure 6. Small TLCP droplets with an average diameter of 0.46 μm were finely dispersed in PBT matrix at lower TLCP content, while TLCP phase existed in the form of the larger domains at higher TLCP content. The size of the dispersed TLCP droplets in PBT/TLCP composites was increased with TLCP content. The PBT/TLCP composites with lower TLCP content exhibited the decrease in the average diameter of TLCP droplets and better adhesion with polymer matrix due to the uniformly distributed TLCP droplets in polymer matrix compared with the composites containing higher TLCP content. The diameter distribution of TLCP droplets in PBT/TLCP composites is shown in Figure 7. For PBT/TLCP composites with 5 wt% TLCP content, the largest proportion of TLCP droplets has a diameter of 0.4 μm , and the average diameter was 0.45 μm . However, for PBT/TLCP composites with 20 wt% TLCP content, the largest proportion of TLCP droplets has 1.6 μm , and the average diameter was 1.68 μm . Wiff *et al.*⁵⁵ reported that the uniform-dispersed and nano-scale fibrous LCP domains can obviously improve the mechanical properties of *in situ* composites by means of the optimal processing condition. The dispersed TLCP in PBT matrix with lower TLCP content had a large deformation, smaller diameter, and narrower diameter distribution compared with the composites containing higher TLCP content. This result was also related to the effect of the compatibility of TLCP on PBT matrix. As described in the previous section, the number of TLCP molecules was increased with further increasing TLCP content



(a) PBT/TLCP (95/5)



(b) PBT/TLCP (80/20)



(c) PBT/TLCP (30/70)

Figure 6. SEM microphotographs of PBT/TLCP composites.

above 10 wt%, and then TLCP tended to link themselves due to the interaction between TLCP molecules.⁴⁰ Therefore, the less interaction occurred between TLCP and PBT phases

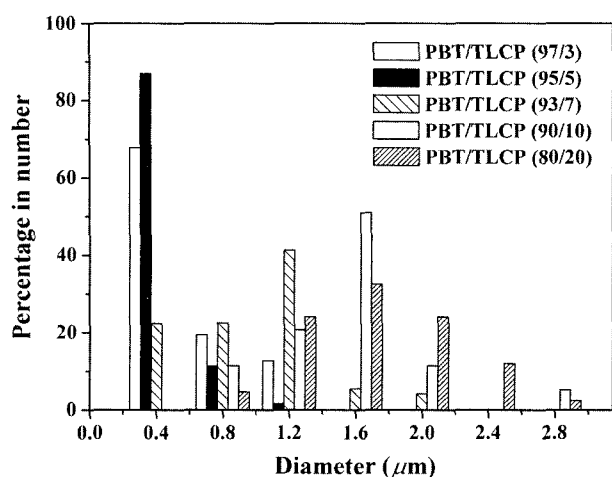


Figure 7. The distribution of diameter of TLCP droplets in PBT/TLCP composites.

resulted in poor compatibility at higher TLCP content.

Non-isothermal Crystallization Behavior. From the industrial point of view, it is very important to understand the non-isothermal crystallization behavior of the polymers if processing techniques occurred under the non-isothermal conditions for preparing engineering plastics were considered. The non-isothermal crystallization processes of PBT and PBT/TLCP composites were performed at different cooling rates. The crystallization occurred at higher temperature with decreasing cooling rate, indicating that the crystallization nucleated at higher temperature with slower cooling rates.⁵⁶ The time for completing the crystallization was reduced with increasing cooling rate, and the relative degree of crystallinity for PBT/TLCP composites is higher than that of pure PBT at the same time for completing the crystallization. The non-isothermal crystallization kinetics can be analyzed by using the extension of the Avrami theory^{57,58} proposed by Ozawa.^{59,60} This analysis accounts for the effect of cooling rate on the crystallization from the melt by the time variable in the Avrami equation with the variable cooling rate term, that is, by replacing t in the eq. (9) with T/a as the eq. (10):

$$1 - X(T) = \exp(-Z_i t^n) \quad (9)$$

$$1 - X(T) = \exp\left[-\frac{K(T)}{a^m}\right] \quad (10)$$

where a is the cooling rate; the exponent n is a mechanism constant depending on the type of nucleation and growth dimension; m is the Ozawa exponent depending on the dimension of crystal growth; Z_i is the growth rate constant involving both nucleation and growth rate parameters, and $K(T)$ is the cooling function related to the overall crystallization rates. The parameters such as Z_i and n explicit physi-

Table IV. The Values of n and Z_c for PBT and PBT/TLCP Composites Obtained from the Avrami Equation

Cooling Rate (°C/min)	PBT		PBT/TLCP (90/10)	
	n	Z_c	n	Z_c
2.5	4.0	0.13	3.2	0.34
5.0	3.2	0.65	3.0	0.67
10.0	3.0	0.96	2.8	0.96
15.0	2.8	0.98	2.7	1.01
20.0	2.6	1.04	2.4	1.04
30.0	2.4	1.05	2.2	1.07
40.0	2.2	1.06	2.1	1.11

cal meaning for the isothermal crystallization, while in the non-isothermal crystallization process the physical meaning of those do not have the same physical significance due to constant change of temperature, thereby influencing the nucleation and crystal growth. Considering the non-isothermal character of the process investigated, Jeziorny⁶¹ suggested that the parameter, Z_i should be corrected as follows:

$$\log Z_c = \frac{\log Z_i}{a} \quad (11)$$

The values of the Avrami exponent (n) and the rate parameter (Z_c) could be determined from the slope and intercept of the plot of $\log[-\ln\{1-X(T)\}]$ versus $\log t$, and these values are shown in Table IV. The Avrami exponent (n) of PBT was in the range of 4.0 to 2.2 depending on cooling rate and the n of PBT/TLCP composites was lower than that of PBT, indicating that TLCP acted as heterogeneous nucleating agent. The dependence of the crystallization kinetics on the temperature is a complex function, and many researches for theoretical models based on the Avrami equation have been performed.⁶²⁻⁶⁴ To describe more effectively the non-isothermal crystallization process for comparison, Liu *et al.*⁶⁴ suggested a convenient procedure for characterizing the non-isothermal crystallization kinetics by combining the Avrami and Ozawa equations. on the basis of the assumption that the degree of crystallinity was correlated to the cooling rate and crystallization time. Therefore, their relationship for the non-isothermal crystallization process can be derived by combining the eqs. (9) and (10) as follows:

$$\log Z_i + n \log t = \log K(T) - m \log a \quad (12)$$

$$\log a = \log F(T) - b \log t \quad (13)$$

where the kinetic parameter, $F(T) = [K(T)/Z_i]^{1/m}$ represented the value of cooling rate chosen at unit crystallization time when the systems have a defined degree of crystallinity; a is the cooling rate, and b is the ratio of the Avrami exponent (n) to the Ozawa exponent (m). According to the eq. (13), the

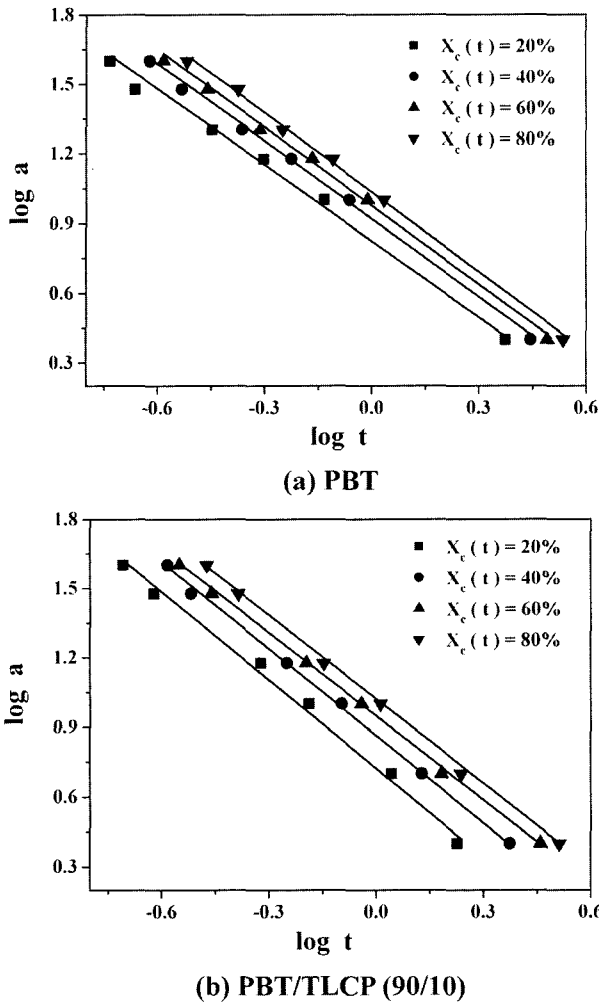


Figure 8. The plots of $\log a$ versus $\log t$ from the combined Avrami and Ozawa equations at different relative degree of crystallinity.

plots of $\log a$ versus $\log t$ at a certain degree of crystallinity are shown in Figure 8, and a linear relationship between $\log a$ and $\log t$ was observed, suggesting this analysis might be effective in modeling the non-isothermal crystallization kinetics. The values of $F(T)$ and b can be estimated from the slope and intercept of the plots, and they are shown in Table V. It can be seen that the value of $F(T)$ was increased with increasing the relative degree of crystallinity, indicating that the higher relative degree of crystallinity was obtained with higher cooling rate. The ratio of the Avrami exponent to the Ozawa exponent varied from 1.06 to 1.15 and from 1.11 to 1.25 for PBT and PBT/TLCP composites, respectively. It is known that the crystallization of polymers is controlled essentially by the nucleation rate and polymer mobility.⁶⁵ In this system for the non-isothermal crystallization of PBT/TLCP composites, TLCP component existed in the nematic liquid-crystalline phase on the heating conditions. Incarnato *et al.*⁶⁶ reported that the presence of nematic domains could

Table V. The Values of b and $F(T)$ for PBT and PBT/TLCP Composites Obtained from the Combined Avrami and Ozawa Equations

Composition (PBT/TLCP)	$X(T)$ (%)	$F(T)$	b
100/0	20	6.67	1.06
	40	8.09	1.11
	60	9.22	1.12
	80	10.69	1.15
95/5	20	5.64	1.11
	40	7.03	1.13
	60	8.19	1.14
	80	9.49	1.16
90/10	20	5.39	1.25
	40	7.31	1.24
	60	8.69	1.19
	80	10.22	1.22
80/20	20	5.99	1.21
	40	7.74	1.20
	60	9.11	1.20
	80	10.80	1.22

provide nucleating sites and reduce the melt viscosity of polymer matrix, especially at higher TLCP content, and they suggested that TLCP might act as a heterogeneous nucleating agent for polymer matrix by providing nucleation sites and as a diluent agent by enhancing polymer mobility.⁶⁷

Activation Energy for Crystallization. The activation energy for the non-isothermal crystallization process can be derived by the combination of cooling rate and crystallization peak temperature, and Kissinger^{68,69} suggested a method for calculating the activation energy for the non-isothermal crystallization as follows:

$$\frac{d[\ln(\Phi/T_p^2)]}{d(1/T_p)} = -\frac{\Delta E_a}{R} \quad (14)$$

where R is the universal gas constant; T_p is the crystallization peak temperature; Φ is the cooling rate, and ΔE_a is the crystallization activation energy. The plots of $\ln(\Phi/T_p^2)$ versus $1/T_p$ for PBT and PBT/TLCP composites are shown in Figure 9. The activation energies of the non-isothermal crystallization for PBT and PBT/TLCP composites were obtained from the slope of the plot of $\ln(\Phi/T_p^2)$ versus $1/T_p$, according to the eq. (14), and the results were shown in Table VI. The activation energy of crystallization for PBT/TLCP composites was lower than that of PBT, and their value was increased with increasing TLCP contents. This result suggested that the incorporation of TLCP might accelerate the non-isothermal crystallization process of PBT matrix, and this acceleration by TLCP component was more effective at low TLCP content.

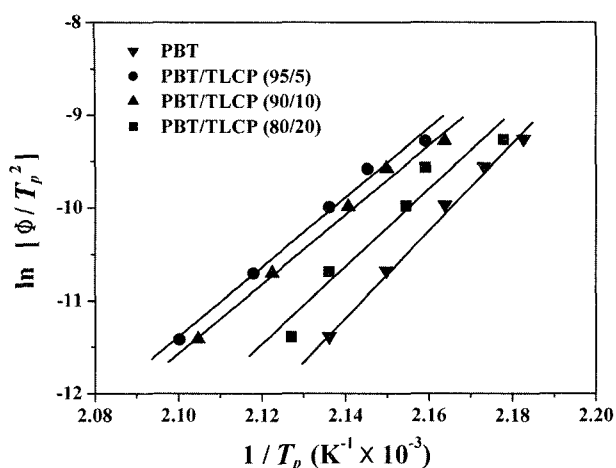


Figure 9. The Kissinger plots for determining the activation energies of the non-isothermal crystallization of PBT/TLCP composites.

Table VI. The Activation Energies for the Non-isothermal Crystallization of PBT and PBT/TLCP Composites Calculated from the Kissinger Method

TLCP Content (wt%)	0	5	10	20
ΔE (kJ/mol)	385.5	308.9	310.3	347.5

Nucleation Activity. Dobreva *et al.*^{70,71} investigated dynamic crystallization kinetics of polymer melts in the presence of nucleating agents, and they suggested the simple method for calculating the nucleation activity of different substrates. It is known that the nucleation activity, ϕ , is a factor by which the work of three-dimensional nucleation decreases with the addition of the foreign substrate.⁷⁰⁻⁷⁵ If the foreign substrate is extremely active, the nucleation activity approaches 0, while for inert particles, it is 1. For the nucleation from the melts near the melting temperature, the cooling rates can be represented as follows:

$$\log a = A - \frac{B}{2.3\Delta T_p^2} \quad (15)$$

where a is the cooling rate; A is a constant; ΔT_p is the degree of supercooling, i.e. $\Delta T_p = T_m - T_p$, and T_p is the temperature corresponding to the peak temperature of the DSC crystallization, and $B = \omega\sigma^3 V_m^2 / 3kT_m \Delta S_m^2 n$ is a parameter related to three-dimensional nucleation (V_m is the molar volume of the crystallizing substance; ΔS_m is the entropy of melting; ω is the geometrical factor; σ is the specific surface energy; n is the Kolmogorov-Avrami exponent, and k is the Boltzman constant). The nucleation activity can be calculated from the following equation.⁷³

$$\phi = \frac{B^*}{B^0} \quad (16)$$

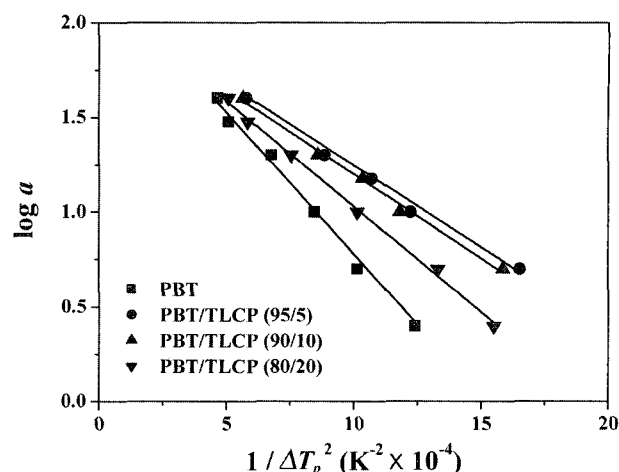


Figure 10. The plots of $\log a$ versus $1/\Delta T_p^2$ for PBT and PBT/TLCP composites.

where B^0 and B^* are the values of B for homogeneous and heterogeneous nucleations, respectively. The values of B^0 and B^* can be obtained from the slope of the plot of $\log a$ versus $1/\Delta T_p^2$ according to the eq. (15), and thus, the nucleation activity was calculated from the eq. (16) by using these values. The plots of $\log a$ versus $1/\Delta T_p^2$ for PBT and PBT/TLCP composites are shown in Figure 10. The nucleation activities of PBT/TLCP composites were decreased with increasing TLCP content, and those values were calculated as 0.54, 0.57, and 0.72, respectively. This result suggested that TLCP could act as a more effective nucleating agent for PBT/TLCP composites with lower TLCP content.

Conclusions

Polymer composites of thermotropic liquid-crystalline polymer (TLCP) and poly(butylene terephthalate) (PBT) were prepared by a melt blending. The incorporation of TLCP can improve the thermal stability of PBT/TLCP composites, indicating that the TLCP may act effectively as thermal stabilizer. The improvement of the compatibility for PBT/TLCP composites with lower TLCP content was attributed to the interaction between PBT chains and flexible PET units in TLCP. The stronger interaction between PBT and TLCP molecules can lead to the greater nucleation effect of TLCP component. The small TLCP droplets with an average diameter of $0.46 \mu\text{m}$ were finely dispersed in the PBT matrix at lower TLCP content, while TLCP phase existed in the form of larger domains at higher TLCP content. The activation energies of the non-isothermal crystallization for PBT/TLCP composites calculated from the Kissinger method were lower than that of PBT, and their values were increased with increasing TLCP contents. This result suggested that the incorporation of TLCP might accelerate the non-isothermal crystallization process of PBT

matrix and this acceleration was more effective at low TLCP content. The nucleation activities of PBT/TLCP composites were increased with even small amount of TLCP component added. The TLCP could act as a more effective nucleating agent for PBT/TLCP composites with lower TLCP content.

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