Thermotropic Liquid Crystal Polymer Reinforced Poly(butylene terephthalate) Composites to Improve Heat Distortion Temperature and Mechanical Properties

Jun Young Kim, Seong Wook Kang, and Seong Hun Kim*

Department of Fiber and Polymer Engineering, Hanyang University, Seoul 133-791, Korea

Abstract: Thermotropic liquid crystal polymer (TLCP)-reinforced poly(butylene terephthalate) (PBT) composites were prepared by melt processing. The improvement in the mechanical properties and the processability of the PBT/TLCP composites was attributed to the reinforcing effect by TLCP phase and its well distribution in the PBT matrix. X-ray diffraction results demonstrated that a slow cooling process leads to the thicker lamellar structures and the formation of more regular crystallites in the composites. The incorporation of TLCP improves not only the tensile strength and flexural modulus but also the heat distortion temperature (HDT) of the PBT/TLCP composites. The HDT values of the composites were dependent on TLCP content. The improvement in the HDT values of the PBT/TLCP composites may be explained in terms with the increased flexural modulus, the development of more regular crystalline structures, and the enhancement of the ability of the composites to sustain the storage modulus by TLCP phase. In addition, the simple additivity rule makes it possible to predict the HDT values of the PBT/TLCP composites.

Keywords: Composites, Heat distortion temperature (HDT), Liquid crystalline polymer (LCP), Poly(butylene terephthalate) (PBT), Reinforcements

Introduction

During the rapid developments in various industries, there has been a great interest in a wide range of applications of high performance polymer composites as advanced industrial materials. Poly(butylene terephthalate) (PBT) resins are semicrystalline polymers with good mechanical properties and excellent processability, and they are used widely as engineering materials in the automotive, electrical, and electronics industries [1,2]. However, there is a continuing practical demand for achieving high performance of PBT with various processing conditions, in order to be utilized practically in advanced industrial fields that demand high performance and low cost. In this regard, polymer composites reinforced with thermotropic liquid crystal polymer (TLCP) have been extensively investigated not only for scientific interest but also for an industrial perspective, because they exhibited excellent mechanical properties, high thermal and chemical stability, and good processability, making it possible to fabricate high performance engineering plastics [3-18].

From an economic point of view and an industrial perspective, one of the major challenges for high performance polymer composites is to optimize the processing operations with low cost. The melt blending of polymers is an effect method for enhancing physical properties and fabricating high performance polymer composites at low cost, leading to the commercial large scale-up. Further, the appropriate combination of cheaper commodity polyester resins with a less expensive TLCP is of growing importance in that they may provide attractive possibilities for improving the mechanical properties of the resultant composites.

The heat distortion temperature (HDT), which commonly represents the upper limit of the dimensional stability of polymers in service without significant physical deformations under a normal load and thermal effect [19], provides important information for product design, including the working temperature of resultant products. Therefore, it is very important to characterize the physical properties of polymers at elevated temperatures in terms of the HDT measurement. The HDT is influenced by various factors such as the melt and mold temperatures, nucleating agents, and various processing conditions, which are often related to the mechanical behavior of polymers. However, the HDT measurements of polymer composites have rarely been investigated to date, and few reports can be found in the literature regarding the effect of TLCP on the HDT values of conventional polyester resins.

In this study, PBT composites reinforced with a TLCP were prepared by a melt processing method to achieve high performance polymer composites with improved processability, and the effects of TLCP on the mechanical properties and the HDT of the PBT/TLCP composites are presented. In addition, the effects of the mechanical properties and crystal structure on the HDT of the PBT/TLCP composites are discussed.

Experimental

Materials and Preparation

The conventional thermoplastic polymer used was the PBT with the intrinsic viscosity of 1.1 d//g and the melt flow index of 20 g/10 min, supplied by Sam Yang Co., Korea. The

*Corresponding author: kimsh@hanyang.ac.kr

TLCP used was the wholly aromatic copolyester synthesized from p-hydroxy benzoic acid (HBA) and 2-hydroxy-6-napthoic acid (HNA) with a molar ratio of 73:27, purchased from Polyplastics Co. Ltd. According to the supplier, the molecular weight (Mw) of the TLCP was approximately 30,000 g/mol. All the materials were dried at 120 °C *in vacuo* for at least 24 h before use, to minimize the effect of moisture. The PBT/ TLCP composites were prepared by melt blending in a twin-screw extruder. The temperature profiles for the blending were 230-265-265-255-255-255 °C, and the screw speed was fixed at 210 rpm. The composite specimens were either quenched by using cold water, or slow-cooled by conditioning at room temperature. The predetermined PBT/TLCP blend compositions were 100/0, 95/5, 90/10, 80/20, 50/50, and 30/ 70 by weight ratio, respectively.

Characterization

Thermogravimetric analysis (TGA) of the PBT/TLCP composites was performed with a TA Instruments SDF-2960 TGA under nitrogen in the temperature range of 30 to 800 °C, employing a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analysis of the PBT/TLCP composites was carried out using a TA Instruments 2010 DSC under nitrogen in the temperature range of 30 to 300 °C, employing a scanning rate of 10 °C/min. The mechanical test specimens were prepared at 265 °C with a Minimax laboratory molder CS-183IM (CSI Co.). The mechanical tests were performed at room temperature using an UTM 10E (United Calibration Co.) according to the procedures in the ASTM D 638 and ASTM D 790 standards, respectively. The values of the mechanical properties used in this study represented the averages over at least five individual measurements. The dynamic mechanical analysis (DMA) of the PBT/ TLCP composites was performed with a TA Instruments DMA-2980 using a dual cantilever in tensile mode at the fixed frequency of 1 Hz and oscillation amplitude of 10 mm, in the temperature range of 30 to 230 °C, employing a heating rate of 3 °C/min. The morphologies of the facture surface for the PBT/TLCP composites were observed using a field emission scanning electron microscope (FE-SEM). The fracture surfaces of the specimens were obtained by quenching and breaking the specimens in liquid nitrogen. Wide-angle X-ray diffraction (WAXD) analysis was performed with a Rigaku Denki X-ray diffractometer using Ni-filtered CuKα X-rays (λ = 0.1542 nm), and the diffracting intensities were recorded at steps of every 2θ = 0.05 ° over the range of 10 ° < 2θ < 35 °. The apparent crystallite size (L_{hkl}) in the PBT/TLCP composites was calculated using the Scherrer's equation [20], L_{hkl} = $K\lambda$/ $\beta\cos\theta$ (where β is the half-width of reflection peak; θ is the Bragg angle; K is the correction factor (K = 0.9), and λ is the wavelength of X-ray beam). Small angle X-ray scattering (SAXS) measurements were performed at the SAXS beamline facility of the Pohang Accelerator Laboratory (PAL) in Korea. The X-ray wavelength used was 0.1542 nm, and the beam

size at the focal point less than 1 mm^2, focused by platinum-coated silicon premirror through a double crystal mono-chromator. Heat distortion temperature (HDT) of the PBT/ TLCP composites was measured under load (1.8 MPa) according to the ASTM D 648 standard, and the values of HDT represented the averages over five individual measurements.

Results and Discussion

In general, the torque of the polymer melts is associated with the melt viscosity. The torque values with the blending time exhibit an apparent maximum during the initial loading of the polymers and then gradually reach a steady-state torque value. The equilibrium torque values of the PBT/ TLCP composites with TLCP content are shown in Figure 1. The equilibrium torque values of the PBT/TLCP composites decreased with increasing TLCP content. The number of
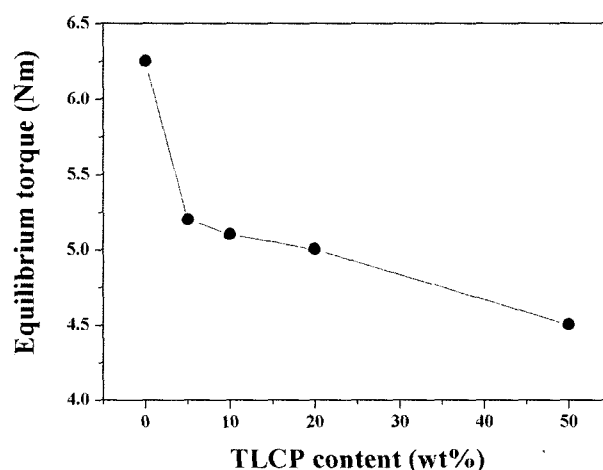

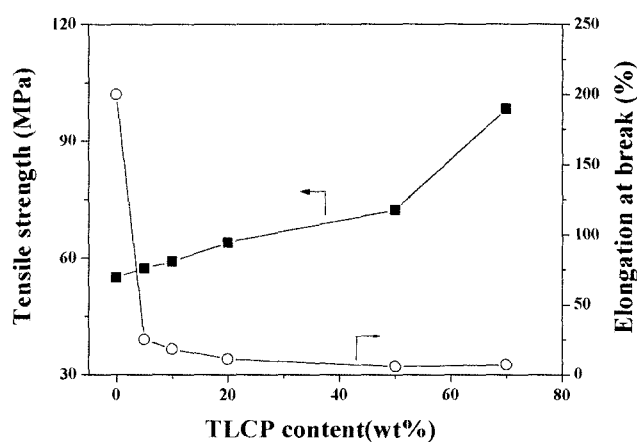**Figure 1.** Equilibrium torque values of PBT/TLCP composites with TLCP content.

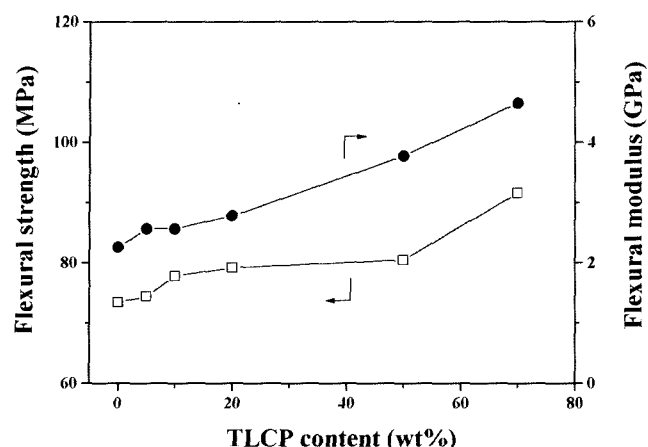**Figure 2.** Variations of the tensile strength and elongation at break of PBT/TLCP composites with TLCP content.

Figure 3. Variations of the flexural strength and modulus of PBT/ TLCP composites with TLCP content.

Figure 4. TGA thermograms of PBT/TLCP composites with TLCP content; (A) PBT, (B) PBT/TLCP5, (C) PBT/TLCP10, (D) PBT/TLCP20, (E) PBT/TLCP50, (F) PBT/TLCP70, and (G) TLCP.

TLCP domains increased with increasing TLCP content, and such domains attempted to lubricate the PBT matrix, implying that the TLCP effectively acts as a processing aid in the PBT matrix.

The mechanical properties of the PBT/TLCP composites with TLCP content are shown in Figures 2 and 3. The mechanical properties of the PBT/TLCP composites significantly depended on TLCP content. As shown in Figure 2, the tensile strength of the PBT/TLCP composites increased with increasing TLCP content, which was attributed to the reinforcement effect of the PBT matrix by incorporating well-distributed TLCP domains and the moderate transfer of the applied stress between TLCP and PBT phases. The values of the elongation at break of the PBT/TLCP composites decreased with increasing TLCP content, and then approached a steady-state condition when TLCP content reached 20 wt%. This result suggests that the introduction of TLCP makes the PBT matrix stiffer, and such a behavior was a typical characteristic of polymer composites [21]. The variations of the flexural strength and flexural modulus of the PBT/TLCP composites are shown in Figure 3. The incorporation of TLCP increased the flexural strength and modulus of the PBT/TLCP composites. The improvement in the mechanical properties of the PBT/TLCP composites may also be related to the development of spherulites in the polymer matrix, because it was expected that during the melt processing, PBT might interact physically with oriented TLCP phase and TLCP domains might act as the nucleating agent [15]. In addition, the improvement in the flexural modulus of the PBT/TLCP composites related to the variation of the HDT values, which will be elaborated in the following section of the HDT measurements.

The TGA thermograms of the PBT/TLCP composites with TLCP content are shown in Figure 4. The initial thermal decomposition of the TLCP occurred at approximately 460 °C, while that of the PBT occurred at 350 °C. The increase in the thermal decomposition temperatures, the maximum decom-
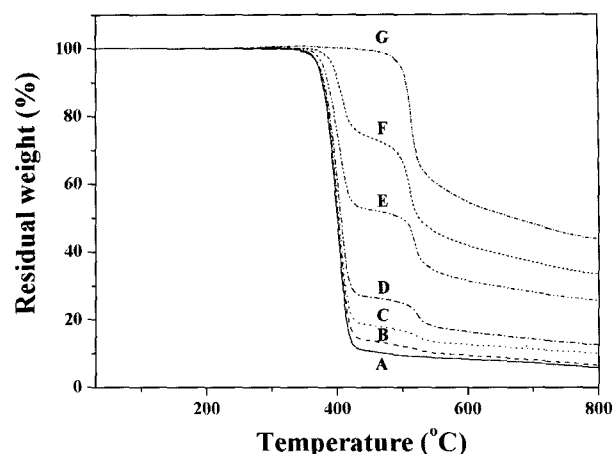
Table 1. DSC results of the PBT/TLCP composites with TLCP content

Materials	T_g^{a} (°C)	T_m^{a} (°C)	ΔH_m^{a} (J/g)	T_c^{b} (°C)	ΔT^{c} (°C)
PBT	57.1	224.4	44.3	178.6	45.8
PBT/TLCP5	56.9	224.9	43.1	189.5	35.4
PBT/TLCP10	57.1	224.5	42.4	190.1	34.4
PBT/TLCP20	56.7	223.8	38.2	189.9	33.9
PBT/TLCP50	56.2	223.4	24.7	190.3	33.1

[a]Values obtained from the DSC heating traces at a heating rate of 10 °C/min, [b]values obtained from the DSC cooling traces at a cooling rate of 10 °C/min, [c]the degree of supercooling, $T = T_m - T_c$.

position temperatures, and the residual yields of the PBT/ TLCP composites with increasing TLCP content indicated that the thermal decomposition reactions of the PBT/TLCP composites were retarded by the presence of rigid TLCP molecular chains. Therefore, the incorporation of TLCP has a positive effect on improving the thermal stability of the PBT/TLCP composites.

The results from the DSC measurements for the PBT/ TLCP composites as a function of TLCP content are shown in Table 1. The addition of TLCP component has little effect on the glass transition temperature (T_g) and melting temperature (T_m) of the PBT/TLCP composites. The increase in the crystallization temperature (T_c) of the PBT/TLCP composites with the introduction of TLCP component, together with the fact that the PBT/TLCP composites have a lower degree of supercooling for crystallization ($\Delta T = T_m - T_c$) with the introduction of TLCP component, suggests that TLCP component can effectively act as nucleating agents in the PBT/TLCP composites, this effect being more pronounced at lower TLCP content. Thus, it can be deduced that the incorporation
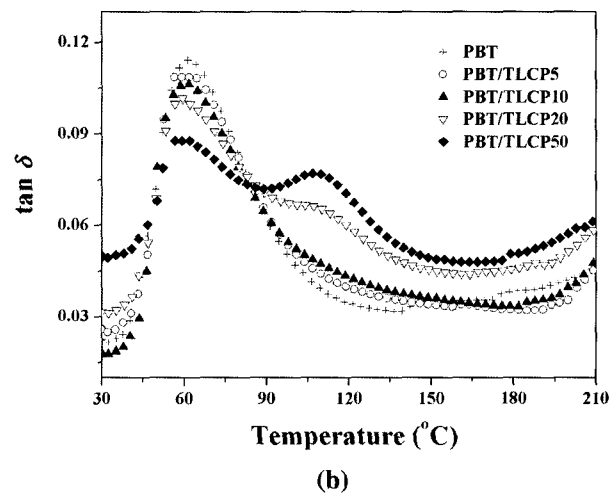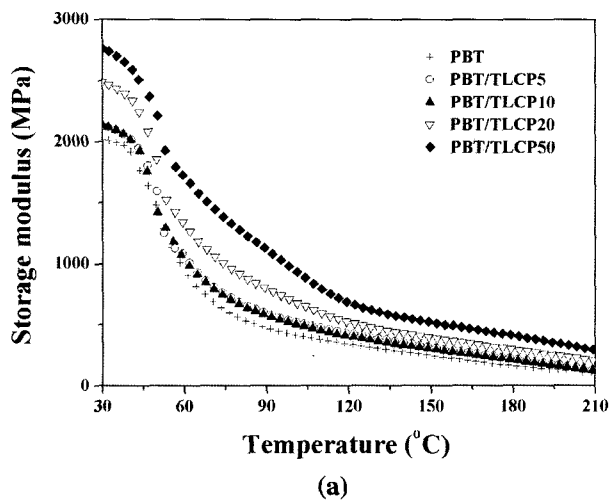
Figure 5. (a) Storage modulus and (b) tanδ of PBT/TLCP composites with TLCP content.

Figure 6. WAXD patterns of (a) PBT/TLCP composites with TLCP content and (b) PBT/TLCP5 composites (A: PBT, B: PBT/TLCP5, C: PBT/TLCP10, and D: PBT/TLCP20).

of TLCP phase can effectively enhance the crystallization of the PBT matrix through heterogeneous nucleation. Jarus *et al.* [22] investigated the relationship between the gradient structures of PP to its HDT, and they suggested that higher crystallization temperature of nucleated PP was responsible for the increase in the HDT values. Therefore, in this study, it is expected that the HDT values of the PBT/TLCP composites are improved with higher crystallization temperature of the composites by a nucleating effect of TLCP phase, which will be confirmed by the HDT measurements.

Dynamic mechanical properties of the PBT/TLCP composites with TLCP content are shown in Figure 5. The storage modulus of the PBT/TLCP composites increased with increasing TLCP content. The increase in the storage modulus of the PBT/TLCP composites with increasing TLCP content may be attributed to the introduction of the rigid TLCP molecules into the PBT phase. The modulus of the PBT/TLCP composites gradually decreased with temperature and
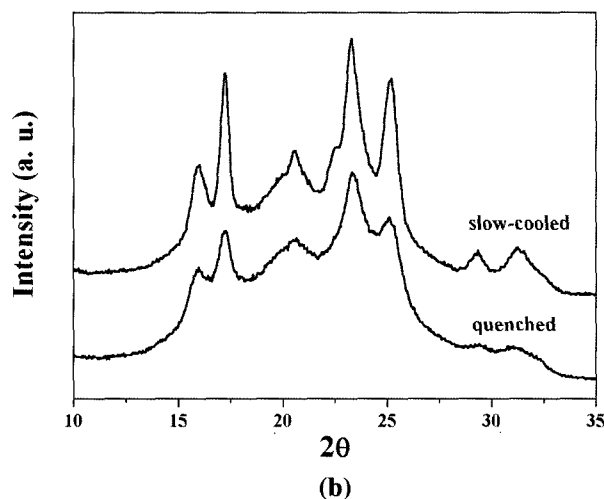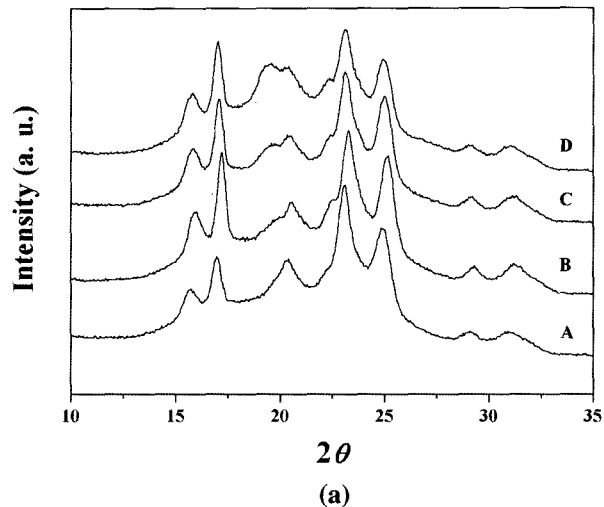
abruptly fell around 50-60 °C, and this transition region was associated with the primary relaxation (i.e., generally T_g) of the PBT phase. The storage modulus of the PBT/TLCP composites below and above T_g increased with increasing TLCP content, and was higher than that of pure PBT, indicating the synergistic effect between TLCP and PBT phases. As shown in Figure 5(b), the PBT/TLCP composites with higher TLCP content ($\geq$20 wt%) exhibited a weak shoulder at approximately 105 °C, which was attributed to the α relaxation peak of the TLCP, corresponding to the materials changing from glassy state to a mobile nematic phase [23]. It can be deduced that the dynamic mechanical properties of the PBT/TLCP composites significantly depend on the weight ratio and the individual properties of component polymers.

The WAXD profiles of the PBT/TLCP composites with TLCP content are shown in Figure 6. In the case of pure

PBT, strong diffraction peaks were observed at approximately 15.8, 17.1, 20.4, 23.1, and 25.0°, which were attributed to (0-11), (010), (011), (100), and (1-11) reflections indicating the α form of the PBT crystals with a triclinic configuration [24]. The positions of the diffraction peaks for the PBT/TLCP composites remained almost unchanged with increasing TLCP content. The PBT/TLCP composites with higher TLCP content ($\geq$20 wt%) exhibited another characteristic peak was observed at approximately 19°, which was attributed to the TLCP equatorial reflection [25]. The WAXD patterns of the slow-cooled and the quenched PBT/TLCP composites are shown in Figure 6(b). As expected, the slow cooling of the polymer composites resulted in sharper and stronger diffraction peaks, and the position of diffraction peaks remained almost unchanged in both the polymer composites. This result indicates that the slow cooling of the polymer composites leads to the formation of larger and more regular crystallites, compared to the quenched polymer composites. The variations of the apparent crystallite size (L_{hkl}) in the direction perpendicular to the (hkl) crystal plane obtained from WAXD patterns of the PBT/TLCP composites by using the Scherrer's equation [20] are shown in Figure 7. On incorporating of TLCP phase into the PBT matrix, the PBT/TLCP composites exhibited smaller L_{hkl} values compared with pure PBT, indicating that the function of TLCP phase as a nucleating agent resulted in the formation of fine and small spherulites in the PBT/TLCP composites. The SEM images of the PBT/TLCP composites are shown in Figure 8. At lower TLCP content, small TLCP droplets were finely distributed in the polymer matrix. However, the TLCP phase existed in the form of larger domains at higher TLCP content. The size of the TLCP droplets increased with TLCP content, which may be attributed to higher probability of TLCP coalescing with increasing TLCP content, resulting in a coarser morphology [16,26].

The SAXS profiles of the PBT/TLCP composites are shown in Figures 9 and 10. The scattering maximum observed in
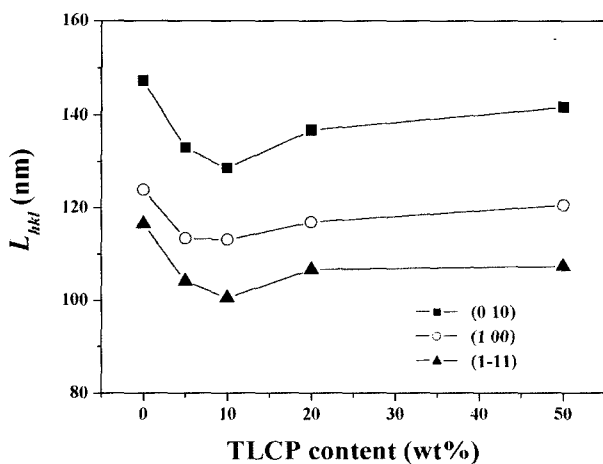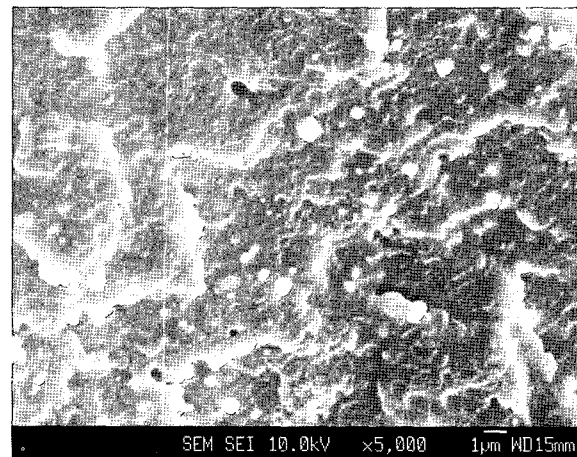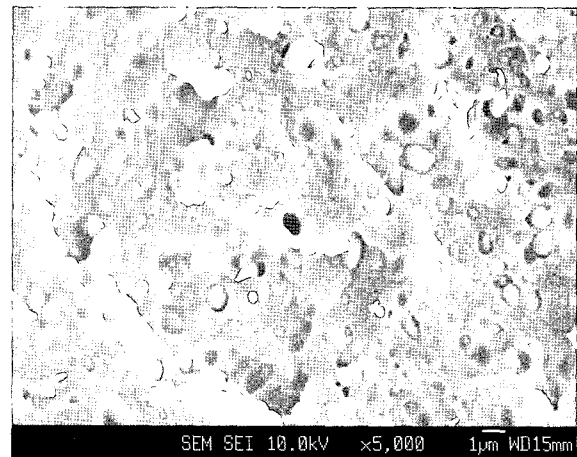
(a)

(b)

Figure 8. SEM microphotographs of (a) PBT/TLCP5 and (b) PBT/TLCP50 composites.

the PBT/TLCP composites shifted to a lower scattering angle with slow cooling, and the scattering intensity increased. The plots of $I^{2}q$ versus θ for the PBT/TLCP composites, reflecting the Lorentz corrected SAXS profiles, are shown in Figures 9(b) and 10(b). From the Lorentz-corrected SAXS profiles, the average long period (L) associated with the lamellar stacks can be determined, using the Bragg relation, $L = 2\pi/q_{max}$ (where $q = 4\pi\sin\theta/\lambda$, is the scattering vector, θ is the scattering angle) [27]. The L value represents the sum of the average thickness of the crystal lamellar thickness and the interlamellar amorphous layer thickness. The increase in the L value of the slow-cooled PBT/TLCP composites may be attributed to the induced thicker and denser lamellar structure and the formation of more regular crystallites in the composites, compared to the quenched composites [28]. The tensile and flexural properties of the slow-cooled and quenched PBT/TLCP composites with TLCP content are shown in Figure 11. The slow-cooled PBT/TLCP composites exhibited higher mechanical properties
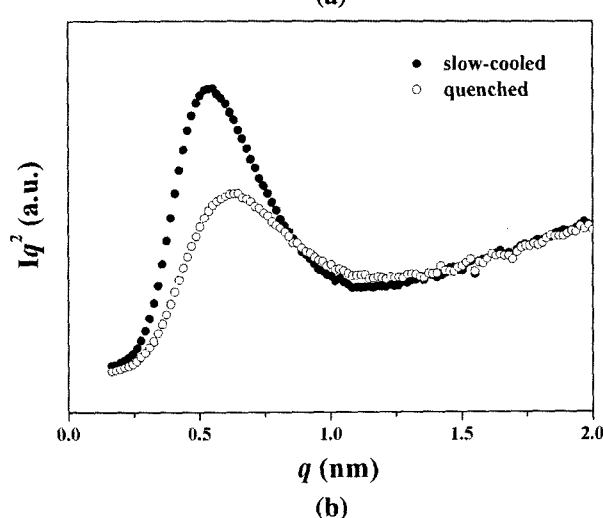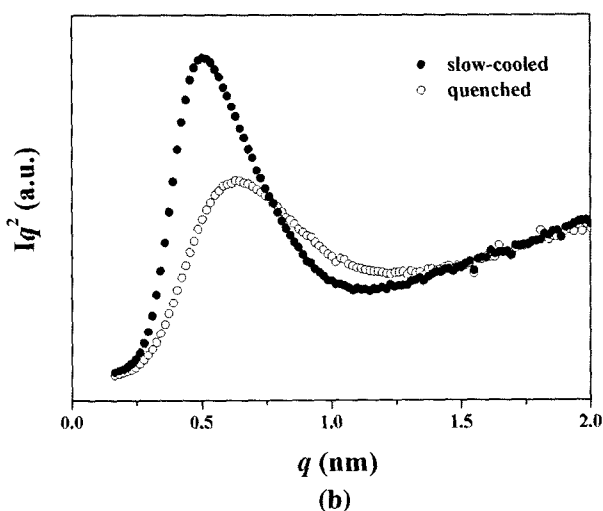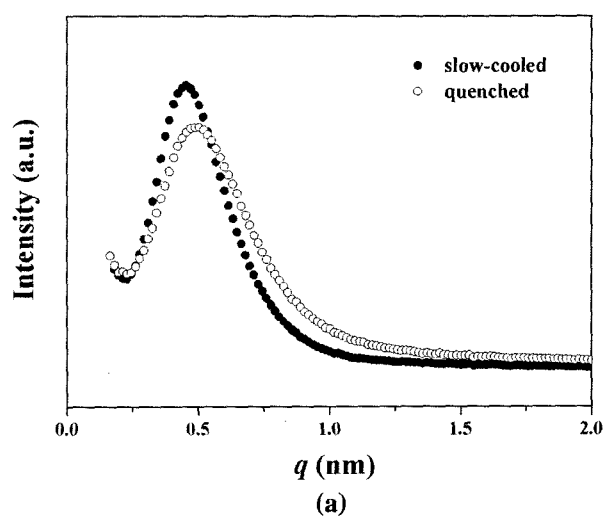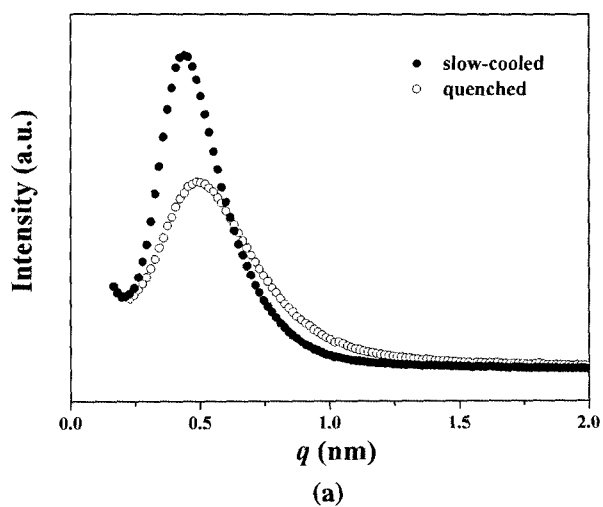
**Figure 7.** Apparent crystallite sizes of PBT/TLCP composites with TLCP content.

Figure 9. (a) SAXS and (b) Lorentz-corrected profiles of PBT/ TLCP5 composites.

Figure 10. (a) SAXS and (b) Lorentz-corrected profiles of PBT/ TLCP10 composites.

compared to the quenched composites over the range of TLCP content studied. This result indicated that the slow cooling process would lead to the formation of larger and more regular crystallites in the polymer composites, resulting in better mechanical properties.

The elevated temperature property, commonly judged by the heat distortion temperature (HDT), is an important factor in evaluating the performance of engineering plastics. The HDT is not necessarily an intrinsic property of a polymeric material but an indirect means for characterizing the physical performance of a polymeric material at elevated temperature [29]. The HDT values are in common use to represent the practical use temperature of thermoplastic polymers, and their analysis is commonly related to the mechanical behavior of polymers. The variation of the HDT for the PBT/TLCP composites as a function of TLCP content is shown in Figure 12. The HDT values of the PBT/TLCP composites were dependent of TLCP content. The HDT values of the PBT/

TLCP composites gradually increased with increasing TLCP content, and this behavior may be explained by the improvement in the modulus of the polymer composites. According to the Nielson's prediction [21], the variation of the HDT value was related to the behavior of flexural modulus with the filler content. The increase in the HDT values of the PBT/TLCP composites with increasing TLCP content is in good agreement with the results of the flexural modulus of the composites as shown in Figure 3, conforming to the Nielson's prediction. That is, the increase in the HDT value of the PBT/TLCP composites was attributed to the improvement of the flexural modulus with increasing TLCP content. In the HDT measurements, the ability of a polymeric material to retain stiffness with increasing temperature is important for a high HDT value [30]. Based on the DMA results, the ratios of E' at 120 °C to that at 40 °C of the PBT/TLCP composites with TLCP content are shown in Figure 13. The modulus ratio of the PBT/TLCP composites increased with
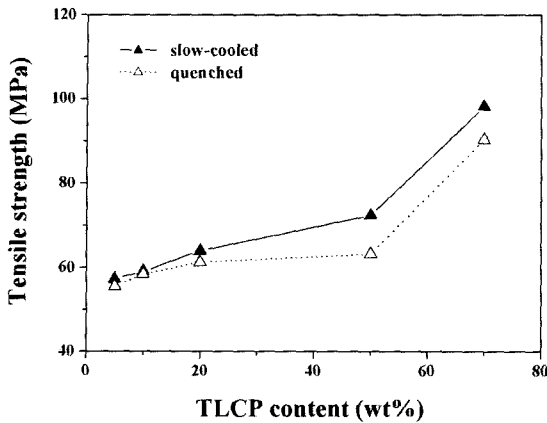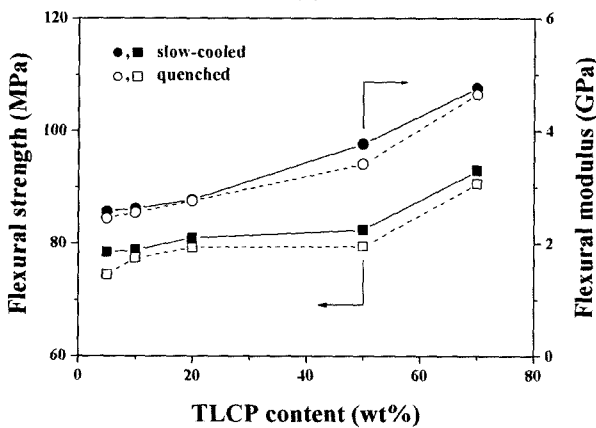
Figure 11. (a) Tensile strength and (b) flexural strength and modulus of PBT/TLCP composites with TLCP content.
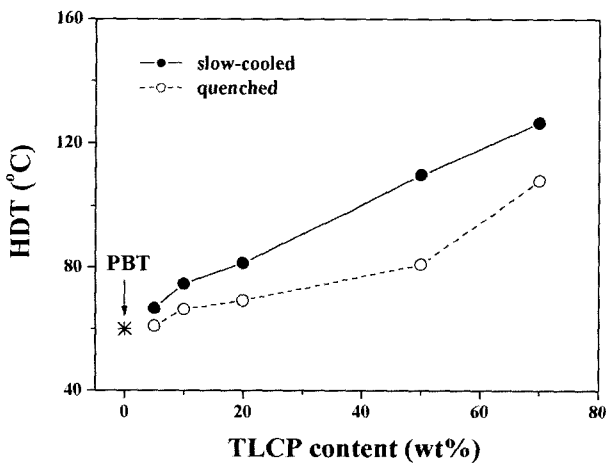

Figure 12. Variation of the HDT values of PBT/TLCP composites with TLCP content.

increasing TLCP content, indicating that the incorporation of TLCP phase enabled the composites to maintain moderate modulus with increasing temperature. Therefore, the ability
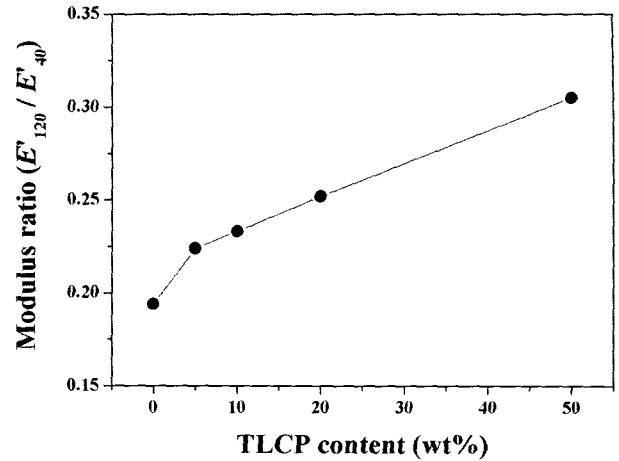

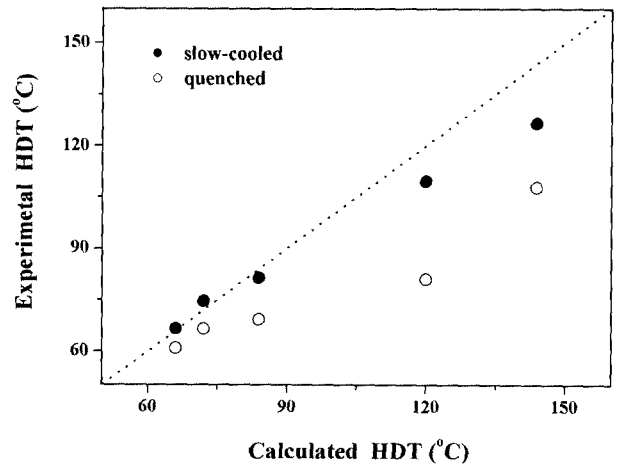**Figure 13.** Modulus ratio of PBT/TLCP composites with TLCP content.

Figure 14. Comparison between experimental and calculated HDT values of PBT/TLCP composites.

of the composites to retain stiffness at elevated temperature, commonly represented by the ratio of the moduli at high and low temperatures, improved with the addition of TLCP phase. This behavior may also contribute to the increase in the HDT values of the PBT/TLCP composites. For the glass fiber-reinforced composites, Thomasson and Groenewood [30] reported that the ratio of the moduli at high and low temperatures, indicating the retention of the higher temperature stiffness, was increased by using more and longer fibers, which was in full agreement with the HDT results.

As shown in Figure 12, the HDT values of the slow-cooled composites were higher than that of the quenched composites. The comparison of theoretical values to experimental data of the HDT for the PBT/TLCP composites is shown in Figure 14, by applying the additivity rule [29]:

$$HDT_{compos} = \phi_{PBT} \cdot HDT_{PBT} + \phi_{TLCP} \cdot HDT_{TLCP} \qquad (1)$$

where HDT_{compos}, HDT_{PBT}, and HDT_{TLCP} are the HDT values of the composites, the PBT, and the TLCP, respectively, and ϕ_{PBT} and ϕ_{TLCP} are the blend composition ratios of PBT and TLCP. As shown in Figure 14, the HDT values of the slow-cooled composites, on the whole, were well fitted to the additivity rule, while the quenched composites showed a larger deviation from the theoretically calculated HDT values. This tendency observed in the quenched composites may be attributed to the lack of the formation of regular crystallites and the development of crystalline structures, compared with slow-cooled composites. In addition, this result suggests the possibility that the HDT value of the polymer composites can be simply predicted by applying the additivity rule.

In summary, the improvement in the HDT values of the PBT/TLCP composites resulted from the better mechanical properties (i.e., an increase in the flexural modulus) of the composites due to the reinforcement effect by TLCP phase, the formation of more regular crystallites and the development of crystalline structures in the composites induced by slow-cooling process, and the enhancement of the ability of the composites to retain high stiffness by TLCP phase.

Conclusion

PBT composites reinforced with a TLCP were prepared by melt blending, and the effects of incorporating TLCP on the HDT and mechanical properties of the PBT/TLCP composites were investigated. The mechanical properties of the PBT/TLCP composites depended upon TLCP content, and they increased with the reinforcement effect by TLCP phase to the PBT matrix. The slow cooling process of the PBT/TLCP composites leads to the thicker and denser lamellar structures and the formation of more regular crystallites in the composites. The incorporation of TLCP phase into the PBT matrix improved not only the tensile strength and flexural modulus but also the HDT values of the PBT/TLCP composites. The improvement in the HDT values of the PBT/TLCP composites resulted from the increase in the flexural modulus of the composites, the formation of more regular crystallites and the development of crystalline structures in the composites, and the enhancement of the ability of the composites to retain high stiffness by TLCP phase. In addition, the HDT value of the PBT/TLCP composites can be simply predicted by applying the additivity rule.

Acknowledgement

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