

In-situ Composite Film of Thermotropic Liquid Crystalline Polymer/Polypropylene: Effect of Film Drawing on Molecular Orientation and Properties

Jareerat Samran^a, Wiriya Meesiri^b, Sauvarop Bualek-Limcharoen^c and Taweechai Amornsakchai^c

^a Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand.

^b Directorate of Armament, Royal Thai Air Force, Donmuang, Bangkok 10210, Thailand.

^c Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand.

* Corresponding author.

Received 5 Feb 1999

ABSTRACT A Blend of thermoplastic, polypropylene, with a thermotropic liquid crystalline polymer (TLCP), copolyester comprising 60 mol% of p-hydroxybenzoic acid and 40 mol% ethylene terephthalate was prepared, using a twin screw extruder. Polymer blend pellets were extruded through a microtruder as thin films, using different draw ratios. Effect of film drawing on molecular orientation and properties was investigated. The order parameter of liquid crystalline domain evaluated from polarized infrared spectra was found to increase with increasing film draw ratio. Morphology of the film observed under an optical microscope revealed increasing TLCP fibre aspect-ratio. Young's modulus of the film measured in the machine direction was found to increase significantly with increasing TLCP fibre aspect-ratio and molecular ordering. Young's modulus of TLCP fibres embedded in PP matrix was estimated using the Halpin-Tsai equation and found to correlate linearly with the fibre aspect-ratio and the order parameter.

KEYWORDS: *In-situ* composite, thermotropic liquid crystalline polymer, film drawing, molecular orientation.

INTRODUCTION

Main chain thermotropic liquid crystalline polymers (TLCPs) are known to possess good thermal and mechanical properties and high dimensional stability.¹ Blends of TLCPs with various kinds of thermoplastics to improve processability and properties of the latter have been intensively investigated.²⁻⁶ These are incompatible blend systems comprising a dispersed phase, i.e. droplets of TLCP, which deform into fibres by elongational force during melt processing. Following melt solidification, the TLCP fibres are frozen in the matrix and hence reinforced the product in a similar manner as the short-fibre reinforced composites. Therefore the name "*in situ* composite" was coined for such a self-reinforced system.⁷

TLCP was found to improve the mechanical properties of the matrix to various degrees depending on processing procedures and conditions which affect morphology and molecular orientation of the blends.⁸⁻⁹ For a thick product like an injected bar, the skin-core effect was found to occur.¹⁰ The skin of the moulded part exhibited longitudinally oriented TLCP fibrils, whereas droplets were formed in the core region. Morphology of the product developed

in the mould depends very much on mould thickness, processing temperature and speed of injection. This in turn results in composites with different mechanical properties. Other forms of composites such as filaments¹¹⁻¹² and films¹³⁻¹⁴ have also been investigated. For these thin-wall specimens the skin-core effect is minimized. However, in the case of blown or extruded films, there is a major problem of anisotropy in physical properties, i.e. the properties measured in the direction along the flow path (machine direction, MD) are different from that in the transverse direction (TD). This problem has been solved to some extent by using a counter-rotating die for thin film extrusion.¹⁵

Correlation of the processing conditions to molecular orientation and mechanical properties of pure TLCP produced as extruded rod and fibres has been investigated.¹⁶⁻¹⁸ The increase in drawn-down ratio was found to increase birefringence, i.e. the difference of refractive indices measured in directions parallel and perpendicular to the fibre axis, which indicated the improvement of molecular orientation.¹⁹ For the *in situ* composite, the elongational flow field was not sufficient to increase the orientation function of TLCP.²⁰ Greater TLCP fibril elongation could be achieved at the exit of the die during spinning of the blend.

In this work, a blend system of polypropylene and TLCP (Rodrun LC3000, a copolyester comprising 60 mol% of p-hydroxybenzoic acid and 40 mol% ethylene terephthalate) was investigated. It is of interest to improve the properties of a commodity polymer like polypropylene. Rodrun LC3000 is chosen to reinforce PP because of their overlapping windows of processing temperature. The specimen was prepared as an extruded film. Thin film has advantages over an injection-moulded specimen, due to the absence of skin-core effect and weld line. For thin film, it is quite simple to evaluate the molecular orientation from the measurement of transmission spectra in the infrared region. Particular attention has focused on the effect of film drawing on the molecular orientation in TLCP fibres and their aspect ratio, and consequently, tensile modulus of the composite.

EXPERIMENTAL

Materials

A thermoplastic polymer matrix used in this study was injection grade polypropylene (PP6331 HMC, Thailand), density = 0.903 g cm⁻³, measured melt flow rate (MFR) 17 g/10 min at 230°C, 2.16 kg loading). Thermotropic liquid crystalline polymer (TLCP) was a copolyester comprising 60 mol% p-hydroxybenzoic acid and 40 mol% ethylene terephthalate (Rodrun LC3000), density 1.4 g cm⁻³, mesophase range from 220 to 280°C, purchased from Unitika Company. TLCP pellets were vacuum dried at 60°C for 12 h before use.

Blending

Melt blending of polypropylene (PP) and 10 wt% TLCP was performed using a co-rotating twin screw extruder (PRISM TSE-16TC) with a screw diameter of 16 mm, L/D 25, intermeshing, at a fixed screw speed of 150 rpm. The processing temperature profile was 180/220/220/225/225°C, representing temperatures at hopper zone, three barrel zones, and heating zone in die head, respectively. Strand exiting the extruder was immediately quenched in a water bath and subsequently pelletized.

Film Extrusion

TLCP/PP blend pellets were extruded using a 16-mm mini-extruder (Randcastle RCP-0625) equipped with a cast film line. The temperature profile was 190/220/230/240°C for the hopper zone, two barrel zones, and slit-die, respectively. Screw speed was 70 rpm. The gap of the die lip was adjusted at 0.65 mm

and the width fixed at 152 mm. Extruded film was drawn as molten blend exiting the die outlet, then quenched on a water-cooled roll and collected by a film assembly with adjustable take-off speed. The film was drawn at the draw ratio (slit width-to-film thickness ratio) of 9, 19 and 33 by adjusting the take-off speeds at 1.6, 3.8 and 6.4 m/min respectively. Film thickness was varied from approximately 20 to 70 µm.

Morphology

Morphology of the thin composite films was directly observed under a polarized optical microscope (Olympus) at the magnification range of 100 to 200 times. Fibre distribution as well as the texture of TLCP phase was also observed. However, for the film thicker than 25 µm, it was quite difficult to see the real domain size, because of the overlapping of fibres in different layers, and hence some areas were out of focus. In order to observe the fibres more clearly, a small piece of each film specimen was extracted with boiling xylene and the TLCP fibres were filtered through a sieve of 200 mesh. The extracted fibres were observed under an optical microscope and the distribution of the fibre aspect-ratio (length-to-diameter ratio) was determined from at least one hundred fibres.

Order Parameter

The order parameter or orientation function (*S*) of the nematic liquid crystalline phase is defined as the following equation,²¹

$$S = 0.5 \langle 3\cos^2\theta - 1 \rangle \quad (1)$$

where θ is the angle between the axis of mesogenic unit and the preferred direction of the nematic phase. $S = 1$ for a phase comprising perfectly aligned molecules and $S = 0$ for the case of random alignment. Infrared dichroism is one of the simple techniques often used to determine the order parameter of liquid crystalline phase.^{17-18,22-24} Absorbance values were measured: A_{\parallel} and A_{\perp} for plane polarized light with the electric vector parallel and perpendicular to the preferred direction (the machine direction), respectively. The dichroic ratio *R*, defined as $R = A_{\parallel}/A_{\perp}$, for a particular absorption band is used to calculate the order parameter from the following equations:

$$S = \frac{(R - 1)}{(R + 2)} \frac{1}{0.5 (3 \cos^2\alpha - 1)} \quad (2)$$

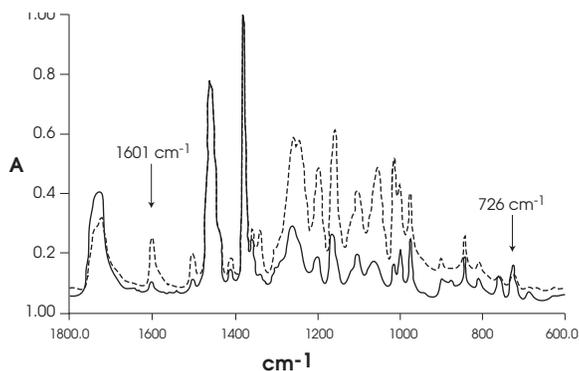


Fig 1. Polarized IR absorption spectra of TLCP/PP recorded at the positions of polarizer parallel (-----) and perpendicular (—) to machine direction of the film.

where α is the angle between the transition moment and the major molecular axis. This equation is reduced to

$$S = (R - 1) / (R + 2) \text{ where } R > 1 \quad (3)$$

for a band whose transition moment is parallel to the major molecular axis (parallel transition moment) and

$$S = 2(1 - R) / (R + 2) \text{ where } R < 1 \quad (4)$$

for a band whose transition moment is perpendicular to the major molecular axis (perpendicular transition moment).

The order parameter of the TLCP phase in TLCP/PP blend was evaluated from the IR absorption spectra measured using Perkin-Elmer FTIR (system 2000) with an aluminium wire-grid polarizer placed in the sample compartment, next to the film specimen. FTIR spectra were recorded at the polarization directions of the polarizer parallel and perpendicular to the machine direction of the film (see Fig 1). Areas under two peaks, the parallel band at 1601 cm^{-1} and perpendicular band at 726 cm^{-1} (corresponding to C-C stretching vibration and C-H out-of-plane bending of para-substituted benzene ring), were used to determine order parameters of TLCP utilizing equations (3) and (4), respectively.

Tensile Testing

Tensile testing was conducted using an Instron mechanical tester (Model 4301), with a grip length of 25 mm, crosshead speed of 50 mm/min, and a full-scale load of 10N. Tensile properties of the dumbbell-shaped specimens (70 mm x 4 mm) were measured

in the machine (MD) and transverse (TD) directions, according to ASTM D412. Each data point was an averaged value obtained from at least ten specimens.

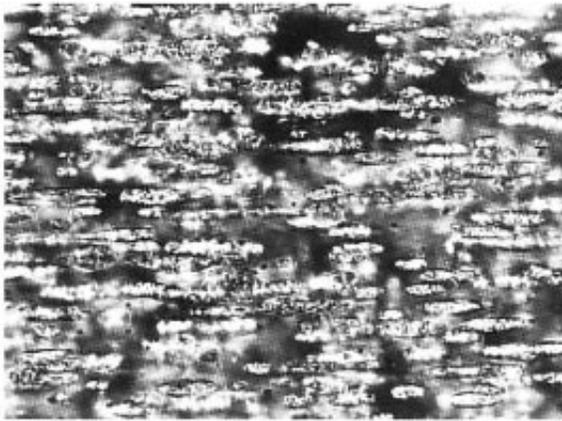
RESULTS AND DISCUSSION

Morphology

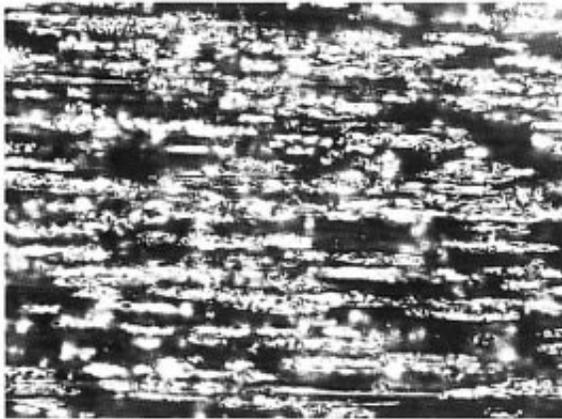
The optical micrographs shown in Figs 2 - 3 are obtained from the TLCP/PP films produced at the draw ratios of 9, 19 and 33. Figs 2a - 2c are photographs of the films, while Figs 3a - 3c are those of TLCP fibres extracted from the films, using hot xylene. The optical micrograph shown in Fig. 2a was taken from the film prepared at the lowest draw ratio. This film is quite thick (ca. $70 \mu\text{m}$) and therefore shows some regions that are out of focus. It can be clearly seen that the apparent aspect ratio of TLCP fibres in this figure is the shortest compared to Figs. 2b and 2c. In addition, it shows a typical schlieren texture of nematic phase which reveals the inhomogeneity of molecular orientation. On the other hand, the texture of TLCP fibres (bright lines) in Fig 2c, which produced at the highest draw ratio, is the most homogenous. This suggests the highest degree of molecular orientation of TLCP domains in the film. In order to see the size and shape of TLCP fibres more clearly, the composite films were extracted with boiling xylene. Photographs of extracted fibres are shown in Figs 3a - 3c. From several photographs, the fibre length (l) and width (d) were measured, and the fibre aspect-ratio (l/d) were calculated. Distribution curves of TLCP fibre aspect-ratio, measured from about one hundred fibres for each specimen of different draw ratios, are presented in Fig 4. From the film of draw ratio 9, the mean fibre aspect-ratio obtained is about 10, with rather narrow range of distribution. Fibres with very small aspect ratio may be filtered out through the sieve. TLCP Fibres extracted from the film of draw ratio 19 and 33 show broader range of distribution and the mean aspect ratio of about 40 and 80, respectively. However, short fibres are also found in the last two cases, which may arise from breakage of long fibres. In general, it can be clearly seen that as the film draw ratio increases, TLCP fibres are more elongated, *ie* the fibre aspect-ratio increases. These results agree with the increase of tensile modulus of the films, discussed in the next section.

Order Parameter

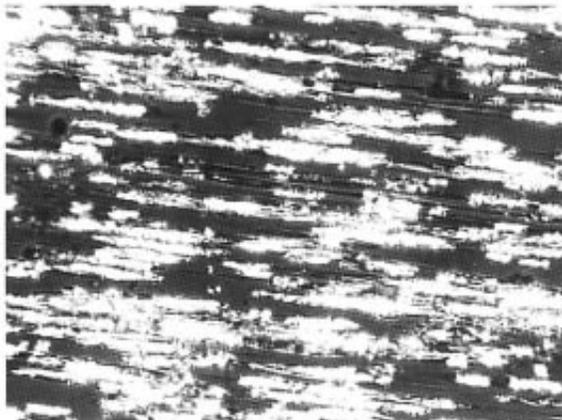
The molecular orientation in polymer specimen is known to determine its strength and stiffness. Hence the order parameter is related to the modulus



(a)

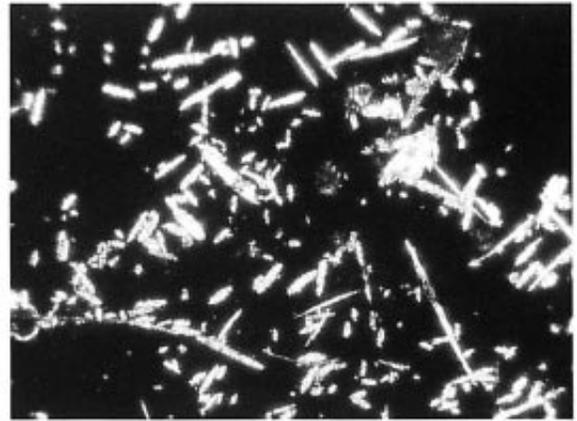


(b)

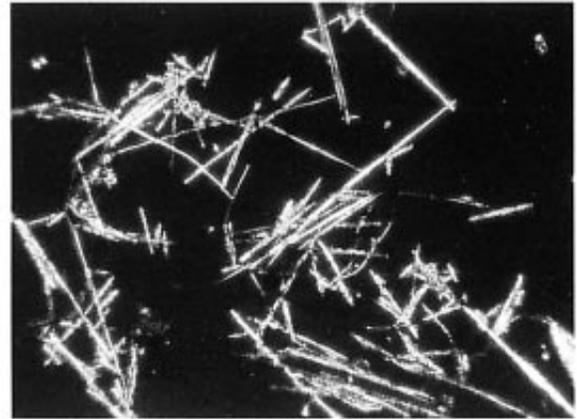


(c)

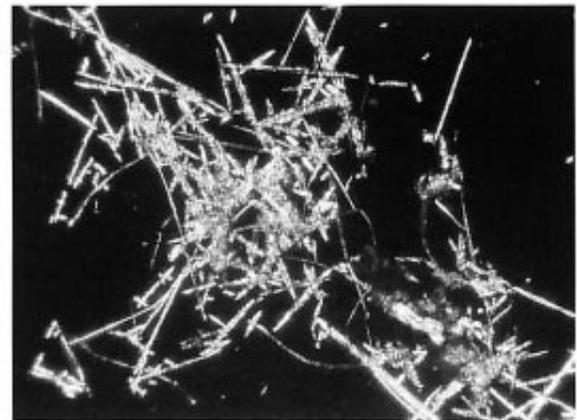
Fig 2. Optical micrographs of TLCP/ PP films produced at different draw ratios,
 (a) 9 (b) 19 (c) 33.



(a)



(b)



(c)

Fig 3. TLCP fibres extracted from films produced at different draw ratios,
 (a) 9 (b) 19 (c) 33.

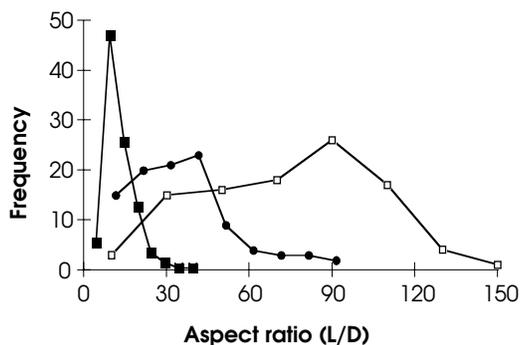


Fig 4. Distribution of aspect-ratio of TLCP fibres obtained from film produced at draw ratios: ■ 9, ● 19 and □ 33.

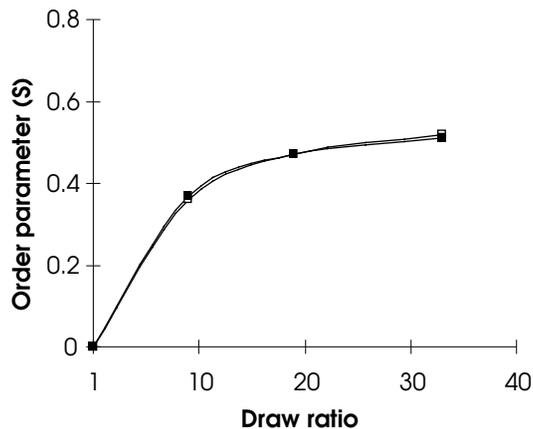


Fig 5. Effect of draw ratio on order parameter of TLCP fibres calculated from the peaks at 1601 cm⁻¹ (□) and 726 cm⁻¹ (■).

of the polymer. The molecular ordering in TLCP phase embedded in PP matrix ought to be one of the parameters determining the strength the fibres which contributes to the composite properties. For thin film specimens, it is rather simple to determine molecular orientation from the anisotropy of absorption spectra (dichroism), especially in the infrared region. Since the selected absorption bands used to measure the dichroic ratio belong to the benzene ring in TLCP molecule, the calculated order parameters, therefore, represent only the molecular orientation of the TLCP phase. The order parameters of TLCP in the composite film plotted as a function of draw ratio are illustrated in Fig 5. The order parameter of TLCP phase is found to increase from 0.37 to 0.52 as the draw ratio increases from 9 to 33. Assuming that without drawing, $S = 0$, ie TLCP appears as spherical droplets, the curves start from the origin. The order parameters calculated from two peaks, at 1601 and 726 cm⁻¹, yield the same results.

Tensile properties

Young's moduli of pure PP and TLCP/PP films prepared at different draw ratios are shown in Fig. 6. The reported results are obtained by measuring in the machine direction (MD) and transverse direction (TD).

Pure polypropylene film, produced using the same processing condition as TLCP/PP composite, exhibits nearly isotropic modulus, i.e., the moduli in both MD and TD are nearly equal. Increasing of draw ratio has no significant influence on the modulus of PP. This might be due to the high flexibility of PP polymer chain and rapid relaxation of these molecules.

The MD modulus of the composite TLCP/PP

film markedly improves with increasing draw ratio. The MD modulus of the composite produced at the draw ratio 33 increases by about 30% from that of the composite film produced at the draw ratio 9 and by about 77% from that of pure PP prepared at draw ratio 33. The results are apparently due to the reinforcement of TLCP fibres and the higher fibre aspect ratio formed at higher degree of film drawing.

For short fibre-filled composites, the longitudinal moduli of the composite (E_c) is related to the fibre modulus (E_f) and matrix modulus (E_m) and fibre aspect-ratio by the well-known equation of Halpin-Tsai²⁵.

$$\frac{E_c}{E_m} = \frac{1 + ABX}{1 - BX} \tag{5}$$

where X is the fibre volume fraction and

$$B = \left[\frac{E_f}{E_m} - 1 \right] / \left[\frac{E_f}{E_m} + A \right] \tag{6}$$

The quantity A is equal to 2(l/d), where l/d is the length to diameter ratio (aspect ratio) of the fibres. We predict the modulus of TLCP fibres embedded in PP matrix by rearranging the Halpin-Tsai equation as,

$$E_f = \frac{E_c(A + X) + AE_m(X - 1)}{\frac{E_c}{E_m}(X - 1) + (XA + 1)} \tag{7}$$

From our results, using the measured values of E_c , E_m , and l/d and $X = 0.07$, the calculated E_f at the film draw ratio of 9, 19 and 33, are 2.99, 6.64 and 7.86 GPa, respectively. The highest value of the modulus is close to the value of flexural modulus of pure TLCP

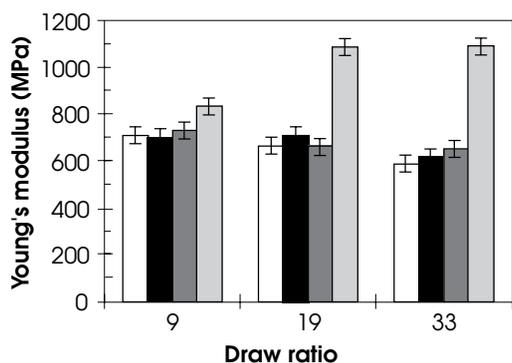


Fig 6. Young's moduli of PP and TLCP/PP films prepared at different draw ratios, measured in machine direction (MD) and transverse direction (TD).

□ PP(TD) ■ PP(MD) ▒ PP/TLCP(TD) ▒ PP/TLCP(MD)

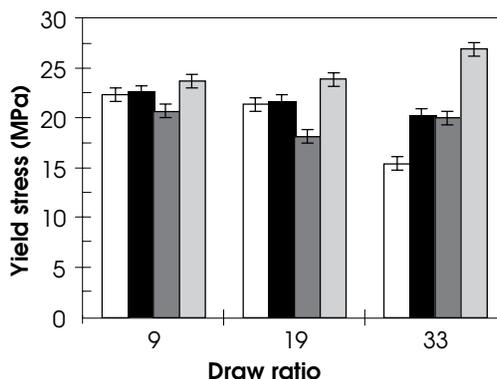


Fig 7. Yield stresses of PP and TLCP/PP films prepared at different draw ratio, measured in machine direction (MD) and transverse direction (TD).

□ PP(TD) ■ PP(MD) ▒ PP/TLCP(TD) ▒ PP/TLCP(MD)

reported by the manufacturer, ie 9.3 GPa. However, it is much lower than elastic modulus of pure TLCP as spun fibre, prepared at a every high draw ratio of 100, which was reported by Dibenedetto¹⁶ at about 35 GPa. The reason for this large difference could be due to the broad distribution of fibre aspect ratio in our sample. The calculated values of E_f are found to correlate linearly with fibre aspect-ratio and also with the order parameter of TLCP phase.

On the other hand, the TD moduli of pure PP and TLCP/PP composite are not significantly affected by increasing film draw ratio. In accordance with the composite theory,^{2,25} the TD modulus of the composite can be estimated by the inverse rule of mixture :

$$\frac{1}{E_c} = \frac{X}{E_f} + \frac{(1-X)}{E_m} \quad (8)$$

For small X, the TD modulus of the composite is dominated by that of the matrix and independent of fibre aspect ratio.

Yield stresses of PP and TLCP/PP films, produced at different draw ratios, measured in both directions are shown in Fig 7. Yield stresses in MD direction of the composite are slightly higher than that of pure PP at draw ratio 9 and 19, but are about 34% improved in the composite at draw ratio of 33. The difference in MD and TD yield stresses of the composite film is larger than that of PP film because of the different morphology of the two systems. When the composite is being stressed perpendicularly to the fibre axis of the dispersed phase, the ends of TLCP fibres with small radius of curvature

could act as stress concentrators.²⁵ Consequently, anisotropy of yield stress of composite films is expected to be higher than that of PP.

It can be concluded that increase of film draw ratio provided an increase in order parameter of TLCP phase and fibre aspect ratio, which match the mechanical results, ie the enhancement of MD Young's modulus. This summarized that better molecular orientation in TLCP phase translates to the better mechanical properties of TLCP,^{17,24} and hence better composite properties.

CONCLUSION

In situ composite films of 10 wt% TLCP/PP were prepared at different draw ratios by extrusion cast film technique. Order parameter of TLCP phase was determined from infrared dichroism. Film morphology was observed under optical microscope and their tensile properties were measured. It was found that as the film draw ratio increased, the fibre aspect ratio increased and so did the order parameter. These results are in good agreement with the enhancement of the film modulus. The modulus of TLCP fibres embedded in PP matrix estimated from the Halpin-Tsai equation was found to correlate well with the order parameter and the aspect ratio of TLCP phase.

ACKNOWLEDGMENT

The financial support of The Thailand Research Fund is gratefully acknowledged.

REFERENCES

1. Luise, RR (1997) in *Applications of High Temperature Polymers*, (Edited by Luise, RR) pp 25-40. Plenum Press, New York.
2. Dutta D, Fruitwala H, Kohli A and Weiss RA (1990) Polymer blends containing liquid crystals: a review. *Polym Eng Sci* 30, 1005.
3. Brown CS and Alder PT (1993) in *Polymer Blends and Alloys*, (Edited by Folkes, MJ and Hope, PS), pp 195-227. Blackie Academic & Professional, Glasgow.
4. Handlos AA and Baird DG (1995) Processing and associated properties of *in situ* composites based on thermotropic liquid crystalline polymers and thermoplastics. *JMS Rev Macromol Chem Phys C35*, 183-238.
5. Machiels AGC, Denys KFJ, van Dam J Nd and de Boer AP (1996) Formation, stability and properties of *in situ* composites based on blends of a thermotropic liquid crystalline polymer and a thermoplastic elastomer. *Polym Eng Sci* 36, 2451-66
6. Jin X and Li W (1995) Correlation of mechanical properties with morphology, and processing parameters for thermotropic liquid crystalline polymer-containing blends. *JMS Rev Macromol Chem Phys C35(1)*, 1-13.
7. Kiss G (1987) *In situ* composites: blends of isotropic polymers and thermotropic liquid crystalline polymers. *Polym Eng Sci* 27, 410.
8. Heino MT, Hietaoja PT Vainio TP and Seppala JV (1994) Effect of viscosity ratio and processing conditions on the morphology of blends of liquid crystalline polymer and polypropylene. *J Appl Polym Sci* 51, 259-70
9. Hull JB and Jones AR (1996) in *Rheology and Processing of Liquid Crystalline Polymers*, (Edited by Arcierno D and Collyer, AA), pp 218-50. Chapman & Hall, London.
10. Baird DG and Wilkes GL (1983) Sandwich injection molding of thermotropic copolyesters and filled polyester. *Polym Eng Sci* 23, 632-6.
11. Qin Y (1994) On the *in situ* generation of reinforcing fibers. *J Appl Polym Sci* 54, 735-42.
12. Qin Y (1994) Drawing behavior of Polyblend fibers from polypropylene and liquid crystal polymers. *J Appl Polym Sci* 54, 873-80.
13. Crevecoeur G and Groeninckx G (1993) Sheet extrusion of *in-situ* composites : influence of processing parameters. *Polym.Eng.Sci.*, 33, 937-43.
14. Hsu TC, Lichkus AM and Harrison IR (1993) Liquid crystal polymer/polyethylene blends for thin film applications. *Polym Eng Sci* 33, 860-62.
15. Chinsirikul W, Hsu TC and Harrison IR (1996) Liquid crystalline polymer (LCP) reinforced polyethylene blend blown film: effect of counter-rotating die on fiber orientation and film properties. *Polym Eng Sci* 36, 2708-17.
16. De Benedetto AT, Nicolais L, Amendola E, Carfagna C and Nobile MR (1989) The effect of hot drawing on the properties of thermotropic polymer fibers. *Polym Eng Sci* 29, 153-62.
17. Kaito A, Nakayama K and Kyotani M (1991) Surface orientation of a liquid-crystalline polymer studied by polarized reflection spectroscopy. *J Appl Polym Sci* 29, 1321-8.
18. Kaito A, Kyotani M and Nakayama K (1995) Effects of shear rate on the molecular orientation in extruded rods of a thermotropic liquid crystalline polymer *J Appl Polym Sci* 55, 1489-93.
19. Pan L and Liang B (1998) A comparative study of *in situ* composite reinforced with different rigid liquid crystalline polymer. *J Appl Polym Sci* 70, 1035-45.
20. Carfagna C, Amendola E, Nicolais I, Acierno D, Francescangeli O, Yang B and Rustichelli F (1991) Blends of a polyetherimide and a liquid crystalline polymer: fiber orientation and mechanical properties. *J Appl Polym Sci* 23, 839-44.
21. Saupe A and Maier W (1961) Methoden zur Bestimmung des Ordnungsgrades nematischer kristallinflüssiger Schichten. *Z Naturforsch*, 16a, 816-24.
22. Kelker H, Hatz R and Wirzing G (1973) Untersuchung des Infrarot-dichroismus in Flüssig-Kristallinen Schichten ohne Verwendung von Polarisiertem Licht. *Z Anal Chem* 267, 161-6.
23. Chingduang P, Bualek S, Phaovibul O and Schrader B (1986) Study of orientation and order of non-mesogenic solutes in liquid crystalline matrix by infrared spectroscopy. *Mol Cryst Liq Cryst* 132, 131-41.
24. Kyotani M, Kaito A and Nakayama K (1993) Structural, mechanical and thermal properties of extruded sheets of a liquid-crystalline copolymer. *J Appl Polym Sci* 47, 2053-63.
25. Nielsen LE (1974) *Mechanical Properties of Polymer and Composites* Vol 2 pp 294-6, 453-510. Marcel Dekker, New York.