

In Situ Modulus Enhancement of Polypropylene Monofilament Through Blending with a Liquid-Crystalline Copolyester

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ABSTRACT: An immiscible blend of poly(propylene) (PP) with a thermotropic liquid-crystalline polymer (TLCP, trade name Rodrun LC5000), a copolyester of 80/20 mol ratio of *p*-hydroxy benzoic acid and polyethylene terephthalate was prepared in a twin-screw extruder. The blend extrudate was fabricated as monofilament by using a single-screw extruder equipped with a fiber line. The as-spun filament was drawn at 120°C to enhance molecular orientation. Morphology, thermal, tensile, and dynamic mechanical properties of both as-spun and drawn monofilaments were investigated. Almost continuously long TLCP fibers dispersed in PP matrix were obtained in the composite as-spun monofilaments. The maximum modulus was found in 15 wt % TLCP/PP composite as-spun filament, an increase of about 2.4 times that of

the as-spun neat PP. For the drawn filaments, the 10 wt % TLCP/PP composite showed a maximum modulus, an increase of about 1.5 times that of the drawn neat PP. The increase in the moduli was attributed not only to the reinforcement by TLCP fibrils with very high aspect ratio but also to the increases in PP crystallinity and molecular orientation through the drawing process. A remarkable improvement in the dynamic mechanical properties of the composite monofilaments was observed, especially in the high-temperature region. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1337–1346, 2003

Key words: composites; liquid-crystalline polymers (LCP); poly(propylene) (PP); monofilaments; fibers

INTRODUCTION

To produce polymeric materials with high modulus and strength, reinforcement with short fibers is a widely applied technique because of the ease of processing and cost effectiveness. In the last two decades, it has been known that short fibers can be formed during processing and fabrication of an immiscible blend of a thermotropic liquid-crystalline polymer (TLCP) and a conventional plastic or thermoplastic elastomer, a so-called *in situ* composite.^{1–4} The TLCP used as the dispersed phase is a linear and rigid polymer with a long relaxation time. It has a low viscosity in the mesophase and can be easily elongated and oriented in the flow direction. The degree of dispersion and fibrillation of the TLCP phase in the matrix phase depends on the processing condition and the rheological behavior of the blend components. The properties of the finished products depend on the

morphology of the blend. Therefore, both the blending conditions and the fabrication methods of the finished products play an important role in the formation of the TLCP fibrils and the degree of molecular ordering in both phases. It has been observed that TLCP fabricated in the form of fiber, sheet, film, and molding specimens shows a decline in modulus as a result of the decrease in degree of molecular orientation.⁵

Poly(propylene) (PP) is one of the polymers most widely used as a construction material with a growing consumption in recent years. So far glass fibers have been used as the major reinforcing element for PP, but this causes difficulty in melt processing because of the increase of viscosity and fiber breakage in the process. Furthermore, the use of glass fibers as a reinforcing filler makes the product difficult to recycle and causes environmental problems. Reinforcement of PP by blending with a TLCP to form an *in situ* composite will help solve both the processing and the environmental problems. Another advantage of TLCP fibers over glass fibers is that TLCP has much lower density ($\sim 1.4 \text{ g/cm}^3$) than that of glass fibers ($\sim 2.5 \text{ g/cm}^3$).

Blending poly(propylene) with different liquid-crystalline polymers using various fabrication techniques such as extruded strands, injection molding, sheet extrusion, fiber spinning, and film extrusion have been studied by several research groups.^{6–23} Among these techniques, materials produced by fiber spinning show superior properties attributed to the

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more efficient elongational force. To prepare *in situ* composites consisting of two components whose melting temperatures differ by about 100°C, Baird et al.²⁴ patented a dual-extrusion process to allow a continuous stream of TLCP into the matrix before melt spinning. Most of the TLCPs used in the works mentioned above were Vectra type [e.g., Vectra A, a copolyester of 6-hydroxy-2-naphthonic acid and *p*-hydroxy benzoic acid (HBA)] and Rodrun LC3000 [a copolyester consisting of 60/40 mol ratio of HBA/poly(ethylene terephthalate) (PET)]. So far as we know, PP blended with Rodrun LC5000 (a copolyester consisting of 80/20 mol ratio of HBA/PET) has scarcely been investigated despite the superior mechanical and thermal properties of the LC5000 compared with those of the LC3000. The main reason is probably because of the difficulty in processing, given their greatly different melting temperatures, which is especially true for the coextrusion method pioneered by Baird et al.²⁴ There was a report by Xu et al.²⁵ on the 30 wt % LC5000/PP/polycarbonate blend prepared by injection molding. A ribbonlike structure was observed in the LC5000/PP binary blend, and a lamella structure was formed in the LC5000/PP/polycarbonate ternary blend.

In the present work, we studied the properties of monofilaments prepared from PP blended with Rodrun LC5000 at various concentrations. Preparation of the specimens was carried out in two steps, using a conventional twin-screw extruder for the purpose of dispersion in the first step and then melt spinning the monofilament by a single-screw extruder equipped with a fiber line. The aim of this work was to investigate the formation of TLCP fibrils in the *in situ* composite monofilaments starting from the spinning step to see how the morphology, crystallinity, and molecular orientation influence the mechanical properties of the filaments. The properties of both the as-spun and drawn filaments were thus thoroughly investigated.

Despite the great difference between the melting temperatures of these two blend components, this work has demonstrated that by using the two-step method, nearly continuous TLCP fibrils dispersed in the PP matrix (at TLCP content as low as 10%) can be generated and give rise to a significant improvement in the modulus of the filaments.

EXPERIMENTAL

Materials

Poly(propylene) (PP, PRO-FAX 6631; HMC Polymer Co., Thailand), with a melt flow index of 2 g/10 min, was used as the matrix. The TLCP used as a reinforcing component was a copolyester of HBA and PET at 80/20 mol ratio (trade name Rodrun LC5000; Unitica Co. Ltd., Tokyo, Japan). The melting temperature of

TLCP is 280°C and the density is 1.4 g/cm³. The materials were vacuum dried at 80°C for 10 h before use.

Blending

Various compositions of PP and TLCP were melt blended in a corotating, intermeshing, twin-screw extruder (PRISM-TSE-16TC; Staffordshire, UK) with a screw diameter of 16 mm, length-to-diameter (L/D) ratio of 25, at an extrusion rate of 150 rpm. The processing temperature profile was 240/280/280/285/290°C, representing the temperatures at the hopper zone, the three barrel zones, and the die head, respectively. The extruded strand was immediately quenched in a water bath, subsequently chopped into pellets, and vacuum dried.

Fabrication of monofilaments

Monofilaments of neat PP and TLCP/PP blends were fabricated by a melt-spinning process using a mini-extruder (RCP-0625; Randcastle Extrusion System, Cedar Grove, NJ), with a screw diameter of 16 mm and L/D ratio of 24, equipped with a fiber line having a single-hole spinneret with a diameter of 1.15 mm. The temperature profile was 245/280/290/295°C, for the hopper zone, the two-barrel zones, and the die, respectively. The screw speed was fixed at 5 rpm. Immediately after the monofilament was extruded from the spinneret, it was quenched in a water bath and passed through a set of rotating godet at a takeoff speed 9 m/min. An as-spun monofilament of diameter about 450 μm with a draw ratio of about 7 (defined as the area ratio of the die and filament cross sections) was obtained at this stage. The filament prepared by this step will be denoted as as-spun monofilament throughout this work. It should be noted here that the monofilament of neat TLCP could not be prepared using the same conditions as described above because of its extremely low melt strength.

In the drawing step, the as-spun monofilament was drawn using the orienting fiber line supplied by Randcastle. Long as-spun filaments were fed through the slow set of rotating godet (diameter = 5 cm; speed = 2 rpm), passing into a silicone oil bath that was maintained at 120°C. The outgoing filament from the bath was taken up by the fast set of godet (diameter = 5 cm; speed 14 rpm), and drawn filaments with the final diameter of about 140 μm were obtained. A silicone oil bath was used instead of an air oven supplied by the manufacturer, to ensure temperature homogeneity. The drawing temperature at 120°C was chosen because it gave the highest value of tensile modulus. The draw ratio of the drawn filament at this stage was approximately 10. Taking into account the initial draw ratio 7 of the as-spun monofilament, the resulting

overall draw ratio of the final drawn monofilaments was therefore 70.

Morphology

Morphology of the cryogenic fracture surface of as-spun monofilament was investigated using a JEOL JSM-5410 (Tokyo, Japan) scanning electron microscope (SEM) operated with an accelerating voltage of 15 kV. The extruded strand and monofilaments were fractured in liquid N₂ and then coated with gold (JEOL JFC-1200) for enhanced surface conductivity.

To see the actual length of the dispersed TLCP fibrils, these were extracted from the matrix with hot xylene and observed under optical microscope (Olympus SC-35, Japan). The optical micrographs of extracted fibrils were taken at a magnification of $\times 40$.

Differential scanning calorimetry

Thermal properties of both as-spun and drawn monofilaments of neat PP and TLCP/PP blends were determined using a differential scanning calorimeter (DSC-7; Perkin-Elmer Cetus Instruments, Norwalk, CT). The samples were analyzed in the temperature range of 50–300°C in heating scan with a rate of 20°C/min under nitrogen atmosphere. The amount of the sample taken for each run was in the range 5–10 mg. The melting temperature and enthalpy of fusion of PP component were determined from the first heating scan to investigate the effect of processing history. The percentage of crystallinity (χ_c) of the PP component in the blend was calculated from the heat of fusion (ΔH_f) of the blend, by reference to the melting enthalpy of the 100% crystalline PP, $\Delta H_f^0 = 209 \text{ J/g}^{26}$:

$$\chi_c (\%) = \frac{\Delta H_f \times 100}{\Delta H_f^0 \times w} \quad (1)$$

where w is the weight fraction of PP in the blend.

Wide-angle X-ray diffraction

To compare the molecular orientation in the as-spun and drawn monofilaments, wide-angle X-ray scattering techniques were applied using a Philips X-ray generator (PW1730/10; Eindhoven, The Netherlands) equipped with a copper target tube, operated with a voltage of 40 kV and a current of 40 mA. A graphite crystal monochromator and a pinhole collimator were used to obtain the Cu-K α radiation ($\lambda = 1.5418 \text{ nm}$). Intensity measurements were made with the area detector (Photonic Science, East Sussex, UK) and area X-ray imaging system (AXIS).

Mechanical testing

Tensile tests of both as-spun and drawn monofilaments were performed at room temperature on an Instron 4301 (Instron Corp., Canton, MA), with a gauge length of 20 mm, extension rate of 50 mm/min, using a load cell of 100 N. At least 10 specimens were measured and averaged for each sample. Ultimate tensile strength, percentage elongation at break, and Young's modulus evaluated by the secant method are presented.

The dynamic mechanical thermal analysis (DMTA) was performed on a DVE-Rheospectoler (DVE-V4; Rheology, Kyoto, Japan) to obtain the dynamic modulus and the loss tangent of both as-spun and drawn monofilaments. The tensile mode was used with an oscillating frequency of 10 Hz and a displacement of 10 μm . The gauge length was set at 5 mm and the heating rate was 2°C/min in a flow of nitrogen. The samples were run from -50 to 300°C. The storage modulus (E') and the loss tangent $\tan \delta = E''/E'$ (where E'' is the loss modulus), were recorded as a function of temperature.

RESULTS AND DISCUSSION

Morphology

The morphologies of various specimens are shown in Figure 1. The figure is divided into two columns and each column shows the results obtained from the blends containing (a) 10 wt %, (b) 15 wt %, and (c) 20 wt % of TLCP. Column I illustrates the SEM micrographs ($\times 200$ magnification) of fracture surfaces of the as-spun monofilaments. Column II shows the optical micrographs ($\times 40$ magnification) of TLCP fibrils extracted from the corresponding as-spun monofilaments derived from column I. The fracture surfaces of as-spun monofilaments show pull-out features of the TLCP fibrils with increasing length and diameter as the TLCP content increases. Some of the TLCP fibrils in the central area are bigger than those located next to the surface of monofilament, especially in the sample with the highest TLCP content. This is attributed to the great tendency for the dispersed phase to coalesce as the TLCP content increases. Furthermore, the coalescence may also be enhanced by the migration of TLCP fibrils toward the middle part because of the velocity gradient of the molten polymer when it was extruded through the spinneret. Such migration and coalescence processes of the TLCP dispersed phase in extensional flow have been elucidated by Gao et al.²⁷ Fiber pull-out at the fracture surface is evidence for a low interfacial adhesion between the two phases. The actual length of TLCP fibrils can be seen in the optical micrographs (column II), where one sees that the extracted TLCP fibrils in all specimens have a substantial length, with diameter width in the range 2–16 μm .

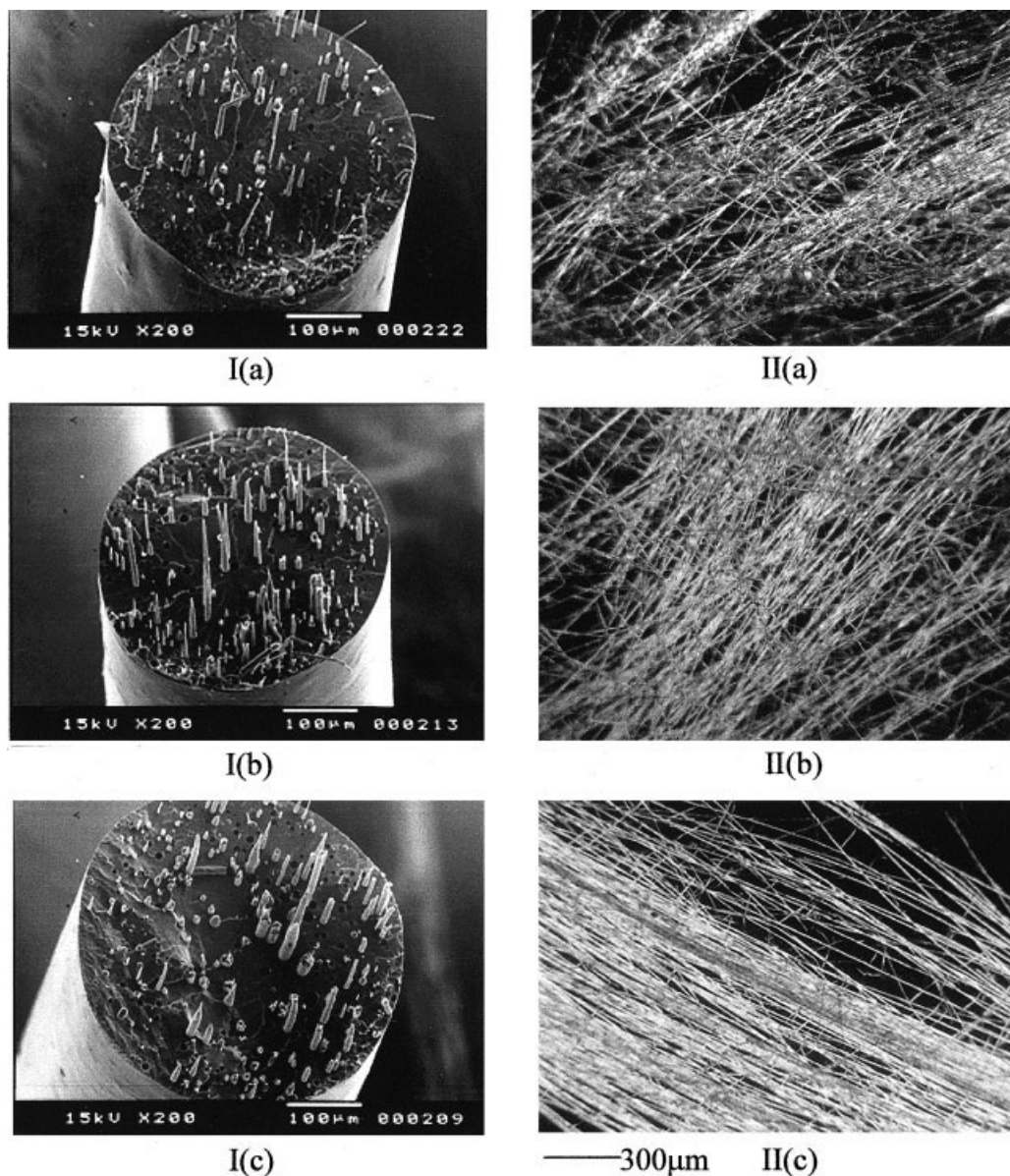


Figure 1 SEM micrographs of as-spun monofilament fracture surfaces (column I) and optical micrographs of extracted TLCP fibrils (column II) of the composites containing (a) 10 wt %, (b) 15 wt %, and (c) 20 wt % TLCP.

That means the fiber aspect ratio (length to width), l/d , is very high (mostly, $l/d > 100$).

The formation of extremely long TLCP fibrils is clear evidence that there is no premature solidification of TLCP phase at the exit die during drawing and illustrates the effectiveness of the extension of molten TLCP domains by elongational force through a narrow die (spinneret). As described in the experimental section, the as-spun filament obtained from the spinneret has actually been subjected to a draw ratio about 7, resulting in the generation of long TLCP fibrils. Further drawing of the filament at this first stage would not render an additional improvement of the modulus because it is well known from the Halpin-Tsai²⁸ prediction for Young's modulus of short fiber-

reinforced composites that the modulus approaches a constant value when the fiber aspect ratio is higher than 100, and this was also experimentally demonstrated by Crevecoeur et al.²⁹ Comparison with the fibril formation in the *in situ* composite films reported earlier by our group^{20-23,30} shows that fabrication of an *in situ* composite as monofilaments is a much more effective route to almost continuously long TLCP fibrils. The reinforcing fibrils with such a high aspect ratio provide effective transfer of stress at the interface, so they are expected to improve the mechanical properties of the composites.

For the drawn filaments, it was not possible to prepare cryogenic fracture surfaces because they were extremely tough. We also tried to extract the TLCP

fibrils from the drawn filament with hot xylene, but the filament shrank significantly. With such a contraction along the filament axis, the fibrils broke into small pieces; thus the true morphology of the drawn filaments could not be presented.

Thermal properties

DSC results of as-spun and drawn monofilaments of neat PP and blends containing 10 and 20 wt % TLCP are presented in Table I. The data shown in the table are the melting temperatures (T_m), heat of fusion of the blend (ΔH_f), and the degree of crystallization of the PP component (χ_c) calculated by eq. (1). Sample-to-sample variations in the DSC measurements were less than 0.8°C for T_m and less than 1% for χ_c . The melting temperatures of all as-spun filaments are approximately at 161°C, whereas those of the drawn filaments are higher (i.e., about 164°C). The shift of the melting point to higher temperature when the polymer specimen was drawn has been observed and explained to be attributed to the increase in extended-chain crystals, which have a higher melting point than that of the folded-chain crystals.^{31,32} The results in the present study reveal that the addition of TLCP into a PP matrix shows no significant influence on the melting temperature of the PP phase, but it has a substantial effect on the level of PP crystallinity. Incorporation of 10 wt % TLCP into a PP matrix leads to a few percent increase of PP crystallinity in the as-spun composite filament. At 20 wt % TLCP, no further marked increase in PP crystallinity could be detected. The enhancement in crystallinity of PP has been reported to be attributed to the nucleation induced by TLCP fibrils in which the molecules are more highly ordered.^{14,15} Similar results were reported by Seppälä et al.³³ for a blend of PP with Vectra A950. They found that blends containing 10% Vectra A gave the maximum PP crystallinity. Upon drawing the as-spun filament at 120°C, some remaining amorphous region and folding crys-

TABLE I
Thermal Properties of As-Spun and Drawn Monofilaments Obtained from the First Heating of DSC Scan: Melting Temperature (T_m), Heat of Fusion of the Blend (ΔH_f), and Degree of Crystallization of the PP Component (χ_c)

TLCP/PP (wt ratio)	T_m (°C)	ΔH_f (J/g)	χ_c (%)
As-spun monofilament			
0/100	161.3	90.7	43.4
10/90	162.0	86.3	45.9
20/80	161.1	97.6	46.7
Drawn monofilaments			
0/100	164.7	106.1	50.8
10/90	164.9	111.2	59.1
20/80	164.2	94.6	56.6

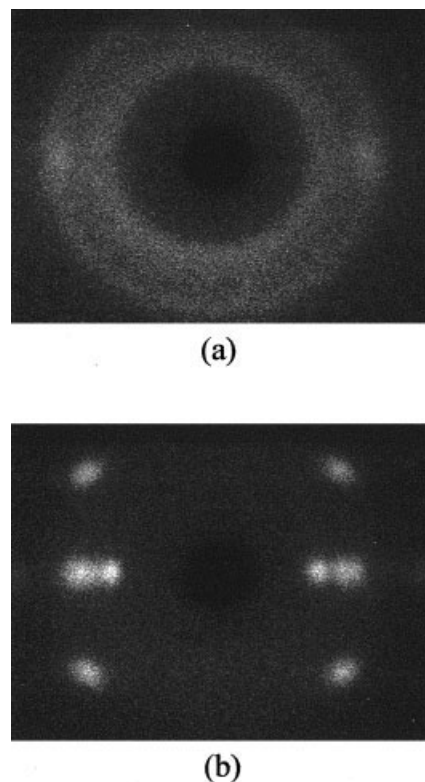


Figure 2 Wide-angle X-ray diffraction patterns obtained at room temperature of 20 wt % TLCP/PP *in situ* composite prepared as (a) as-spun monofilament and (b) drawn monofilament. The fiber axis is in the vertical direction.

tallites were forced to align to form unfolded crystals. Therefore the degrees of PP crystallization in the drawn neat PP and 10 wt % TLCP/PP filaments are about 7 and 13% higher than that in the corresponding as-spun filaments, respectively. The highest amount of PP crystallinity (59%) was observed in the drawn filament containing 10 wt % TLCP.

X-ray diffraction patterns

Figure 2(a) and (b) show two-dimensional X-ray diffraction patterns for as-spun and drawn monofilaments of 20 wt % TLCP/PP, respectively. The amorphous halo appearing in Figure 2(a) is apparently from the PP component in the as-spun filament. The two diffused spots on the equator that overlap with the outer ring apparently belong to the TLCP fibrils (monofilaments are aligned on the vertical axis). The crystalline reflections shown in Figure 2(b) clearly demonstrate the high molecular orientation of both components in the drawn filament, similar to that reported by Qin et al.¹⁵ The results clearly show that the molecules are highly ordered in the drawn filament and this supports the improvement in the mechanical properties discussed in the next section.

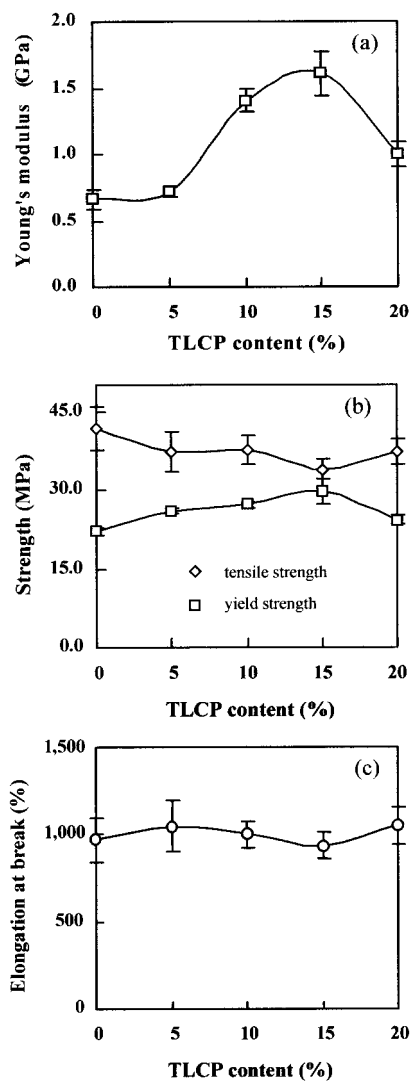


Figure 3 Tensile properties of as-spun monofilaments as a function of TLCP content: (a) Young's modulus, (b) yield and tensile strengths, and (c) elongation at break.

Tensile properties

The effects of the TLCP content on the tensile properties of the as-spun and drawn monofilaments are shown in Figures 3 and 4, respectively. For the as-spun monofilaments, the addition of TLCP has relatively little effect on the strength or elongation at break values. However, there is a substantial enhancement in the tensile modulus. The 15 wt % TLCP composite as-spun filament shows a maximum modulus of about 2.4 times that of the neat PP as-spun filament. This substantial increase is attributed to the reinforcement of the PP matrix by the uniaxial alignment of anisotropic TLCP fibrils with very high aspect ratios. The fact that this enhancement reaches a maximum for the 15% TLCP sample indicates that some coalescence of the fibrils has taken place in the 20% TLCP sample. This is confirmed by examination of the fracture surface shown in Figure 1. Although the modulus of the

as-spun filament shows a substantial enhancement through the addition of the TLCP, it is fair to say that the mechanical properties overall are rather modest because of the soft PP matrix, which exhibits the so-called smectic phase.³⁴ The tensile strength of the as-spun PP and the composite filaments is in the range 34–42 MPa. All filaments exhibit a yield point [Fig. 3(b)].

Further drawing of the filament at 120°C leads to major improvement of the mechanical properties through the generation of a highly oriented PP matrix, as can be seen from the X-ray pattern [Fig. 2(b)]. This leads to the expected increase in modulus of about 7 times for the neat PP and the filaments do not exhibit a yield point. Again the addition of the TLCP has little influence on the strength or elongation at break values. However, as for the as-spun monofilaments there

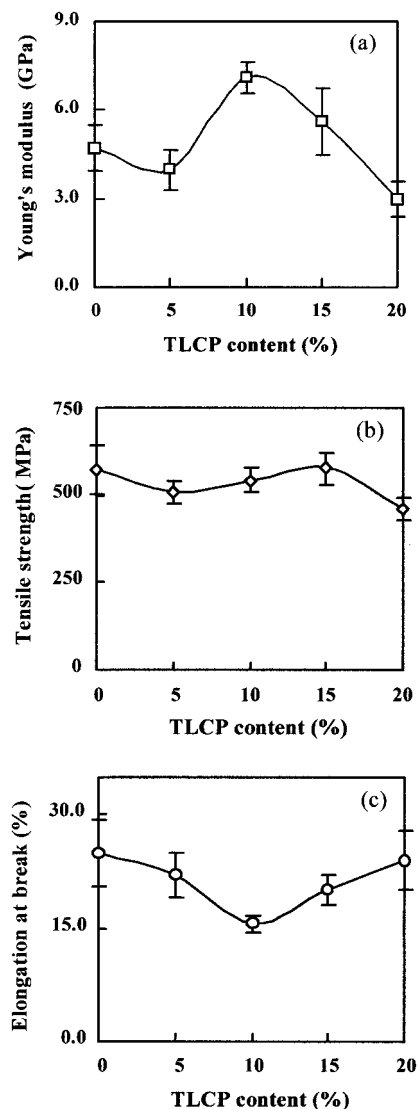


Figure 4 Tensile properties of drawn monofilaments as a function of TLCP content: (a) Young's modulus, (b) tensile strength, and (c) elongation at break.

TABLE II
Comparison Between Values of the Tensile Moduli of Neat PP and TLCP/PP Composite Prepared in the Forms of Monofilament, Injection-Molded, Film, and Plaque

Fabrication	%TLCP	Tensile modulus ^a		%Increase over PP	Reference
		Neat PP	TLCP/PP		
As-spun filament	10%LC5000	0.66 GPa	1.41 GPa	114%	This work
Drawn filament	10%LC5000	4.7 GPa	7.1 GPa	50%	This work
As-spun filament	10%LC3000	1.08 Ntex ⁻¹	1.21 Ntex ⁻¹	12%	15
Drawn filament	10%LC3000	13.49 Ntex ⁻¹	10.52 Ntex ⁻¹	-22%	15
As-spun filament	10%VectraA	1.08 Ntex ⁻¹	1.18 Ntex ⁻¹	3%	15
Drawn filament	10%VectraA	13.49 Ntex ⁻¹	14.01 Ntex ⁻¹	4%	15
Drawn filament	10%LC3000	8.53 Ntex ⁻¹	5.56 Ntex ⁻¹	-35%	18
Drawn filament	10%SBH	3.7 GPa	4.1 GPa	11%	6
Injection-molded	20%LC5000	0.91 GPa	1.62 GPa	52%	25
Film	10%LC5000	0.74 GPa	1.18 GPa	131%	37
Film	10%LC3000	0.62 GPa	1.09 GPa	117%	21
Plaque	20%LC3000	1.38 GPa	1.63 GPa	18%	11
Plaque	20%VectraA	1.38 GPa	2.56 GPa	85%	11

^a 1 tex = weight in grams of 1-km-long filament.

is a significant variation of the modulus with TLCP content in the drawn filaments. The maximum enhancement is observed for the 10 wt % TLCP drawn composite filament (7.1 GPa), an increase of about 1.5 times that of the pure drawn PP filament (4.7 GPa). It was found that a draw temperature of 120°C resulted in the maximum enhancement in modulus over that of the pure PP filament. At this temperature, the TLCP is solid and hence at best the TLCP fibrils remain unchanged. However, although it is the case that further drawing leads to an overall modulus enhancement, there is clearly one or more factors to be accounted for. The modulus of the 20 wt % TLCP drawn filament is lower than that of the pure drawn PP filament and the enhancement ratio compared to PP for the drawn filament is lower than that for the as-spun filaments. We attributed this to some breakage of the TLCP fibrils during drawing at 120°C and to some debonding at the PP/TLCP interface. In fact, it would appear from simple inspection of the data [comparing Figs. 3(a) and 4(a)] that the level of reduction from the "optimum" values increases with increasing fraction of the TLCP. In other words, the secondary drawing after the spinning substantially enhances the modulus of the matrix but also degrades the effectiveness of the reinforcement by the dispersed TLCP phase.

For short fiber-filled composites, the longitudinal modulus of the composite (E_c) is related to the fiber modulus (E_f), matrix modulus (E_m), and fiber aspect ratio by the well-known Halpin-Tsai equation²⁸:

$$\frac{E_c}{E_m} = \frac{1 + ABX}{1 - BX} \quad (2)$$

where X is the fiber volume fraction and

$$B = \left[\frac{E_f}{E_m} - 1 \right] / \left[\frac{E_f}{E_m} + A \right] \quad (3)$$

The quantity A is equal to $2(l/d)$, where l/d is the length-to-diameter ratio (aspect ratio) of the fibers. From our results, using the measured values for the drawn 10 wt % TLCP/PP filament, $E_c = 7.1$ GPa, $E_m = 4.7$ GPa, l/d assumed to be 100, and $X = 0.07$; the calculated E_f value for TLCP fiber is about 40.7 GPa. This derived value is in good agreement with the value of 40 GPa measured by Zachariades³⁵ for Rodrun LC5000 neat filaments. Nagamae et al.³⁶ used X-ray techniques to evaluate the modulus of 105 GPa for crystalline regions of LC5000. In this work, the modulus of the TLCP fibrils has contributions from both crystalline and noncrystalline components.

We have compared the moduli of as-spun and drawn monofilaments obtained in this work with those reported in the literature, emphasizing the cases where a low content of TLCP (up to 20%) was incorporated. Table II compares the values of tensile moduli for the PP matrix and the *in situ* composites that were fabricated in different forms, including monofilaments,^{6,15,18} injection-molded specimens,²⁵ films,^{21,37} and plaques.¹¹ It can be seen that the drawn filaments prepared in this work show a higher modulus than that reported for composite filaments containing LC3000 and SBH (a copolyester of sebacic acid, hydroxyl benzoic acid, and 4-4'-hydroxybiphenyl). It is interesting to note that the addition of a TLCP does not always lead to an enhancement of the modulus (see Qin et al.¹⁵ and Miller et al.¹⁸). This in part may be attributed to the lower mechanical performance of the TLCP fiber itself (LC3000 in the studies by Qin and Miller and colleagues just cited), as well as the processing conditions. The use of a specific modulus in

the data reported in Qin et al.¹⁵ and Miller et al.¹⁸ results in an apparently lower enhancement as a result of the difference in densities between PP and the TLCP. Not surprisingly, the drawn filament prepared in this work exhibits a higher modulus than those reported in composites in the form of films and moldings. However, the as-spun filaments exhibit moduli in broad accord with those found in films and moldings, suggesting that in all those systems the flow field and thermal profile generates a soft isotropic PP matrix, as observed in this work. It is interesting to note that where the same matrix and TLCP have been used (this work and Saengsuwan et al.³⁷), there is a similar enhancement in the modulus despite the difference in geometry of the final products.

By comparing all the results shown in Table II, it can be concluded that the improvement in the modulus of the *in situ* composite drawn monofilaments obtained in this work is relatively high (i.e., from 4.7 GPa in the neat drawn PP filament to 7.1 GPa after incorporation of 10 wt % LC5000).

Dynamic mechanical thermal properties

DMTA scans for as-spun and drawn monofilaments are shown in Figures 5 and 6, respectively. Each figure presents the plots of (a) logarithmic storage modulus (E') and (b) loss tangent ($\tan \delta$) versus temperature for neat PP and blends containing 10 and 20 wt % TLCP. From Figure 5(a), it is seen that the storage moduli of the blend as-spun monofilaments are significantly higher than that of the neat PP over the whole range of temperatures being investigated. For example, the E' values at 25°C for as-spun monofilaments of neat PP and the composite with 10 wt % TLCP are 0.79 and 1.9 GPa, respectively. When the temperature increases, the storage modulus of PP as-spun filament decreases much faster than that of the blends. This is attributed to the reinforcement effect of the TLCP fibrils. Therefore, both the dimensional stability and the thermal stability of the as-spun blend monofilaments are much improved over those of the as-spun neat PP monofilament.

In the case of drawn filaments [Fig. 6(a)], a very substantial increase in storage modulus of all specimens compared to that of the as-spun filaments is achieved as a consequence of the high molecular orientation in the PP phase, as evident in the X-ray pattern. The increase in storage moduli of the drawn filaments is in good agreement with the increase in the values of Young's moduli. In the temperature region below 70°C, E' values of the drawn neat PP and blends are nearly the same. This demonstrates the important role of the matrix. However, in the temperature region higher than 70°C, the moduli of the blends are somewhat higher than that of the neat PP. The improvement arises from the reinforcing effect of TLCP fibrils,

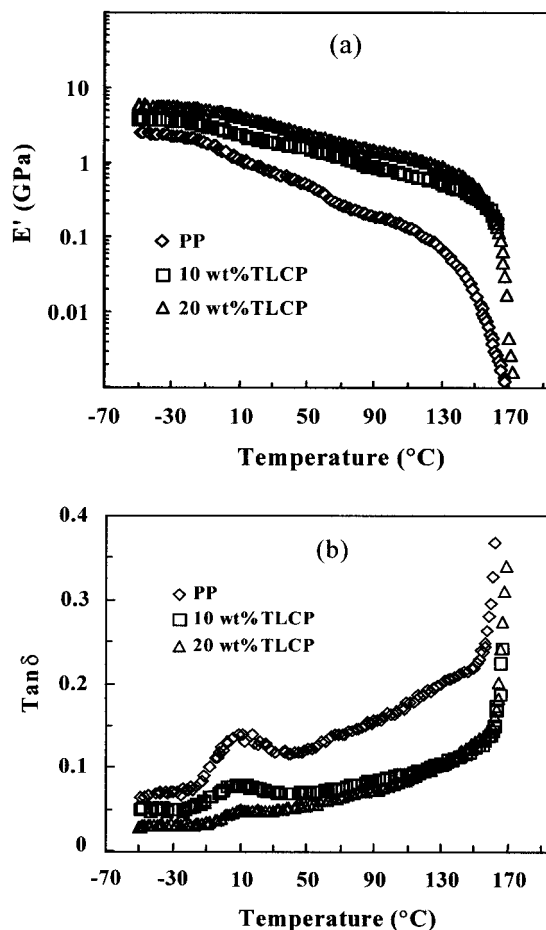


Figure 5 Storage modulus (a) and $\tan \delta$ (b) as a function of temperature for the as-spun monofilaments of neat PP and the blends containing 10 and 20 wt % TLCP.

which are more thermally stable than the PP matrix and inhibit relaxation of the PP matrix.

In Figures 5(b) and 6(b), the $\tan \delta$ curves are shifted along the vertical axis to avoid overlap. The $\tan \delta$ versus temperature plots of as-spun monofilaments presented in Figure 6(b) show only one peak around 10°C, corresponding to the glass transition (β -relaxation) of the PP component, as previously reported by Gupta et al.³⁸ and Amash et al.³⁹ Upon drawing, this peak disappears and a new broad peak occurs around 100°C [see Fig. 6(b)]. The suppression of the peak at 10°C indicates the reduction of the molecular mobility that results from the increasing degree of orientation in the PP matrix. The new broad peak that appeared around 100°C is attributed to the crystalline α -relaxation of PP as described by Amash et al.³² A small shift of the loss peak to higher temperature in the blends compared to the neat PP arises from an increase in the PP crystallinity upon blending with TLCP, as evident and already discussed in the DSC results. In addition, the decrease in the peak area of $\tan \delta$ in the blend is attributed to the decrease in PP content. From the DMTA results, it can be concluded that the modulus

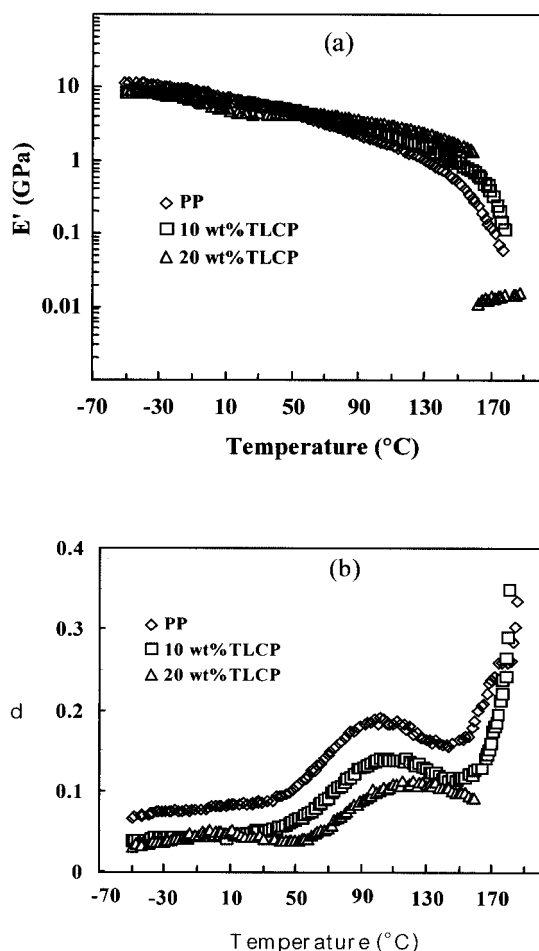


Figure 6 Storage modulus (a) and $\tan \delta$ (b) as a function of temperature for the drawn monofilaments of neat PP and the blends containing 10 and 20 wt % TLCP.

as well as the thermal stability of both as-spun and drawn PP monofilaments can be enhanced by incorporation of TLCP fibrils.

CONCLUSIONS

Immiscible blends of PP with TLCP (80/20 mol ratio of copolyester HBA/PET) were prepared in a twin-screw extruder and fabricated in the form of monofilament using a mini-extruder equipped with a fiber line. The morphology, thermal properties, molecular orientation, and both tensile and dynamic mechanical properties of both as-spun and drawn monofilaments were investigated. It was observed that almost continuously long TLCP fibrils were formed in the as-spun monofilament, resulting in an effective reinforcement of the PP matrix. The as-spun filament of 15 wt % TLCP/PP displayed a maximum improvement in Young's modulus (i.e., about 2.4 times that of the as-spun filament of neat PP). After drawing the as-spun filaments at 120 $^{\circ}\text{C}$, the drawn filaments exhibited an almost three- to sevenfold increase in Young's

moduli and an approximately 12- to 17-fold increase in tensile strength compared with that of the as-spun filaments. The drawn monofilament of 10 wt % TLCP/PP showed the highest modulus (i.e., about 1.5 times that of the drawn filament of neat PP). The lower level of enhancement in the tensile modulus with the addition of the TLCP for the drawn composite filament might be attributed to fiber breakage during the cold drawing at 120 $^{\circ}\text{C}$. In conclusion, the improvement in tensile moduli of the composite monofilaments is attributed to the reinforcement by TLCP fibrils with very high aspect ratio, together with the increase in the crystal structure in PP matrix through nucleation by TLCP fibrils and the enhancement of molecular orientation. Dynamic mechanical properties of both as-spun and drawn composite monofilaments also showed a substantial improvement compared with those of the neat PP filaments, especially in the high-temperature region, as a result of the more thermally stable TLCP fibrils, which inhibit relaxation of the PP matrix.

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