Rheology, Morphology and Tensile Properties of Thermotropic Liquid Crystalline Polymer/ Polypropylene *In-Situ* Composites

Sauvarop Bualek-Limcharoen, Sayant Saengsuwan, Taweechai Amornsakchai, Banchob Wanno*[+]

Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand
[+]Present address: Department of Chemistry, Faculty of Science, Mahasarakham University, Mahasarakham 44150, Thailand

Summary: Blends of various grades of polypropylene (PP) with a thermotropic liquid crystalline polymer (TLCP), namely a copolymer of p-benzoic acid and ethylene terephthalate (60/40 mole ratio) were prepared as extruded films. A thermoplastic elastomer styrene (ethylene-butylene) styrene (SEBS) was used as a compatibilizer. Melt viscosities of all specimens were measured using a plate-and-plate rheometer with oscillating mode in the shear rate region of 1 - 200 rad/s. Addition of SEBS compatibilizer resulted in an increase of the blend viscosity. Observation of the blend morphology revealed an improvement of TLCP dispersion. The TLCP fiber aspect ratio (length to diameter) in the extruded film also increased after addition of SEBS. As a result, the film modulus in extrusion direction was enhanced. The tensile strength of the film specimen was also increased due to an improvement of interfacial adhesion.

Introduction

Polymer blend containing a thermotropic liquid crystalline polymer (TLCP) and a thermoplastic resulting in a so-called *in-situ* composite has been known to exhibit excellent mechanical properties due to a self-reinforcing effect of the dispersed TLCP fibrils[1-4)]. The final properties of *in-situ* composites depend on their phase morphology, which was affected by several important factors. These are, for examples, TLCP content, processing conditions, viscosity ratio (disperse phase to matrix phase) and the interfacial adhesion. Processing conditions including temperature, shear and extensional forces strongly affect the molecular orientation of the TLCP phase as well as the TLCP fiber aspect ratio. The effect of viscosity ratio on the morphology of *in-situ* composites has been investigated. Most fibrillation was achieved when the viscosity of TLCP is lower than that of the matrix[5-6)]. Addition of compatibilizer was found to improve the

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dispersion of TLCP phase and in some cases enhance the ultimate mechanical properties of the blends$^{7-11)}$. This was expected to be due to the reduction of the interfacial tension.

We have reported the effect of melt viscosity of PPs on fibrillation of TLCP in the *in-situ* composites which were prepared as extruded films drawn at different draw ratios$^{12)}$. We found that the films prepared from the more viscous matrix generated TLCP fibrils with higher aspect ratio. Incorporation of an elastomeric compatibilizer, SEBS, was found to improve fibrillation of the TLCP disperse phase. However, the effect of addition of compatibilizer on the blend viscosity was found to be opposite when comparing the melt flow index data and those measured using a capillary rheometer. This discrepancy might be due to different range of shear rate being investigated. Since the shear rate at the die of film extruder was estimated to be in the range of 20 - 45 s^{-1}, the rheological behavior of the blends in this region should be investigated more closely. This report is a continuation of the previous work. The results of viscosity measurements at low shear rate using a plate-and-plate rheometer in the oscillation mode are given, together with the results of the effect of processing temperature, matrix melt viscosity and compatibilizer on tensile properties of *in-situ* composite films.

Materials and Methods

Four grades of polypropylene (PP) used in this study were obtained from HMC Polymer Co., namely, PRO-FAX 6531, PW583, 6331 and 6231, with the measured values of melt flow index (MFI) 5, 9, 14 and 28 (ASTM D1238), respectively. These PPs will be denoted as PP5, PP9, PP14 and PP28 throughout this paper. The dispersed phase is a thermotropic liquid crystalline polymer, a copolyester of p-hydroxy benzoic acid and ethylene terephthalate (60/40 mole ratio), melting point 220 °C, purchased from Unitika Co. All materials were dried in a vacuum oven at 70°C for at least 12h before use.

Blending and film extrusion

Melt-mixing of 10 wt% TLCP in each PP matrix was carried out in a co-rotating, intermeshing, twin-screw extruder (PRISM-TSC-16-TC). Thereafter, the dried blend pellets were extruded using a mini-extruder (Lancastle-RCP-0625) equipped with a cast film line using conditions described in our previous report$^{12)}$. In the film extrusion step, two different temperature profiles used were 190/220/220/240°C and 220/240/255/255°C, representing the temperatures at the hopper zone, two-barrel zones and the die, respectively. The film draw ratio (die gap to film thickness) was fixed at 30.

Viscosity measurements

The test specimens were first melt-pressed into approximately 1-mm thick sheets. Melt viscosities of all specimens were measured at 240°C using a plate-and-plate rheometer (Haake RT20) in oscillation mode with the plates of diameter 20 mm and a gap of 1 mm. The tests were run in the frequency range from 1 to 200 rad/s.

Tensile Testing

Tensile testing was conducted using an Instron mechanical tester (model 4301), with grip length of 25 mm, cross-head speed of 50 mm/min and a full scale load cell of 100N (ASTM D412). Tensile properties of the dumbbell-shape specimens were measured in the parallel or machine (MD) and transverse directions (TD). At least ten specimens were measured and averaged for each blend.

Results and discussion

Rheological behavior

Melt flow curves of all grades of neat PPs and pure TLCP measured at 240°C are shown in Fig. 1. All polymers show shear thinning effect, i.e. the complex viscosity, η^*, decreases with the increase of shear rate. As expected, PP with lower value of MFI exhibits higher complex viscosity. In the lower range of shear rate, the differences in

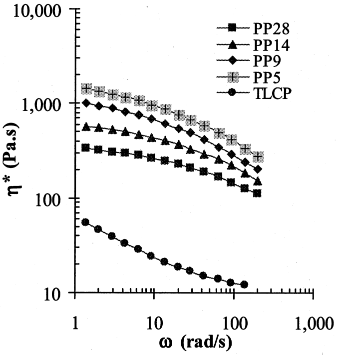


Figure 1. Melt flow curves of pure PPs and TLCP at 240 °C.

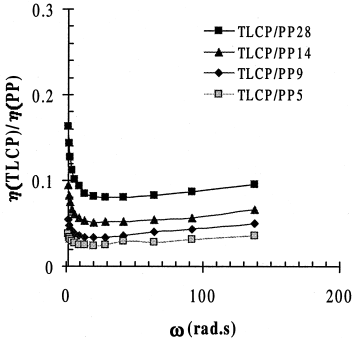


Figure 2. Viscosity ratio, η(TLCP)/ η(PP) versus shear rate at 240 °C.

viscosity among the matrices are greater than those in the higher shear rate region. This indicates the higher resistance to flow due to entanglement of higher molecular weight polymer when low shear stress was applied13). Also presented in Fig. 1 is the flow curve of pure TLCP. It is about one decade lower than those of the matrices and exhibits stronger shear thinning behavior, especially in the lower range of shear rate.

The viscosity ratios of TLCP to the matrix polymer, η(TLCP)/η(PP), plotted as a function of shear rate are illustrated in Fig. 2. These values are less than 0.10 at shear rate higher than 10 rad/s. The values of viscosity ratio obtained in this work agreed well with the values in the overlapping range of shear rate obtained from the capillary rheometer12).

Similar trend of the melt flow curves of TLCP/PPs blends is seen in Fig. 3. Despite of the substantially lower viscosity of TLCP, addition of 10 wt% TLCP into PPs does not much alter the viscosities of the matrices. Both, positive or negative deviations in the complex viscosity of a polymer matrix have been observed when another polymer dispersed phase is added but such behavior is not yet fully understood14).

In our previous report12), the viscosity measured in the high shear rate region (10^2 - 10^4 s^{-1}) using a capillary rheometer was found to decrease when SEBS is added into the blend. In contrast, the viscosity measured using melt flow rate tester was found to increase. Therefore, we have to investigate the rheological behavior of these blends more closely in the low shear rate region using a plate-and-plate rheometer.

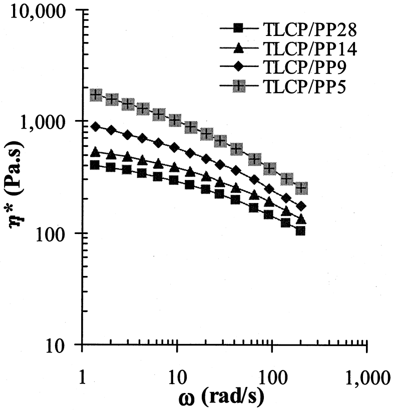


Figure 3. Flow curves of 10% TLCP/PP blend at 240 °C.

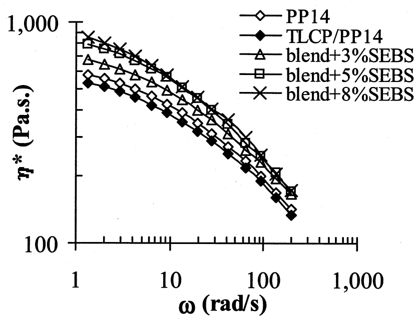


Figure 4. Flow curves of 10 %TLCP/PP containing 3, 5 and 8 wt.% SEBS at 240 °C

Fig. 4 presents the results demonstrating the effect of addition of 3, 5 and 8 wt. % of SEBS on viscosity of TLCP/PP14 blend. It is seen that the flow curve of the blend is slightly lower than that of pure PP but after addition of SEBS the blend viscosity becomes higher and levels off at about 5 % of SEBS. The result is in good agreement with the trend observed in the change of MFR[12)].

We propose that the increase of melt viscosity after addition of SEBS at very low shear rate would be due to the presence of SEBS at the interface, with the two ends (styrene blocks) diffused into the TLCP phase and the EB middle block into the PP matrix. Hence this would enhance the possibility of the molecules at the interface to entangle and thus resists the flow at low shear rate.

Morphology

Optical micrographs of TLCP fibrils extracted (using hot xylene as described in ref. 12) from composite films are shown in Fig. 5. The fibrils extracted from uncompatibilized films prepared from PP5, PP9 and PP14 are shown in the first row Ia, Ib and Ic, respectively, and those of the corresponding systems containing 3% SEBS are shown in the second row IIa, IIb and IIc. It is clearly seen that in the more viscous PP matrix (low MFI) longer TLCP fibrils are formed with more homogeneous texture, suggesting high degree of molecular ordering inside the fibrils. For compatibilized systems, thinner TLCP fibrils are created, hence fibrils with higher aspect ratio are obtained. As seen in

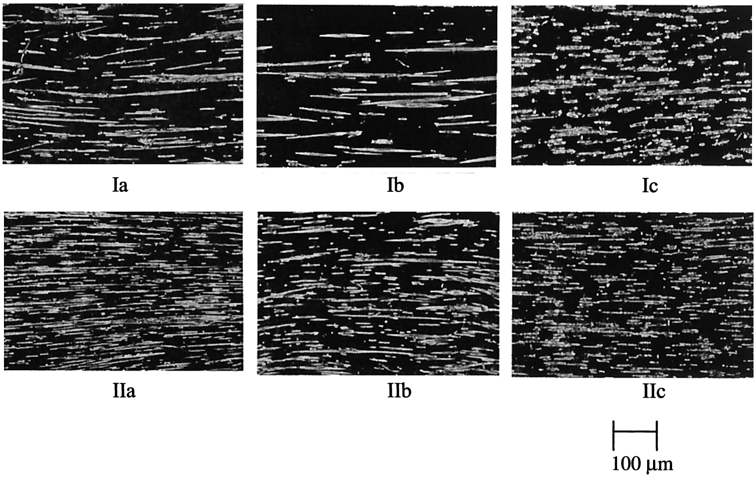


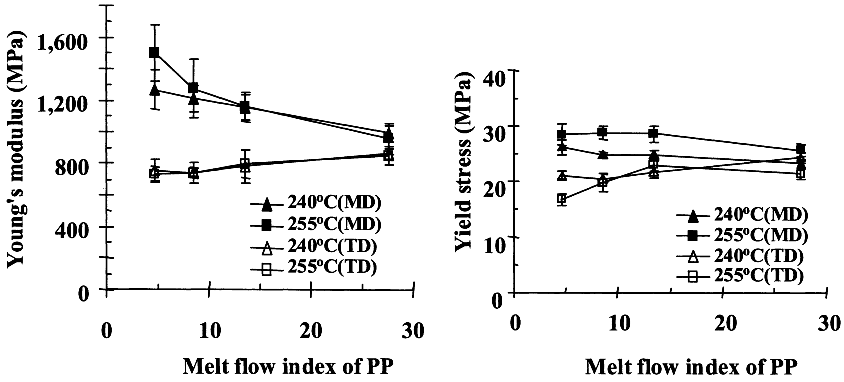
Figure 5. Extracted TLCP fibrils from composite films prepared from matrices (a) PP5 (b) PP9 (c) PP14, without SEBS (row I) and with 3 wt.% SEBS (row II).

the previous section, the viscosity of the blend system increases with addition of 3% SEBS, which indicates stronger interaction at the interface. Therefore the stress transferred from the matrix to the dispersed phase is more effective.

Tensile properties

Effect of processing temperature and matrix melt viscosity

The Young's moduli and yield stresses of the composite films prepared from PPs of different MFI using the die temperatures of 240 and 255°C are illustrated in Fig. 6. It is seen in Fig. 6a that moduli in both parallel (MD) and transversal direction (TD) of the films prepared at these two temperature profiles are equal, except the MD modulus of TLCP/PP5 which shows higher value for the film prepared at the die temperature of 255°C. Considering the effect of increasing matrix viscosity (decreasing of MFI), MD moduli were found to increase sharply, but the TD values slightly decrease. In other words, the anisotropy in modulus increases with the increase of the matrix melt viscosity. For the films prepared from PP5, 9, 14 and 28 matrices at the die temperature of 255°C, MD moduli are by 100, 70, 45 and 14 % higher than the corresponding TD values. This is a result of the uni-axial orientation of TLCP fibers with increasing aspect ratio when the matrix viscosity is increased. Fig. 6b shows the yield stresses of the same series of specimens. It is seen that the MD yield stresses of all specimens prepared at



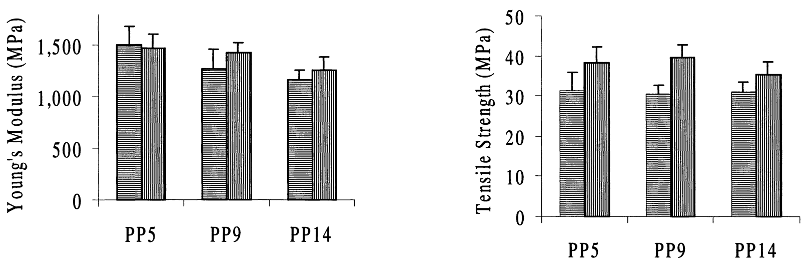
(a) (b)

Figure 6. Effect of processing temperature on (a) Young's modulus and (b) yield stress of TLCP/PP composite films prepared at 240 °C and 255 °C. Data measured in parallel (MD) or transversal direction (TD).

255 °C are slightly higher than those prepared at 240 °C but the TD yield stresses are approximately the same at both temperatures. No influence of the matrix melt viscosity on yield stress is observed. This means that the yield stress is independent of TLCP fiber aspect ratio.

Effect of compatibilizer

For the films prepared at 255 °C, addition of 3 wt.% of SEBS could enhance the Young's modulus of the blends comprising PP9 and PP14 (see Fig. 7a) by about 10 %. This is due to the increase of TLCP fiber aspect ratio. However, though thinner TLCP fibrils are formed after addition of SEBS into TLCP/PP5 blend, no improvement of the modulus is obtained. Since the thinner fibrils are prone to break down more easily than the thicker ones, lower fiber aspect ratio may be observed in this system. Fig. 7b shows the increases in tensile strength of all blends. This is a result of the better interaction at the interface due to the anchoring effect of the SEBS, as evident from the increase of the compatibilized blend melt viscosity.



(a) (b)

Figure 7. Young's modulus (a) and tensile strength (b) in MD direction of TLCP/PP (▤) and TLCP/PP/SEBS (▥) prepared from various grades of PP.

Conclusions

Addition of 10 wt.% of TLCP into PP matrices of different melt viscosity resulting in an enhancement of MD modulus to a different degree, more viscous matrix gives higher MD modulus. Addition of SEBS into the blend increases the complex viscosity in the low shear rate region, indicating an improvement of interfacial adhesion. As a result, better dispersion of TLCP phase and hence fibrils with higher aspect ratio were obtained. This effect leads to the enhancement of Young's modulus and tensile strength of composite films.

Acknowledgements

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