JOURNAL OF Applied Polymer SCIENCE

Reinforcing Properties of Poly(trimethyleneterephthalate) by a Thermotropic Liquid Crystal Polymer

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ABSTRACT: A thermotropic liquid crystalline copolymer (TLCP) having a trimethylene terephthalate (TT) unit and a triad terephthaloyl mesogenic unit was synthesized and its blends with poly(trimethylene terephthalate) (PTT) were prepared for TLCP-reinforced fiber spinning. The TLCP, PTT, and their blends were characterized in terms of their thermal, mechanical, and morphological properties. In the hot-drawn fibers of 20 wt % TLCP/PTT blend, the well-oriented fibrils were observed at higher temperature ($>T_m$) than the PTT melt by polarizing optical microscope. With scanning electron microscopy images of cryogenically fractured surfaces of the blends, the TLCP were well dispersed in 0.3 to 0.5 μm in domain size. Interfacial adhesion between the TLCP and PTT seemed fairly good. The TLCP acted effectively as a reinforcing material in PTT matrix, it led to an increase of initial modulus and tensile strength of the blend fibers as TLCP's content increased. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41408.

KEYWORDS: blends; liquid crystals; polyesters

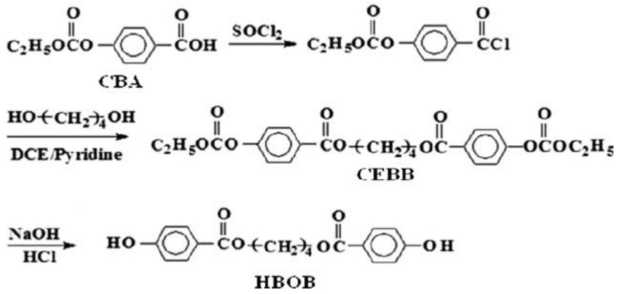
Received 1 May 2014; accepted 13 August 2014
DOI: 10.1002/app.41408

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is one of the most common aromatic polyesters used in structural materials and textile industry. Even though PTT is a tough and ductile material in the unnotched state, the presence of sharp notches or curvature in the material leads to failure in a brittle manner. The notched impact strength and tensile modulus of PTT can be enhanced by the incorporation of rubber-like filler.[1–3] However, this toughening technique usually requires a substantial amount in filler which, in turn, implies a significant loss in elastic modulus and processability. Using a thermotropic liquid crystalline copolymer (TLCP) which could be compatible with PTT instead of adding filler-like materials is an interesting way to solve this issue.

TLCPs have received much attention in terms of the processability using conventional compounding equipment. Due to the shear-thinning effect of the TLCP melts, these polymers exhibited low melt viscosity and slow relaxation time. Furthermore, under appropriate processing conditions, the TLCP could orient in the flow direction and extend into fibrous structures. This fibrillar morphology of TLCP is able to induce self-reinforcement to the matrix polymer.[4,5] Except in a few cases, however, most TLCP blends are incompatible with poor interfacial adhesion and result in lower mechanical properties than the predicted values.[6] The dispersion of TLCP in the matrix and the adhesion force between matrix and TLCP used as an additive are more important than any other factors in the polymer-reinforcing system.[7–9] To increase interfacial adhesion and compatibility of the polymer blend, several methods have been attempted as follows; it blended a TLCP block/graft-copolymer in which it includes the matrix polymer moiety in the copolymer structure or a TLCP as a compatibilizer in which it has the similar molecular structure with the matrix polymer for increasing the interfacial adhesion and compatibility.[10] Besides, the method that was intended to improve interfacial adhesion with matrix polymer while the side chain of TLCP acts as a kind of solvent-like materials in the blends.[11] The polymer blending with TLCP having mesogenic unit in the long side chain has been reported.[12,13] The greatest feature of PTT is that it has excellent elasticity comparable to nylon and spandex.[14,15] However, in PTT, the gap between glass transition temperature (T_g) and crystallization temperature (T_c) is very narrow—only 25°C.[15] Therefore, when producing film or fiber, the optimum processing temperature for drawing is generally determined within this narrow range in the case of PTT. It makes the design of process and optimum conditions difficult, and furthermore PPT has weaker mechanical properties than other polyester fibers.

In our previous reports, various structure–property relationships of liquid crystalline polyesters were identified for improving



Scheme 1. Synthetic route of HBOB.

compatibility and mechanical properties when blended with engineering plastics.[16–21] The TLCP blends with engineering plastics such as PET, PTT, and PBT showed improved compatibility and reinforced mechanical properties through a simple chemical interaction such as transesterification.[20] The sequence distribution of the transesterified blends of TLCP and PBT tended to approach that of a statistical binary copolymer.[21]

Another approach to improve fibrillation was by drawing the TLCP/thermoplastic blends. Drawing promotes fibrillation especially with appropriate TLCP content because it facilitates the deformation of the large TLCP domains into fibrils under the applied extensional flow. The mechanical and structural relationship with drawing has been reported by several authors.[22–25] It was determined that as draw ratio (DR) increased, the tensile modulus increased due to the improvement in the molecular orientation and the higher aspect ratio of the TLCP fibrils.

In this study, a newly designed TLCP on the basis of our earlier studies, was synthesized for enhancing the compatibility with PTT and the properties of in situ blends containing the TLCP and PTT were studied. The TLCP was designed as a form of random copolymer including a trimethylene terephthalate (TT) unit and a trimesogenic unit.

EXPERIMENTAL

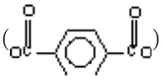
Materials and Instruments

4-Hydroxybenzoic acid, ethyl chloroformate, and trifluoroacetic acid (Aldrich) were used as purchased without further purification. Terephthaloyl chloride was sublimated, thionyl chloride, pyridine, and tetrahydrofuran were purified by distilling and refining after fully refluxing with triphenyl phosphite, sodium hydroxide, calcium hydride. Ethylene glycol, 1,3-propanediol, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, 1-chloronaphthalene (1-CN) were used by distilling under reduced pressure after stirring for 24 h with vacuum dried $MgSO_4$ and calcium hydride. PTT powder (Hyosung) was also vacuum dried at 50°C for 48 h.

FT-IR (Shimadzu 8601PC), FT-NMR (JEOL JNM-LA300), differential scanning calorimeter (DSC TA-2010), thermogravimetric analyzer (TGA TA-2050), melting point apparatus (Fisher-John's) were used for identification and characterization of the compounds and the blends. And a cross-polarizing microscope (Zeiss) with a heating stage (Linkam THMS-600 with TP-92 temperature programmer) was used to examine and confirm the phase structure of polymer blends. Scanning electron microscopy (SEM) (Hitachi S-4700) for morphology of the blends, and UTM (Shimadzu AGS-500D) for mechanical properties were used. For blending and extrusion of compounded polymer and PTT, laboratory hot-press (Carver), mini-max molder (CSI-183 MMX), and mini-extruder (Rand castle RC-025) were used.

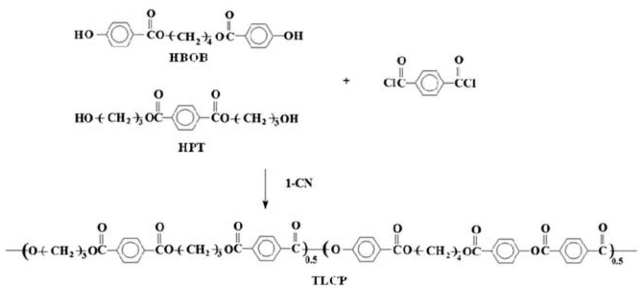
Syntheses

For the synthesis of the TLCP, a monomer, 1,4-bis(*p*-hydroxybenzoyloxy)butane (HBOB) was synthesized according to our previous report[11] with minor modifications which is shown in Scheme 1. Bis(3-hydroxypropyl)terephthalate (HPT) was synthesized according to the method described by Kim et al.[26] A TLCP having dimesogenic unit and PTT unit was polymerized by polycondensation as shown in Scheme 2.

For the monomer, HBOB, synthesis, at the first onset *p*-(carbethoxy)benzoic acid was chlorinated followed by reacted with *n*-dihydroxybutane to obtain 1,4-bis(*p*-carbethoxy benzoyl oxy) buthane (CEBB). The CEBB was hydrolyzed and recrystallized in methanol–water solvent to produce HBOB, yield: 83%. Melting point and elemental analyses were obtained, mp: 188°C, *Anal.* Calcd: C 65.0%, H 5.4%; Found: C 65.1%, H 5.5%. And for the other comonomer, HPT, 1,3-propanediol 14.23 mL (0.1775 mol) was dissolved into pyridine 6 mL under an argon flow, and THF 24 mL and then after terephthaloyl chloride 8 g (0.0393 mol) was dissolved into THF 45 mL in vigorous stirring at 0°C, added it slowly using a dropping funnel. After the reaction was conducted for 6 h at room temperature, half of the solvent was evaporated at 60°C. The final product was precipitated by dropping the residues into 300 mL cold water and white crystals were obtained and recrystallized in water. Structure identification was performed with IR and NMR Spectra. IR spectra (KBr pellet): 3300–3377 cm^{-1}(O—H stretching), 2961 cm^{-1}(Ar. C—H stretching), 2916 cm^{-1}(aliph.C—H stretching), 1713 cm^{-1} (C=O stretching), 1510 cm^{-1} (C=C stretching), NMR spectra ($CDCl_3$): δ 1.97–2.03 ($—CH_2\underline{CH_2}CH_2OH$), δ 3.75–3.79 ($—CH_2CH_2\underline{CH_2}OH$), δ 4.31–4.69 ($—\underline{CH_2}CH_2CH_2OH$), δ 8.02~8.15().

Blending and Fiber Spinning

Samples of TLCP synthesized and PTT were mixed with proper composition and tumbled for 72 h. The blends were extruded using 1/4 inch mini extruder (Randcastle RC-025) after dried in a vacuum dryer at 100°C for 24 h. The temperature profiles of the extruder were 215, 250, and 255°C at zone 1, zone 2, and zone 3, and 260°C at die zone, respectively. The rotation rate of



Scheme 2. Synthetic route of the TLCP.

Table I. General Properties of TLCP and PTT

Polymer	η_{inh}[a]	T_g[b] (°C)	T_{cc}[b] (°C)	T_m[b] (°C)	T_i[b] (°C)	T_d[c] (°C)	L.C. phase
TLCP	0.69	89		270	320	361	Nematic
PTT	0.92	47	177	228	-	320	

[a] Inherent viscosities of polymer were measured at a concentration of 0.5 g/dL in trifluoroaceticacid/chloroform = 7/3 (v/v)mixture at 35°C.
[b] Glass, crystallization, melting, isotropic temperatures were measured by DSC thermograms.
[c] Degradation temperature was obtained from 5% reduction in weight on TGA thermograms.

screw was adjusted to 30 rpm and the residence time in the extruder was less than 2 min. To minimize thermal decomposition, the time was shortened as much as possible. The distance between die and take-up device was about 1 m and take-up speed was 76 m/min. Post-treatment (cold- and hot-drawing) of fiber was conducted in two steps, cold-drawing at 90°C and hot-drawing at 190°C using a home-made drawing device.

Characterization

Solution viscosities of PTT and the polymer synthesized were measured in thermostat of 35°C by making 0.5 g/dL solution with trifluoroacetic acid/chloroform (7/3, v/v) mixed solvent. Melt flow index (MFI) was determined using a melt flow indexer (LMI 4000 Series, Dynisco) according to ASTM D 1238. The instrument was warm at 235°C for 15 min. The 6 g of polymer was added in piston. Bring the weight on piston, polymer will melt and flow pass dyne for 10 s. The melted polymer was weighed for calculated MFI. The glass transition (T_g) temperatures, crystallization, and melting temperatures of the blends in various compositions were measured with a DSC equipped with a coolant-circulated intracooler at a scan rate of 10°C/min in the range 0–250°C. The second heating runs for melt-quenched samples were chosen to remove previous thermal history and to make the T_g more clear and obvious. In addition, to examine the morphology and phase behavior of the samples, a polarized-light optical microscope (Carl Zeiss, Zeiss Jena) with a heating and freezing plate (Linkam THMS-600 with TP-92 temperature programmer) was used to examine the phase structure of the polymer blends. The interface morphology was observed by SEM.

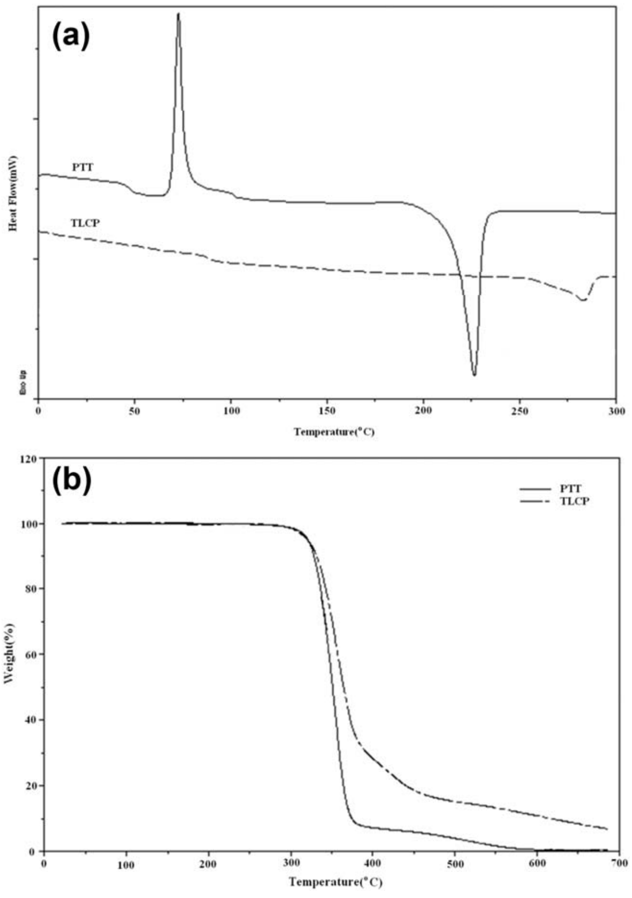


Figure 1. DSC (a) and TGA (b) thermograms of TLCPs and PTT at a heating rate of 10°C/min.

Mechanical properties of the fibers of PTT and TLCP/PTT blends were measured using UTM of Shimadzu. Cross head speed was set up at 10 mm/min and the length of fiber samples was 50 mm. For each sample, the values reported are the average of 10 specimens. The diameter of each sample was measured using polarization microscope and the DRs were determined by calculating the ratios (DR = R^2/r^2) of cross-sectional area of as-spun fiber and hot drawn fiber.

RESULTS AND DISCUSSION

Syntheses

For polymer synthesis, HBOB 12.20 g (0.03697 mol) and HPT 3.50 g (0.01231 mol) were put into a reactor which contained 80 mL 1-CN and stirred it at 130°C under an argon air atmosphere. After the reactants were dissolved completely, terephthaloyl chloride 10 g (0.04925 mol) was added. Then the fibrous

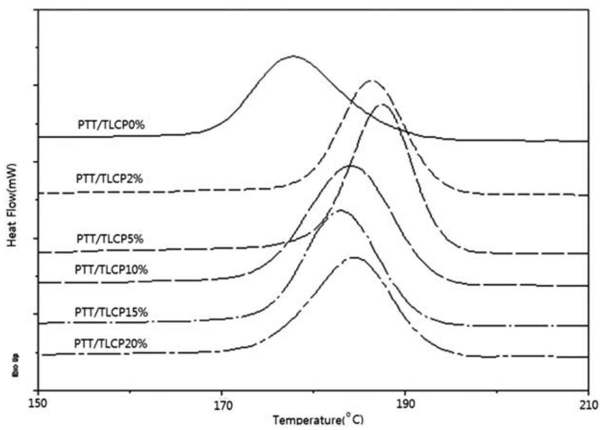


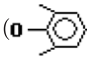
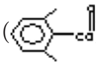
Figure 2. DSC thermograms on cooling of PTT and TLCP/PTT blends at a cooling rate of 10°C/min.

Table II. Thermal Properties of TLCP/PTT Blends

	Heating[a]					Cooling[a]		
TLCP/PTT (wt %)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)	MFI (g/10 min)
0/100	47	72	37.42	226	53.82	177	46.64	20.5
2/98	48	73	46.88 (47.9)	227	55.47 (56.68)	186	51.34 (52.46)	32.5
5/95	48	74	45.28 (47.6)	227	58.86 (61.95)	187	53.71 (56.53)	40.0
10/90	48	73	44.94 (49.9)	226	60.65 (67.38)	183	56.74 (63.04)	48.5
15/85	49	73	45.52 (53.5)	227	57.85 (68.05)	182	54.07 (63.6)	54.4
20/80	51	74	43.29 (54.11)	226	55.72 (69.65)	182	53.21 (66.51)	50.5
100/0	89	–	–	270	10.12	–	–	–

[a] The values are those obtained from second heating and cooling (10°C/min) runs, and the values in parentheses were calculated based on the amount of PTT in the blends by a mixing rule.

product was precipitated by dropping it into hot methanol after reacting it at 180°C for 48 h. White polymer powder was obtained by vacuum drying at 100°C for 48 h after washing it in hot methanol and water several times. Melting point of polymer was 270°C, and yield rate was 92% (20.2 g).

The polymer synthesized was identified using FT-IR and ^{1}H-NMR υ_{OH} (3300–3377 cm^{-1}) and $\upsilon_{C=O}$ (1730 cm$^{-1)}$) appeared newly in HBOB. And at δ 7.36–7.41 (), δ 8.14–8.43 () for the aromatic rings and at δ 2.02–2.21

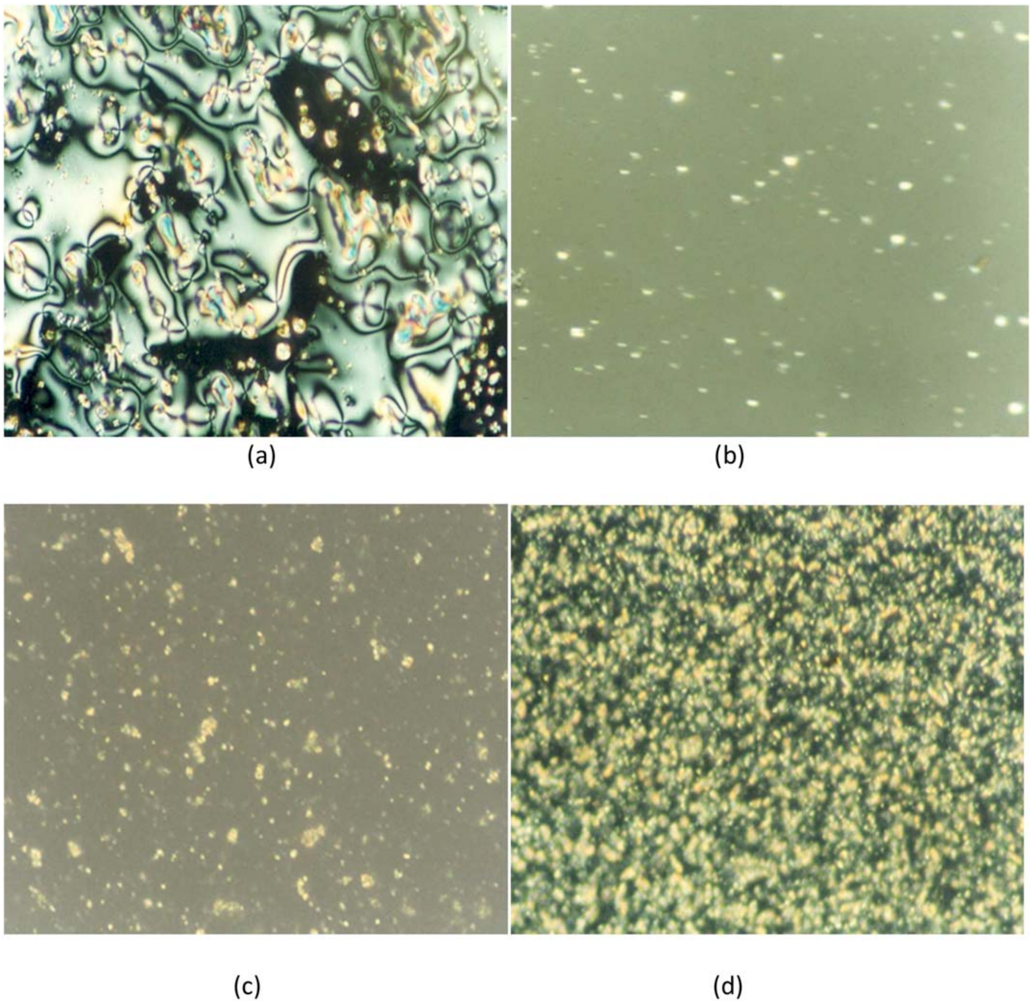


Figure 3. Polarized optical micrographs of (a) of TLCP taken at 290°C (200×), and (b) 5 wt %, (c) 10 wt %, and (d) 20 wt % TLCP/PTT blends taken at 260°C (200×). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

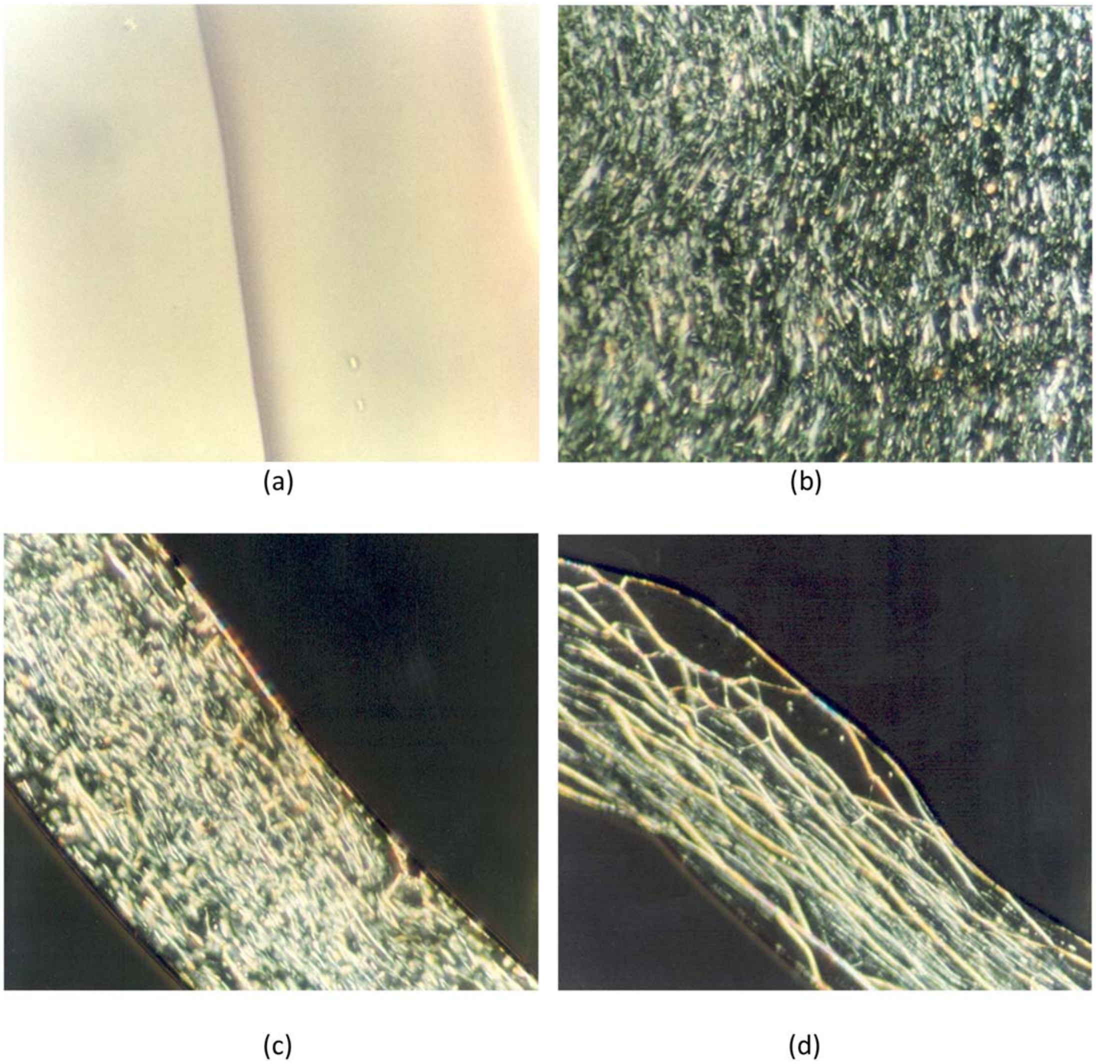


Figure 4. Polarized optical micrographs of PTT and 20 wt % TLCP/PTT blend fibers taken at 260°C. (a) PTT, (b) as-extruded, (c) cold-drawn (DR: 4.0) and (d) hot drawn (DR: 7.4). (200×). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$(\text{—OCH}_2\underline{\text{CH}_2}\underline{\text{CH}_2}\text{CH}_2\text{O—})$, δ 2.38–2.44 $(\text{—OCH}_2\underline{\text{CH}_2}\text{CH}_2\text{O—})$, δ4.60–4.67 $(\text{—O}\underline{\text{CH}_2}\text{CH}_2\text{CH}_2\underline{\text{CH}_2}\text{O—})$, and δ 4.83 $(\text{—O}\underline{\text{CH}_2}\text{CH}_2\underline{\text{CH}_2}\text{O—})$ for the aliphatic hydrogens. Solution viscosity of the polymer synthesized was 0.69 g/dl. Table I shows physical properties of TLCP and PTT used in this experiment.

Thermal Properties

DSC and TGA thermograms of the TLCP/PTT blends and the neat polymers were obtained (Figures 1 and 2). Thermal properties of the blends are shown at Table II. For the TLCP/PTT blends, the difference between the two T_gs (PTT = 89°C, TLCP = 47°C) was too small to define the resolution of two T_gs by DSC. In DSC thermograms of TLCP/PTT blends showed cold crystallization and melting peak at around 74 and 227°C, respectively, which are not changed much from those of PTT.

With regard to all DSC analysis of the blends, after a first scan up to 260°C to provide the same thermal history for all samples, followed by steadily cooling to 20°C, the second runs were recorded at a heating rate of 10°C/min. As shown in Table I, T_g, T_m (melting point), and T_i (isotropic temperature) of TLCP were 89, 270, and 320°C, respectively. Table II shows thermal properties of the TLCP/PTT blends in different composition. Glass transitions of pure PTT and pure TLCP were shown at 47 and 89°C, respectively. The thermograms of the blends containing from 2 to 20 wt % of TLCP are very similar to that of PTT. These peaks changed only slightly with blend composition. T_gs of the blends were increased with increasing TLCP content, for example, 48°C in 2 wt % TLCP and 51°C in 20 wt % TLCP. The changes in enthalpies of melting and crystallization of the blends are in contrast with the values calculated based on the simple mixing rule (Table II). Besides, as the amount of TLCP increases, there seems to be shifts of C=O stretching at 1728 cm^{-1} to lower wave numbers which has been commonly reported for the transesterification of aromatic polyesters.[27] From this result, it is estimated that there is partial miscibility between the TLCP prepared and PTT by in situ transesterification reaction. It can be ester-exchanged easily between these two polymers because of the same TT units linked by ester bonds in both TLCP and PTT. This is comparable to our earlier observation that the blend of TLCP (TR4) and poly(butylene

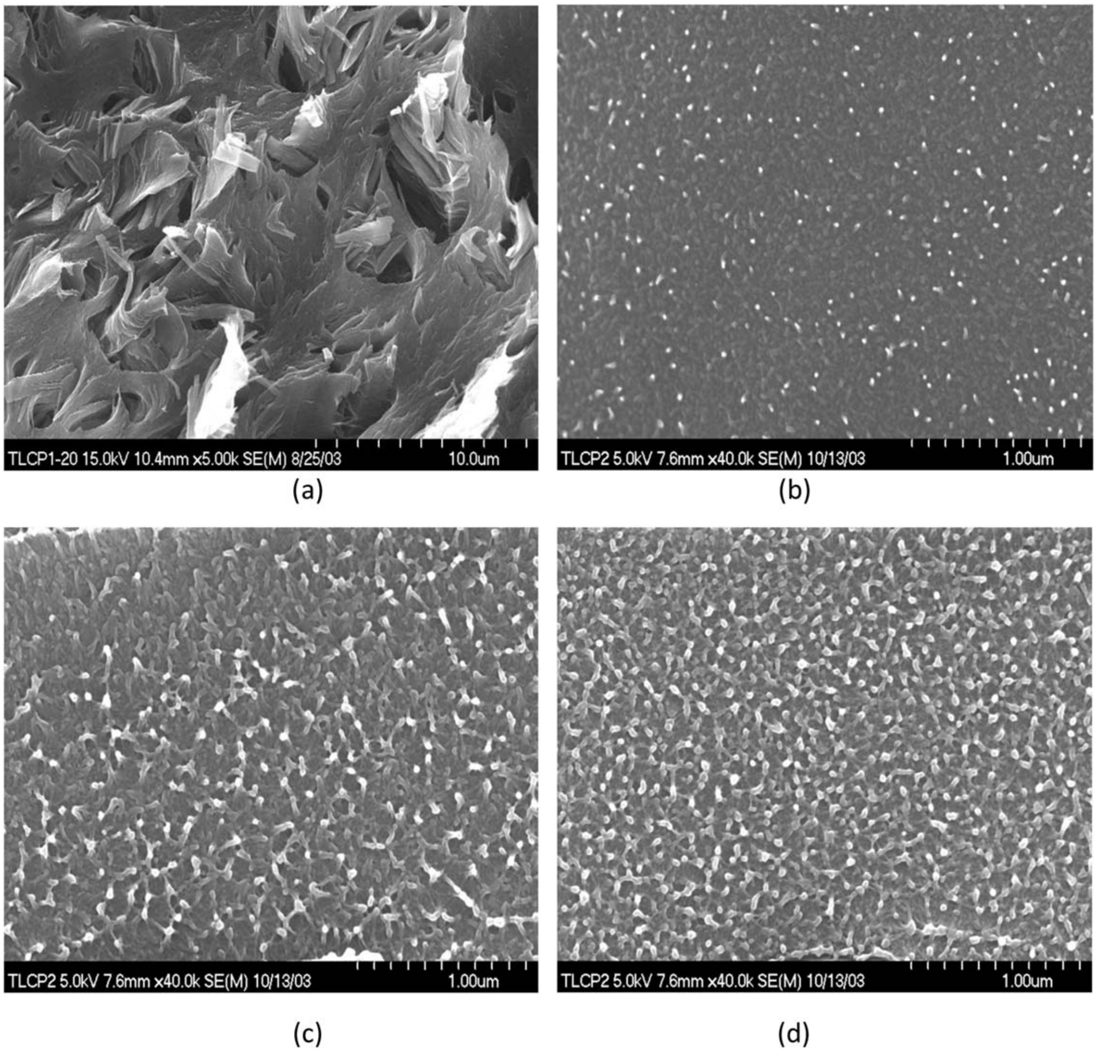


Figure 5. Scanning electron micrographs of the fractured surface of (a) TLCP and (b) 5 wt %, (c) 10 wt %, and (d) 20 wt % TLCP/PTT as-spun blend fibers.

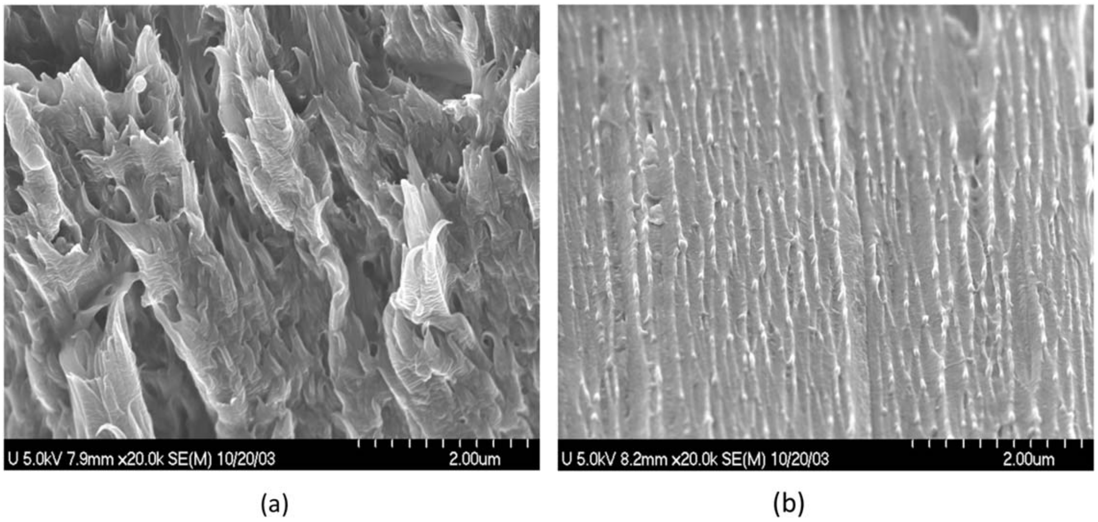


Figure 6. Scanning electron micrographs of the fractured surface of 20 wt % TLCP/PTT hot-drawn fibers.

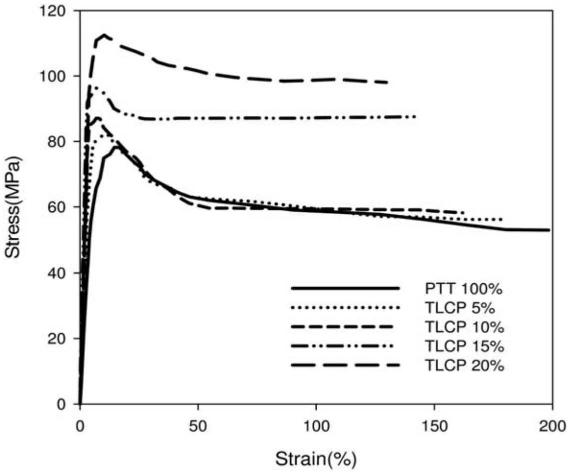


Figure 7. Stress–strain curves of the as-spun PTT and blended with TLCP, 5, 10, 15, 20% (DR = 0).

terephthalate) revealed transesterification reaction between the polymers blended, and the monomer sequence distribution of the blend tended to close that of a statistical copolymer composed of each repeating units of component polymers.[20] The transesterification can also occur between PTT and polycarbonate at the temperature range often used for melt blending or processing.[27] The possibility for transesterification should not be excluded in view of the effect of processing temperature and time.

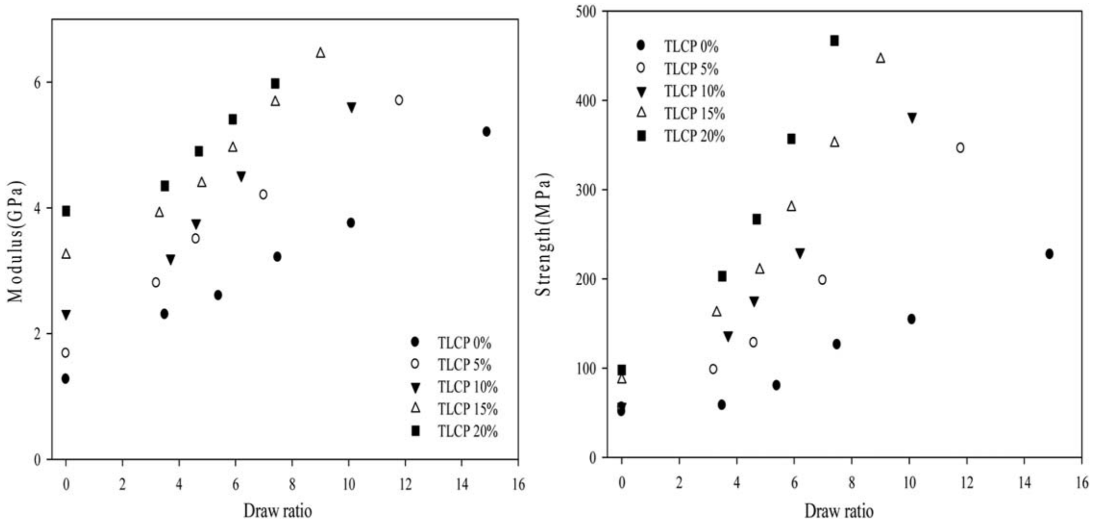
The crystallization point of pure PTT was 177°C, conversely, those of the blends with the TLCP showed much higher temperature for crystallization from the melt. It means that the TLCP is ascribed to nucleating agent in the blends.

MFI of the blends was measured to investigate flow properties of TLCP/PTT blend melts The MFI of PTT was 20.5 g/10 min. As shown in Table II, MFI of the TLCP/PTT blend was increased significantly with increasing TLCP content. As small amount of the TLCP was added to PTT matrix, MFI was suddenly increased from 20.5 of pure PTT to 32.5 of TLCP 2% blend. Thereafter, it was increased monotonically to about 48.5 for up to 10 wt % of the TLCP. It is expected from the measured MFI results that fluidity and spinnability of TLCP/PTT blends would be considerably improved by addition of small amount of TLCP. This might be expected from molecular orientation and fibrillation of the TLCP in the blend. The TLCP can act as a processing aid as well as a reinforcing agent and in the blends. In contrast, the MFI at 80/20 decreases as only 50.5 g/10 min probably due to the ratio at 80 : 20 as considerably incompatible polymer blends.

Morphology

The nature of liquid crystal phases and anisotropy formed by the TLCP having TT unit was identified by observing the optical textures of the polymer melt on a polarizing microscope. The TLCP showed strong stir-opalescence and threaded schlieren structure with two and four brushes simultaneously [Figure 3(a)] which are typical characteristics of nematic.[28]

Figure 3(b–d) depicted microscopic pictures observed by a polarizing microscope which show that many fine liquid crystal domains were formed in bulk blend melt at 260°C. It is obviously seen that the domain size of the dispersed LC mesophase is increased with increasing TLCP content. There are, however, no macrophase separations between TLCP and PTT up to 20% TLCP content. The TLCP/PTT blends were extruded and spun by extrusion followed by cold- and hot-drawing method. Fiber properties such as birefringence, fiber diameter and mechanical properties were observed using the maximum DR of the used drawing method. Effects of DR on optical texture and fiber diameter of TLCP/PTT blend fibers are shown in Figure 4. There is no birefringence or fibrillation at pure PTT extrudate as expected [Figure 4(a)]. Birefringence of the blend fibers increased with increasing DR, indicating that molecular orientation was developed along the fiber axis with increasing DR. The considerably high birefringence of the TLCP/PTT blend fibers



(a) (b)

Figure 8. Tensile modulus (a) and tensile strength (b) versus spinning DR of the TLCP/PTT blends.

which were not drawn additionally can be explained by the effects of TLCP phase and high DR applied during cold- and hot-drawing the extrudates. Although TLCPs are incorporated as a minor component into the PTT matrix, they can form highly elongated domains parallel to the flow direction and the oriented domains result in higher birefringence of the blend fibers [Figures 4(c,d)]. These results were attributed to the fact that the TLCP fibrils were generated and oriented in the flow direction by applied shear-force during extrusion processing. To confirm the fibrillation of the TLCP generated in PTT matrix, the fracture surfaces of the extrudates obtained from the pure and the three blends containing up to 20 wt % TLCP in the PTT matrix were examined by SEM observation as shown in Figures 5 and 6. The 5% TLCP/PTT blend shows fine TLCP domains 50–70 nm in size [Figure 5(b)]. The 10% TLCP/PTT also shows fine dispersion with domain size 60–80 nm in diameter [Figure 5(c)]. But the LCP domain in the 20% TLCP/PTT blend is much bigger and closely packed owing to agglomeration of the TLCP [Figure 5(d)]. Elongated particles observed at low TLCP content seem to be disappearing and formation of cocontinuous phase with increasing TLCP content. Adhesion between the TLCP and the matrix appears to be fairly good. Therefore, it can be concluded that processability of the TLCP/PTT blend was improved by the incorporation of TLCP into the PTT matrix because of thermotropic liquid crystal characteristics, such as oriented fibril structures of TLCP generated during the melt processing.

Mechanical Properties

Mechanical properties of blend fibers were measured under the tensile strength, elongation at break and modulus. The tensile strength at yield of the blend fibers (100/0, 95/5, 90/10, 85/15, and 80/20 in PTT/TLCP ratio) were measured and shown in Figures 7 and 8. The tensile strength at yield and modulus were found to be 51 MPa, 2.6 GPa for pure PTT. The observed values of tensile strength and modulus at yield of the blend fibers are shown increase in its mechanical properties as the TLCP content is increased in blend compositions.

The dependence of the tensile strength and modulus of the blend fibers with various TLCP content on the DR is shown in Figure 8(a,b), respectively. The highest values in mechanical properties of the blend fiber are 467 MPa in tensile strength and 5.98 GPa in flexural modulus at DR 7.4 in the blend of 20% TLCP. The tensile strength and modulus of the fibers were improved with increasing TLCP content and DR, and this was attributed to both the development of more ordered structures with well-distributed TLCP domains in the PTT matrix and the improvement of the orientation for the TLCP component in the blends. This result indicated that the molecular orientation and mechanical properties of the blend fibers were improved by the DR increasing. It may also be associated with the existence of an oriented phase of the TLCP in the matrix as fibrillar structures with higher aspect ratios of the TLCP fibrils. Kim et al.[2] reported that the improvement of mechanical property was attributed to the fact that oriented fibril structure was formed by thermotropic liquid crystal nature of the PHB component in TLCP and by applied shearing force during melt compounding. Generally, the formation of fibrillar structures is essential for improving the mechanical properties of as-spun fibers. The development of a fibrillar structure in the PTT matrix could enhance the tensile strength and modulus of the blend fibers. That is, the improvement of the tensile strength and modulus of the PTT blend may have been caused by TLCP fibrils with higher fibrillation in the matrix. Compared with those of the PTT fibers not containing the TLCP component, the tensile strength and modulus of the PTT were improved with increasing TLCP content at all DR investigated, and this was attributed to the development of TLCP fibrils with a high aspect ratio due to molecular orientation in liquid crystal phase. This suggests that the TLCP synthesized may have acted as a reinforcing agent with compatibility in the blends because of the well-distributed TLCP fibrils in the polymer matrix. Therefore, the improvement of the mechanical properties of the PTT by the introduction of the TLCP component may have been caused by both the formation of the highly elongated TLCP fibrils and the reinforcement of the polymer matrix by the TLCP component.

CONCLUSION

A newly designed TLCP was synthesized for enhancing the compatibility with PTT and the properties of in situ blends containing the TLCP and PTT were identified. The TLCP was designed as a form of random copolymer including a TT unit and a trimesogenic unit. It can be concluded that mechanical reinforcement and processability of the TLCP/PTT blend were improved by the incorporation of TLCP into the PTT matrix because of thermotropic liquid crystal characteristics, such as oriented fibril structures of TLCP generated during the melt processing.

ACKNOWLEDGMENT

This study was supported by research fund from Chosun University, 2010.

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