

CHAPTER 2

Literature Review

Blends of melt processable polymers and liquid crystalline compound, have been studied in many researches. The reviews cover liquid crystalline compound with low molecular weight and also high molecular weight. The main aim of blending high molecular weight liquid crystalline compound (liquid crystal polymer, LCPs) into polymers is to make reinforcing fillers and increase mechanical properties of matrix polymer. Only few researchers have reviewed about low molar mass liquid crystal. The literatures in this field are therefore rarely found.

Buckley, A. Conciatori, A. B. and Calundann, G. W. [1984] investigated the blends of low molecular weight liquid crystalline compound and polyolefin / polyester. The main polymers were plasticized and the melt viscosity of blends reduced by as much as 25 to 30 percent compared with the main polymers.

Cogswell, F. N., Griffin, B. P. and Rose, J. B. [1984] explained the melt processable compositions comprising melt processable polymers and liquid crystal polymers. The melt viscosity of such compositions was less than that of the melt processable polymer in absence of the liquid crystal polymer at least 10 percent.

Siegmann, A., Dagan, A., and Kenig, S. [1985] prepared the polyblends of a liquid crystalline aromatic copolyester (based on 6-hydroxy-2-naphthanoic acid (HNA) and p-hydroxybenzoic acid) and an amorphous polyamide (PA) by melt mixing. The rheological behavior of blends was very different from pure component and viscosity of blends changes very significantly. Only 5 % composition of LCP blends to system could reduce the viscosity 20 – 25 times. The tensile mechanical behavior of the blends was increased, similar to polymer composites. The two-phases morphology was found, depending on their compositions.

Blizard, K. G., and Baird, D., G. [1987] characterized the morphology of blends of polycarbonate and nylon 6,6 with the copolyester of 60%HBA-40% PET. They found that some extensional flows are required for the coalescence and extension of the particulated LCP phase. Only 10 to 30 percent of LCP is required for the viscosity reduction of those polymers.

La Mantia, F. P., Valenza, A., Paci, M. and Magagnini, P. L. [1990] investigated the blends of nylon 6 and a liquid crystal copolyesteramide (LCP). The blends have been extruded at two different temperatures. The influence of the LCP content on the viscosity of the blends is better, see Figure 2-1 and Figure 2-2 (in the next page) where the viscosity is reported as a function of the composition at fixed shear rate. A deep minimum is shown at both temperatures at a concentration range of the LCP component of 10-20% at 260°C and 5-20% at 290°C. The reduced viscosity has been interpreted in term of formation of fibril and immiscibility between two phases.

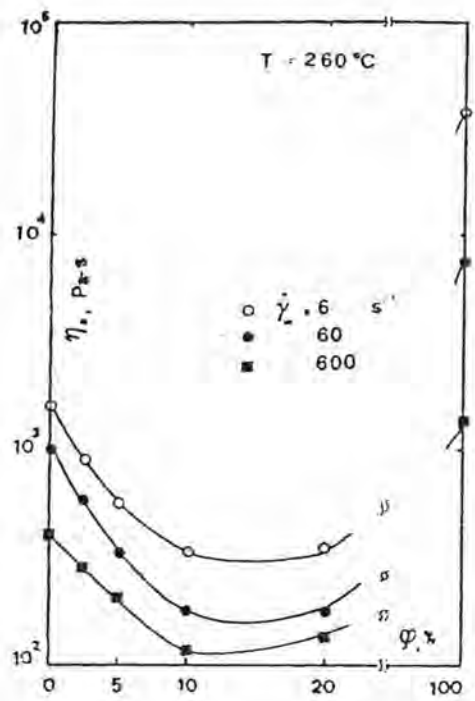


Figure 2-1 Viscosity vs LCP content at fixed shear rates. $T = 260^\circ\text{C}$ [La Mantia, et. at., 1990].

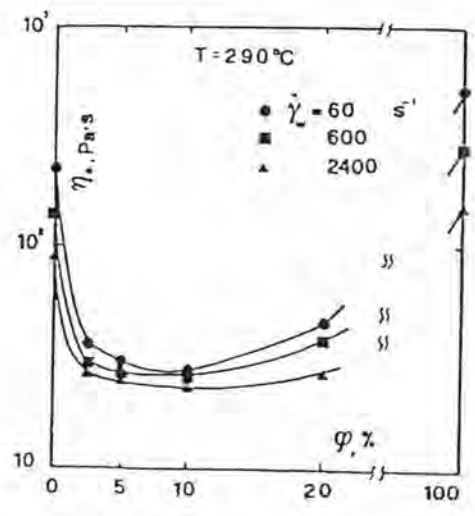


Figure 2-2 Viscosity vs LCP content at fixed shear rates. $T = 290^\circ\text{C}$ [La Mantia, et. at., 1990].

Kulichikhin, V. G., et al. [1991] studied LC copolyester (PES) "Ultrax4002" and polysulfone in terms of the morphology and characteristics of the extrudates. The reinforcement of an isotropic matrix by LC polymers leads to a specific change in the strength properties of compositions. A maximum increase in the strength and initial modulus was observed for blends containing not more than 10% LC polymer.

Heino, M. T. and Seppala, J. V. [1992] investigated blends of a polyester-type thermotropic liquid crystalline polymer (LCP) (Vectra A950) with polyethylene terephthalate (PET), polypropylene (PP), and polyphenylene sulfide (PPS) respectively. They concluded that LCP was found to act as a significant reinforcement for all matrixes studied. The tensile strength and elastic modulus of the blends increased with increasing LCP content, while the strain at break and the draw-ratio decreased. The improvement in strength and stiffness was most significant at higher LCP contents (20-30 wt%). However, at these compositions, the effect of draw ratio was greater. Moreover, they found that the mechanical properties of their blends were closely related to the blend morphologies. The melt viscosity of LCP and the pure matrix were quite similar in the shear rate range used in processing. However, at some shear rates, PP was slightly less viscous than LCP blend.

Beery, D., Kenig, S. and Siegmann, A. [1992] studied the shear and elongational viscosities of a thermotropic liquid crystalline polymer (LCP) polycarbonate (PC), and their 20%LCP in 80%PC blend by using a capillary rheometer. The LCP used was a wholly aromatic copolyester, composed of hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA) with 73/27 molar ratio. Experimental results have shown that shear viscosities and entrance pressures are practically independent of the entrance

angles. The entrance pressure drop was small in the case of PC and the reached 50% of the total pressure drop for LCP. The 20%LCP blend exhibits intermediate viscosity values. The elongational viscosities of the three materials studied are the function of elongation rate, and can be described by power law equations.

Lin, Y. C., Lee, H. W. and Winter, H. H. [1993] studied the miscibility and viscoelastic properties of blends of a segmented block copolyester (LCP) and poly(ethylene terephthalate). They found that addition of a small quantity of LCP has a dramatic effect on rheology. For example, an addition of 2 wt% LCP reduces the viscosity by about 60%. This effect is most pronounced for PET of higher molar masses. The melt viscosity decreases exponentially with the LCP content in the range of composition where the blends are miscible. But there was no significant further reduction of viscosity when the LCP content exceeds 50 wt%. The addition of LCP also changes the distribution of the relaxation times of PET and broadens the zero- shear viscosity regime.

Li, W., et al. [1994] studied the phase morphology and miscibility of binary blends of polyarylethersulfone (PES) and liquid crystalline polymer (LCP) of p-oxybenzoate and ethylene terephthalate units. They observed the phase inversion in the blend, when they contained 50 wt% or more of the LCP.

Lee, S., Mather, P. T. and Peason, D. S. [1996] investigated the phase behavior and rheology of binary blends of polycarbonate (PC) and a liquid crystalline polymer (LCP). Results of DSC and optical microscopy have indicated that the LCP is solubilized in the mixture for weight fractions of LCP less than about 0.05 and shows partial miscibility with PC over the rest of the composition range. Moreover, they suggested that there is some

interaction between the separate isotropic and anisotropic phases, with complex viscosities of the blends being intermediate between pure components.

Kulichikhin, V. G., Parsamyan, I. L., Lipatov, Y. S., Shunski, V. F., Getmanchuk, I. P., Babich, V. F., and Postema, A. R. [1997] investigated the rheological and mechanical properties of two phase polymer blends containing a liquid crystalline copolyester (LCP) of PHB/PET plus isotactic polypropylene (iPP) with various composition and concentration. The results shows that the perfect fibrillation of the disperse LC phase into iPP matrix in capillary flow was observed at LCP concentration more than 20%wt and temperature more than 488K. This effect leads to the decrease of the blend viscosity and the reinforcing effect of the mechanical characteristic of the blends at the same time.

Campoy, I., Gomez, M. A., and Macro, C. [1998] studied the structure and thermal properties of the blends of PA6 and a liquid crystalline copolyester (LCP) based on 2,6 hydroxynaphthoic acid (HNA) and p-hydroxybenzoic acid (PHB). The melt blending was carried out in a Haake Rheocod System 60 rheometer at 290^oC, rotor speed of 50 rpm and mixing time about 50 minutes. The results show that the depression of the thermal transition temperature of PA6 had been attributed to an improvement of the compatibilization between the PA6 and LCP for the blend with higher LCP content.

Van Eijndhoven-Rivera, M. J., Wagner, N. J., and Hsiao, B. [1998] investigated the rheological properties of the immiscible blends of thermotropic liquid crystal based on HX-8000 series and polybutylene terephthalate (PBT) on the cone and plate, parallel plate and capillary rheometer to complete the wide range of shear rate. Figure 2-3 shows the reduction of viscosity of the blends at various composition of LCP. They provided

evidence concerning the possible mechanism for the anomalous viscosity reduction in immiscible TLCP blends.

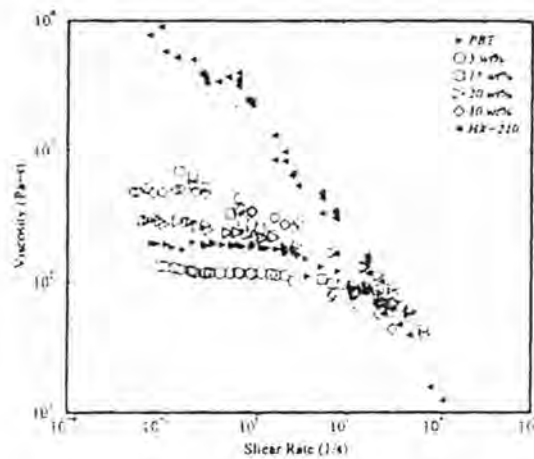


Figure 2-3 Shear viscosity of PBT and PBT/LCP blends at various compositions

[Van Eindhoven-Rivera, et. al., 1998]

Meng, Y. Z., Tjong, S. C. and Hay, A. S. studied the melt blend of a novel polyarylether , poly(phthalazinone ether ketone sulfone) copolymer, PPESK and a liquid crystalline copolyester based on Vectra A950. The PPESK is a high performance polymer that was characterized by an extremely high T_g , high stability but poor processability. The melt blend of PPESK and LCP at various compositions (5-35%) was investigated for the rheological behavior by a capillary rheometer. The results show in Figure 2-4 that at 340°C , the viscosity of PPESK/LCP blends were significantly lower than that of the pure PPESK over the study range of shear rate. It was indicated that the processability of PPESK was greatly improved by blending with LCP.

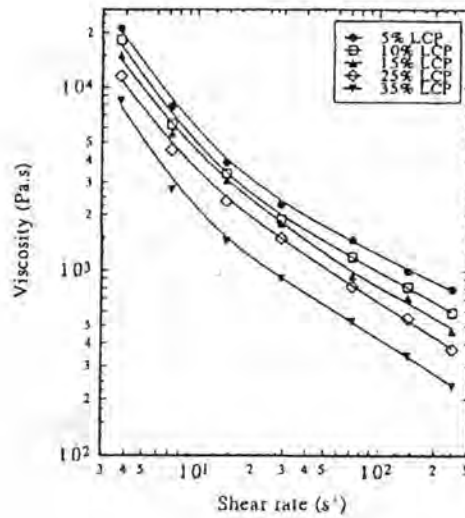


Figure 2-4 Viscosity of PPESK/LCP blends at 340°C [Meng, et. al., 1998]

Meng, Y. Z. and Tjong S. C. [1998] investigated the maleic anhydride compatibilized polyamide6 (PA6-MAP) blends with a liquid crystalline copolyester (LCP₁) and a copolyester containing 60:40 PHB/PET (LCP₂). The rheological measurements were carried out by capillary rheometer. The results were shown in Figure 2-5 at 300°C and 280°C and Figure 2-6 at 265°C and 235°C respectively. The shear viscosity of the blends was significantly changed from that of the pure PA6-MAP while tensile strength of PA6-MAP-LCP₁ represented the fibril-reinforced behavior of LCP. In other word, the tensile of blends was increase with percent composition of LCP₁ increase. On the other hand, the tensile strength appeared to decrease significantly with percent composition of LCP₂ content. This was due more to the LCP₂ phase dispersed into porous and foamy structure than the extended fine fibril.

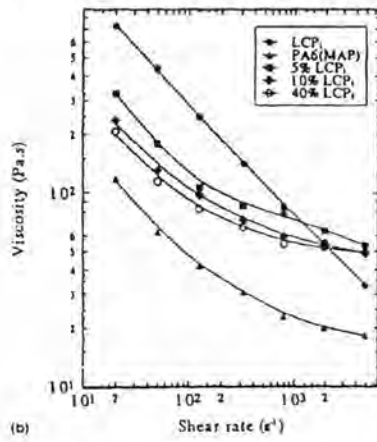
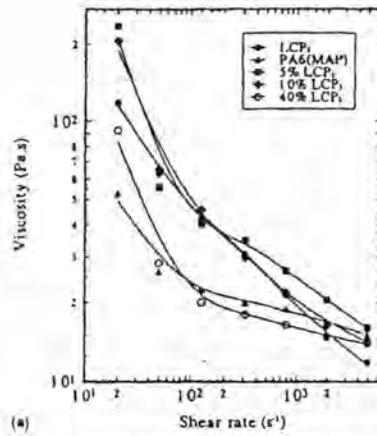


Figure 2-5 Viscosity vs shear rate of PA6-MAP-LCP₁ blends at (a) 300°C (b) 280°C [Meng, et. al., 1998]

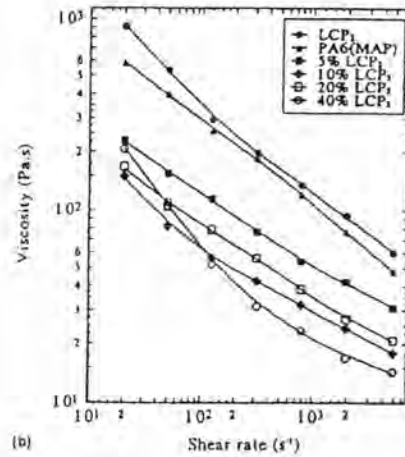
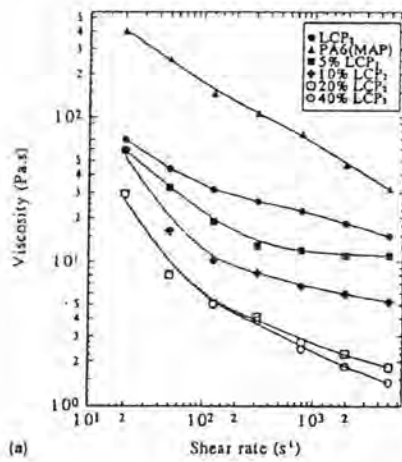


Figure 2-6 Viscosity vs shear rate of PA6-MAP-LCP₂ blends at (a) 265°C (b) 235°C [Meng, et. al., 1998]

Meng V. Z., and Tjong, S. C. [1999] investigated the binary blends of polyvinyl chloride (PVC) and a liquid crystalline copolyester containing 60%PHB and 40% PET. The blends were prepared by injection moulding. The mechanical, thermal, rheological properties and morphology of these blends were investigated. The results showed that the tensile strength and modulus of the blend tend to increase with increasing LCP content for the blends containing LCP content below 15wt%, and they decrease significantly with further increasing LCP content. DSC and DMA showed that PVC and LCP are partially miscible for the blend with LCP content < 15wt% and miscible for the blends with LCP content >15wt%. The torque measurement indicated that the viscosity ratio between the LCP and PVC matrix is much smaller than unity. This implied that LCP fibrillation is likely to occur in the PVC/LCP blends. However, SEM observations revealed that fine fibrils are only formed in the skin layer of the blends containing LCP content < 15wt%. Two-phase morphology disappeared in the blends with LCP content above 15wt% owing to the decomposition of LCP during processing.

Xie, X. L., Tjong, S. C., and Li, R. K. Y. [2000] studied the ternary blend of poly(butylene terephthalate, PBT), polyamide6,6 (PA6,6) and a liquid crystalline copolyester based on p- aminobenzoic acid (ABA) and poly(ethylene terephthalate, PET). The thermal, rheological and mechanical properties were investigated. The results showed that the melting temperature of PBT/PA6,6 phase tended to decrease with increasing LCP content. The torque rheometer showed that the viscosity of the blends decreased dramatically at higher LCP concentration. Finally, the tensile tests showed that the stiffness and tensile strength of ternary in situ composites were generally improved with increasing LCP content.