

Thermal, Morphological and Rheological Study of Polytrimethylene Terephthalate/Thermotropic Liquid Crystalline Polymer Binary Blend

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The miscibility of thermotropic liquid crystalline polymer (TLCP) and polytrimethylene terephthalate (PTT) blends was investigated with thermal, morphological and melt viscoelastic analyses. The blend samples containing 5, 10 and 15 % of TLCP were prepared by both in an internal mixture and a modular twin screw extruder. The results obtain from DSC showed the heat of fusion and heat of crystallization of the blend samples was found to be slightly lower than those predicted from additive rule and indicated small compatibility between PTT and TLCP phases. Cryogenically fractured surface of the blend samples examined by SEM. The SEM showed a matrix-dispersed type morphology in which TLCP phase was uniformly dispersed in polymer matrix. The shear viscosity as well as melt elasticity of the TLCP were matched quarter than PTT matrix. The melt flow behaviour of TLCP showed an appreciable viscosity up turn and a non-terminal storage modulus (G') at low shear rate range while PTT showed a sudoplastic type flow behaviour.

Key Words: Thermotropic liquid crystalline polymer, Poly trimethylene terephthalate, Miscibility, Binary blend.

INTRODUCTION

Thermotropic liquid-crystal polymers (TLCPs) are among attractive because fibres due to their potential applications as ultra-high strength fibers. They have also been used as high-performance finished products of their good properties, excellent thermal endurance and chemical stability. It is well known that the addition of a small amount of a TLCP, because of its low melt viscosity can reduce the melt viscosity of polymer blends, thereby enhancing the process ability.

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Recently blending of thermotropic liquid crystalline polymers (TLCP) with commercial thermoplastics has attracted a considerable attention because TLCP can intrinsically exhibit a high degree of molecular order in the melt state. TLCP under appropriate processing conditions, can be deformed into fibrils, these fibrils then act as a reinforcement component for the thermoplastics matrix.

Since the 1990s, there have been a great number of studies of TLCP blends with commercial thermoplastics¹⁻²⁶. Many kinds of commercial plastic polymers have been used as a matrix to make blends with TLCP, which included polypropylene^{9-11,13,14,18,20,26}, polyethylene²⁴, nylon^{3,19,21,22}, polycarbonate^{12,25}, polyesters [poly(ethylene terephthalate) (PET), Poly(butylenes terephthalate) (PBT) and poly(ethylene2,6 naphthalate) PEN^{4,5,23,27}, Poly(methyl methacrylate), epoxy and others^{8,12,15,16}. The fibrillation of TLCP in a thermoplastic melt is a complex process, which can be affected by many factors such as miscibility between TLCP and the matrix, TLCP content, viscosity ratio of TLCP to the matrix, processing temperature, shear and elongational flows, as well as processing history. Most pairs of TLCP and thermoplastics are immiscible so that there is an interface separating the two phases. The poor interfacial tension between the two phases is considered to be the main reason for the melt slip that often results in a negative deviation from the rule of mixture^{23,27,28}. The shear viscosity ratio of TLCP to the polymer matrix is well known to be important in governing fibrillation of TLCP. It is often observed that a shear viscosity ratio ($\eta_{TLCP}/\eta_{matrix}$) between 0.01 and 1.0 1/s TLCP droplet deformation^{12,17,25,26}. Here, the matrix viscosity is required to be greater than that of TLCP to allow efficient transfer of shear stress from the matrix to the dispersed TLCP domains for deformation of TLCP droplets. For example, He and Bu¹² studied the effect of viscosity ratio the fibrillation of TLCP in poly(ether sulfone) and observed that the deformation of TLCP domains was controlled by the viscosity ratio. When the viscosity ratio was very low (0.01), TLCP fibrils were formed.

Choi *et al.*¹⁷ found that when the viscosity of liquid crystalline polymer (LCP) was lower than that of polystyrene, fine LCP fibril structure was formed, whereas the spherical form of LCP was observed when the viscosity of the other LCP was higher than that of polystyrene.

However, when some commercial TLCP such as Vectra A950 or B950 are used as a dispersed phase and blended with low melt viscosity polymer. Such as polypropylene or nylon often results in a viscosity ratio of TLCP to the matrix to be greater than 1^{18,19,22}.

In this case, fibrillar structures of LCP could be formed at relatively high shear rates, as reported by Postema and Fennis¹⁸ for the blends of PP and Vectra A950. Thus, the criteria for determination of the LCP fibrillation

by using the low viscosity ratio ($\eta_{\text{TLCP}}/\eta_{\text{matrix}} < 1$) become invalid. Here, to avoid the conflict, one may have to consider the original characteristics of a given TLCP. For example, the rigid chains of vectra LCPs give much higher viscosity than the relatively flexible chains of Rodrum LCPs. It also seems that the former tends to form fibrillar structures more easily in the nematic state under appropriate shear flow conditions than the latter.

In literature, there is no report on effect of elongational viscosity ratio on TLCP fibrillation in a thermoplastic matrix. In fact, compared to a shear condition, TLCP fibrillation should be more favoured by extensional conditions. This is because similar to a fiber spinning process an extensional flow is more effective at elongating the TLCP droplets into fibrils rather than a shear flow²⁹.

The main objective of the present work was to study the properties and miscibility PTT/TLCP binary blend.

EXPERIMENTAL

TLCP used in this study is a copolyester of 4-hydroxy-benzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA). The material is produced by TiconaTM with a trade name of vectra A950. The liquid crystalline polymer does not have a sharp transition temperature. Instead, there is a broad and relative low melting temperature 285 °C for this polymer. The conventional thermoplastic used in this research was with an intrinsic viscosity of 0.92 dl/g which was supplied by Zimmer co.

All the material was dried at 100 °C in oven for 24 h before being used to minimize the effect of moisture. The PTT/TLCP samples containing 5, 10 and 15 % of TLCP were prepared by both in an internal mixture and a modular twin screw extruder. The blending composition and sample codes are shown in Table-1. The temperature of internal mixture was 290 °C and the temperature of heating zones set to 270, 275, 280, 285, 285 and 270 °C and the rotor speed was kept at 50 rpm.

TABLE-1
BLENDING COMPOSITION AND SAMPLE CODES

Sample No.	PTT (%)	TLCP (%)
PTT1	100	0
PTT2	95	5
PTT3	90	10
PTT4	85	15
TLCP	0	100

Characterization: For thermal analysis experiments was performed using differential scanning calorimeter (DSC). The samples were first heated

to 290 °C at 5 °C/min (first heating), held for 5 min to remove the thermal history and quenched to room temperature. Each sample was reheated to 290 °C at 10 °C/min (second heating). In this procedure, the glass-transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) were obtained. The morphologies of the blend samples were observed with a scanning electron microscope (SEM). The measured blend samples were broken in liquid nitrogen and then the fracture surfaces were sputter-coated in vacuum with gold before scanning to prevent charging in the electron beam.

The melt flow behaviour and viscoelastic properties were studied by using a rheometric mechanical spectrometer (RMS). Pure PTT, TLCP and blend samples melt-pressed into circular disks of 1 mm in thickness and 25 mm in diameter. Before each measurement the measuring chamber was heated to 290 °C.

RESULTS AND DISCUSSION

Differential scanning calorimetry is used to analyze the thermal transition in polymer blends. Normally, miscible polymer blends are evidenced by a single T_g or the T_g of one of the polymer components is shifted towards that of the other. In the case of LCP blends, however, the DSC traces of LCPS often fail to provide any useful information. Sometimes T_g can not be observed at all and if one or both polymers are crystalline, direct and reliable information will be hard to obtain. Since both the degree of crystallinity and the melting point of a crystalline polymer can be expected to decrease with increasing content of the LCP component, indirect information on compatibility in LCP blends can be obtained from the melting and crystallization transitions. It has been noted in many miscible thermoplastic/LC blends, a second component prevents the perfect crystallization of matrix and lowers its melting temperature. The addition of a small amount of LCP to a semi-crystalline thermoplastic actually enhances crystallization processes of the thermoplastic phase, apparently because LCP acts as a nucleating agent, causing the thermoplastic crystals to nucleate on the surface of the LCP domains.

The melting-point depression is an important property of crystalline polymer blends. When certain blends are miscible, melting point depression may occur. It is a fundamental phenomenon in characterizing the corresponding. In general, thermodynamic considerations predict that the chemical potential decreases with the addition of miscible diluents. When one component is crystallizable, its decrease in chemical potential leads to a depression of the melting point. In most cases, melting point depression has been reported in amorphous polymer and crystalline polymer blends. Recently, however, there have been several reports about melting point depression in

semi-crystalline polymer pairs. Wei and Tyan reported melting point depression in the solution blend of TLCP and PEN. This suggests that if the T_m of one blend component is significantly different than that of the other component, the component having a lower T_m plays a role of diluents and decreases the melting temperature of the blends.

DSC thermograms of the blend samples are depicted in Fig. 1 and the relevant explanations are given in Table-2.

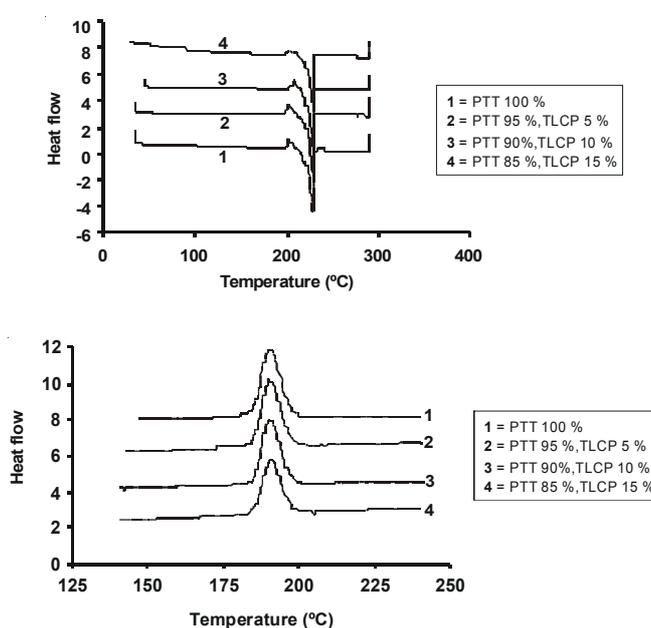


Fig. 1. DSC thermograms PTT/TLCP blends at a heating rate of 5 °C/min

TABLE-2
THERMAL CHARACTERISTICS OF PTT/TLCP
BLENDS FROM DSC MEASUREMENT

Sample	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m^* (J/g)	ΔH_f^* (J/g)	ΔH_c^* (J/g)	ΔH_c (J/g)
PTT	56.76	229.41	190.33	56.65	56.65	60.57	60.57
PTL 5	55.59	229.19	190.17	53.77	49.64	57.54	55.58
PTL 10	56.61	229.27	190.28	50.98	46.72	54.51	52.68
PTL 15	55.67	229.24	190.44	48.02	44.68	51.48	48.89

T_m = melting temperature, T_g = glass transition temperature, T_c = cold crystallization temperature, ΔH_m^* = heat of fusion of the blends, ΔH_m , heat of fusion based on the mass of PTT/TLCP in the blends, ΔH_c^* = heat of cold crystallization of the blends, ΔH_c , heat of cold crystallization based on the mass of PTT in the blends.

The T_g of pure TLCP was 67 °C and PTT was 56.76 °C. Although the T_g value of TLCP are not distinct in Fig. 1. The blend samples showed only a single T_g while the T_g for each sample shifted in the blends represents miscibility or partial miscibility. This result too showed heat of fusion (ΔH_f) and heat of crystallization (ΔH_c) of the blends was found to be slightly lower than those predicted from additive rule indicating small compatibility between PTT and TLCP phases.

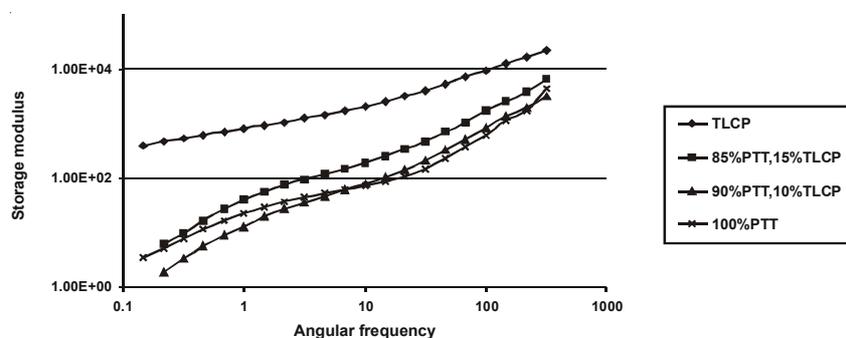
Rheology: The miscibility of the polymer blends can be roughly determined from the deviation of the viscoelastic function from that predicted by the log-additively rule mentioned previously. Three types of deviation can occur (1) positive, (2) negative and (3) positive/negative. For immiscible polymer blends, the positive deviation is expected and for miscible blends the negative deviation should result.

Shear rate plays a vital role in promoting fibrillation of TLCP. When a polymer melt enters the capillary from the convergent region, the melt flow will be rearranged into a shear viscosity profile and this shear velocity profile is dependent on shear rate. Here, it is worth noting that the shear rate changes from a maximum value at the wall to the zero value at the centre of the capillary. The dispersed TLCP fibrils or small droplets closest to the wall will be highly sheared and aligned in the flow direction. Depending on shear rate, the state of the dispersed TLCP phase may vary between ellipsoids and microfibrils at a temperature in the nematic temperature range. The typical skin-core morphology is a result of shear rate effect, where TLCP fibrils are formed only in the skin region and spherical and/or ellipsoidal forms of TLCP exist in the core or center region. Fig. 2 illustrates the storage modulus and complex viscosity (η^*) measured at 290 °C for PTT, TLCP and their blends as a function of shear rate.

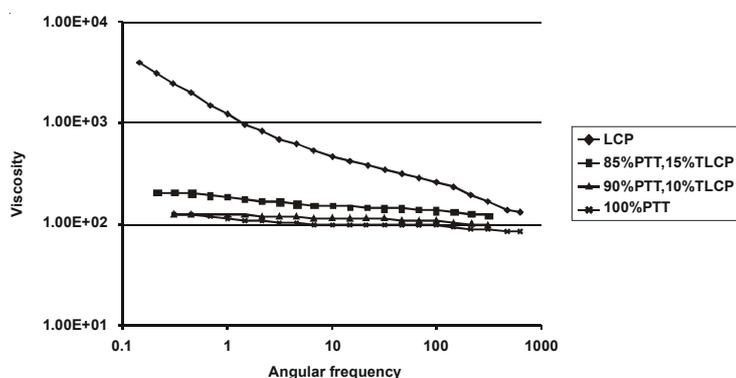
Within the shear-rate range studied (0.1-1000 s^{-1}) the shear viscosity for PTT decreased slightly with an increasing shear rate, suggesting a slight shear-thinning behaviour, whereas TLCP exhibits a shear-thinning behaviour at low shear rates. The flow behaviour of TLCP showed an appreciable viscosity upturn and a non-terminal storage modulus (G') at low shear rate range while PTT showed a pseudo plastic type flow behaviour. By comparing these results one may note that the melt viscoelastic behaviour of the blend samples is predominantly determined by PTT matrix.

Morphology: Scanning electron microscopy (SEM) is the most widely used technique in the study of blends. The shape, distribution and size of the TLCP particles in the matrix depend on several factors, such as TLCP content, viscosity ratios of the matrix and the processing condition. In addition, the morphology is affected by interfacial adhesion between the components. The interfaces are sharp in polymer blends with poor adhesion. High porosity of the material is also an indication of low interfacial adhesion. In certain

cases scanning electron micrographs have also given clear evidence of good interfacial adhesion. In miscible blends all the TLCP particles have some matrix over their surfaces and there are no open rings around the particles of TLCP. Typically, the diameter of a TLCP particle size in miscible blends is less than 1 μm , while the diameter in immiscible blends is 1 to 5 μm or larger. Many researchers have attempted to link the mechanical properties of blends to the morphology of the TLCP domains. Thus, a good reinforcement is achieved when TLCP phases are well deformed and elongated during processing. The shape and orientation are retained during solidification and fibres are permanently oriented in the flow direction.



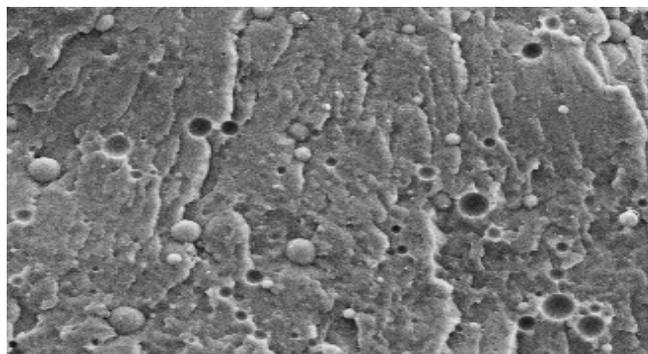
(a) complex viscosity



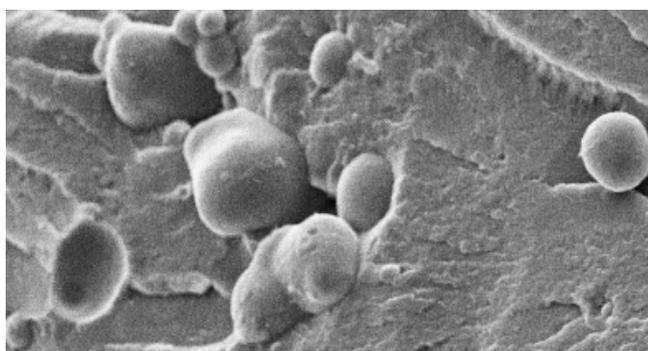
(b) storage modulus

Fig. 2. Results of melt viscoelastic measurements

Typical SEM micrographs of the blend samples is shown in Fig. 3. In all the blend samples the TLCP phase was uniformly dispersed in the PTT matrix. The average TLCP diameter was smaller for the blend samples prepared by extruder compared to those produced by internal mixer.



(a)



(b)

Fig. 3. SEM micrographs of PTT/TLCP binary blend: a) modular twin screw
b) internal mixture

Conclusion

From the results of melt viscoelasticity, morphology and thermal analyses, it was demonstrated that PTT and copolyester based TLCP are not miscible in molten state but they are compatible such that in their blends containing to so that 5, 10 and 15 % of TLCP.

Such that a matrix-disperse type morphology in which the TLCP particles were finely dispersed in PTT matrix were found for all blends sample.

REFERENCES

1. F.P.La Mantia, *Thermotropic Liquid Crystal Polymer Blends*, Technomic Publishing Co, Lancaster, PA.
2. C.L. Jackson and M.T. Shaw, *Int. Mater. Rev.*, **36**, 165 (1991).
3. F.P.La Mantia, A. Valenza, M. Paci and P.L. Magagnini, *Polym. Eng. Sci.*, **30**, 7 (1990).
4. W.G. Perkins, A.M. Marcell and H.W. Frerking Jr., *J. Appl. Polym. Sci.*, **43**, 329 (1991).
5. A. Zaldua, E. Munoz, J.J. Pena and A. Santamaria, *Polymer*, **32**, 682 (1991).
6. C. Carfagna, L. Nicolais, E. Amendola, C. Carfagna Jr. and A.G. Fillippov, *J. Appl. Polym. Sci.*, **44**, 1465 (1992).

7. H.G. Schild, E.S. Kolb, R.A. Guadiana, Y. Chiang and W.C. Schwarzel, *J. Appl. Polym. Sci.*, **46**, 959 (1992).
8. D. Dutta, R.A. Weiss and K. Kristal, *Polym. Eng. Sci.*, **33**, 838 (1993).
9. A. Datta, H.H. Chen and D.G. Baird, *Polymer*, **34**, 759 (1993).
10. Y. Qin, D.L. Brydon, R.R. Mather and R.H. Wardmann, *Polymer*, **34**, 1196, 1202, 3597 (1993).
11. Y. Qin, *J. Appl. Polym. Sci.*, **54**, 735, 873 (1994).
12. J. He and W. Bu, *Polymer*, **35**, 5061 (1994).
13. A. Datta and D.G. Baird, *Polymer*, **36**, 505 (1995).
14. H.J. O'Donnell and D.G. Baird, *Polymer*, **36**, 3113 (1995).
15. P.L. Magagnini, M. Paci, F.P. La Mantia, I.N. Surkova and V.A. Vasnev, *J. Appl. Polym. Sci.*, **55**, 461 (1995).
16. J.P. Souza and D.G. Baird, *Polymer*, **37**, 1985 (1996).
17. G.D. Choi, S.H. Kim and W.H. Jo, *Polymer J.*, **28**, 527 (1996).
18. A.R. Postema and P.J. Fennis, *Polymer*, **36**, 505 (1995).
19. Y. Seo, S.M. Hong and K.U. Kim, *Macromolecules*, **30**, 2978 (1997).
20. M.M. Miller, J.M.G. Cowie, D.L. Brydon and R.M. Mater, *Polymer*, **38**, 1565 (1997).
21. Y.Z. Meng and S.C. Tjong, *Polymer*, **39**, 99 (1998).
22. Y. Seo, B. Kim and K.U. Kim, *Polymer*, **40**, 4483 (1999).
23. L. Minkova and P.L. Magagnini, *Polymer*, **42**, 5607 (2001).
24. C.K. Chan, C. Whitehouse, P. Goa and C.K. Chai, *Polymer*, **42**, 7847 (2001).
25. L.P. Tan, C.Y. Yue, K.C. Tam, Y.C. Lam and X. Hu, *Polymer Int.*, **51**, 398 (2002).
26. M.W. Lee, X. Hu, C.Y. Yue, L. Li, K.C. Tam and K. Nakayama, *J. Appl. Polym. Sci.*, **86**, 2070 (2002).
27. Y.C. Lam, C.Y. Yue, Y.X. Yang, K.C. Tam and X. Hu, *J. Appl. Polym. Sci.*, **87**, 258 (2003).
28. D.S. Park and S.H. Kim, *J. Appl. Polym. Sci.*, **87**, 1842 (2003).
29. L. Li, C.L. Chan, C.Y. Yue, Y.C. Lam and K.C. Tam, *J. Appl. Polym. Sci.*, **91**, 1505 (2004).

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