CHAPTER II

LITERATURE REVIEW

Liquid crystal have been known for over 100 years by Austrian botanist, Fridrich Reintzer [Cowies, 1991]. He noted that chloesteryl esters formed opaque liquids on melting, which became subsequently clear when heating to higher temperature.

There are a number of commercial applications based on these materials. Low molar mass liquid crystal have been used as plasticizers for the thermoplastic polymers, electro-optics applications, optical recording media, and membranes [Dutta et al., 1990]. High molar mass liquid crystalline polymers have been primarily used in polymer blends as a processing aids and as an incipient reinforcing phase "self-reinforced" materials [Dutta et al., 1990]. In this work, only low molar mass liquid crystal were used to blend with polystyrene (PS) and poly (bisphenol A carbonate) (PC) respectively. So, the literature review will involve only about low molar mass liquid crystal applications. The literature in this field is rarely found.

Kroneberg, B., Bassignana, I., and Patterson, D. [1978] studied the phase behaviour of N-(p-ethoxybezylidine)-p-n-butylaniline (EBBA) with polystyrene (PS) and polyethylene oxide (PEO), respectively. The width of the miscibility gap between EBBA and PS or PEO increased with increasing molar mass of the polymer. Thermal hysteresis properties were observed from nematic and isotropic transition temperature ($T_{N\text{-}I}$) in heating and cooling processes.

Dubault, A., Casagrande, C., and Veyssie, M. [1982] constructed the phase diagram of flexible polymers, namely, polystyrene (PS) and polyethylene oxide (PEO) in nematic solvents, i.e. p-azoxyanisole (PAA) and N-(p-ethoxybezylidine)-p-n-butylaniline (EBBA), respectively. The mixtures (PS with EBBA, PEO with PAA) were prepared and kept in the glass tubes which were sealed under vacuum. Firstly, each sample was homogenized by smooth shaking at a temperature when the low molar mass nematic solvent was isotropic (just above the clearing temperature of the nematic solvent). Secondly, the samples were dipped into a heated bath which permitted a visual observation of the sealed tubes at the lower temperature than the clearing point.

A typical phase diagram of flexible polymer in nematic solvent is shown in Figure 2-1. Φ_o is the concentration of an isotropic homogeneous solution. $T_i(\Phi_o)$ is the temperature which defines the upper coexistence curve that the first nematic droplet appears. The isotropic and nematic phases coexist until the temperature reaches $T_n(\Phi_o)$. At $T_d(\Phi_o)$ another phase separation process may occur; there appears an isotropic fraction rich in polymer in equilibrium with a nematic solution.

In the mixtures of PS with EBBA and PEO with PAA, they observed a biphasic region consisting of isotropic and nematic phases, and a biphasic region width was increased as the polymer molar mass increased. A homogenous nematic phase was not observed when average molecular weight of the polymer was greater than 10,000.

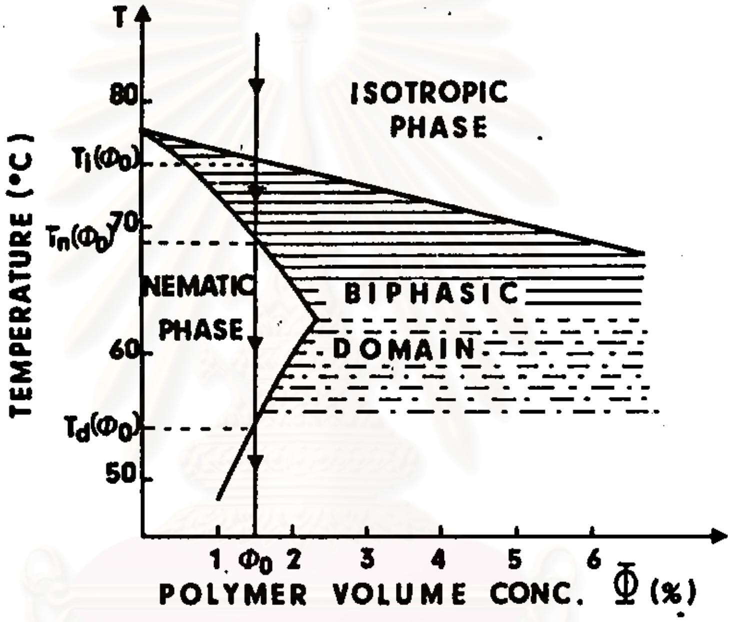

Figure 2-1 A typical phase diagram of flexible polymer in nematic solvent [Dubault et al., 1982]

Huh, W. and Weiss, R. A. [1983] studied the rheological and thermal properties of composites of polystyrene (PS) and two liquid crystalline low-molecular-weight additives: terephthal-bis-4-n-butylaniline (TBBA) and N-(p-ethoxybezylidine)-p-n-butylaniline (EBBA), respectively. Both additives act as plasticizers as evidenced from continuous decreasing in the glass transition and the melt viscosity of the blends. TBBA and EBBA were found to be miscible with PS at all temperatures when liquid crystal concentration was below 11 and 40 percent, respectively. Partial phase diagrams of the two systems were presented and discussed.

Buckley, A., Conciatori, A B., and Calundann, G. W. [1984] used low molecular weight liquid crystalline compound to plasticize polyolefin and polyester. The melt viscosities of blends were reduced by as much as 25 to 30 percent compared to the melt viscosities of the pure polyolefin and polyester.

Patwardhan, A. A. and Belfiore, L. A. [1988] used UNIFAC-FV (Universal Quasi-Chemical Functional-Group Activity Coefficient including Free Volume Correction) group contribution thermodynamic to predict the phase behaviour of blends of poly(ethylene glycol) (PEG) with p-hexyloxybenzoic acid (HOBA) and bisphenol-A-polycarbonate (PC) with p-pentyloxycinnamic acid (POCA). Experimental results based on differential scanning calorimetry (DSC) and high-resolution carbon-13 solid state NMR spectroscopy (^{13}CNMR) were used to construct the phase diagrams. Blends of PC/POCA were partially miscible. This conclusion was based on the depression of T_g of the blend for liquid crystal concentrations in the range 0-15 weight percent as shown in Figure 2-2. Blends of PEG/HOBA were completely immiscible.

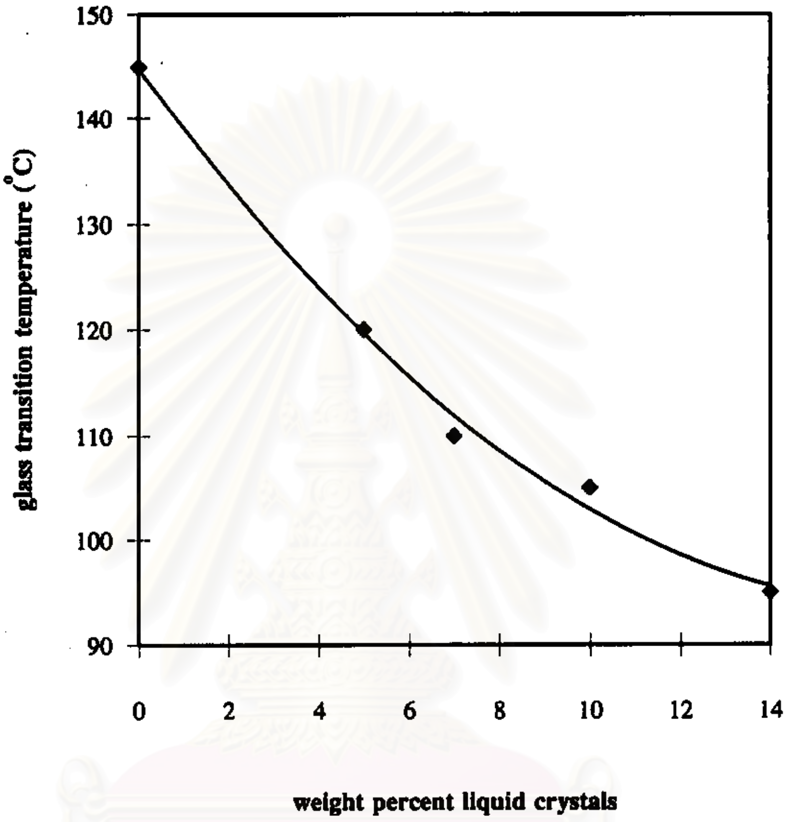

Figure 2-2 Glass transition temperature depression in blends of bisphenol-A-polycarbonate and p-pentyloxycinnamic acid [Patwardhan and Belfiore, 1988].

There are a number of works that observed the phase behaviour of the polymer-polymer blends and constructed the phase diagrams of the blends using a variety of experimental techniques.

An exanple is the work of Organ, S. J., and Barham, P. J. [1993] who studied the phase separation in a blend of poly(hydroxybutyrate) with poly (hydroxybutyrate-co-hydroxyvalerate) (HV). The blend had been studied using differential scanning calorimetry (DSC), polarizing microscopy and electron microscopy.

The information obtained from the DSC experiments were combined in the diagram shown in Figure 2-3. The dashed curve showed the approximate position of the boundary for liquid-liquid phase separation. The dotted curve showed where the crystals obtained in practice change from being predominantly mixed to phase separated.

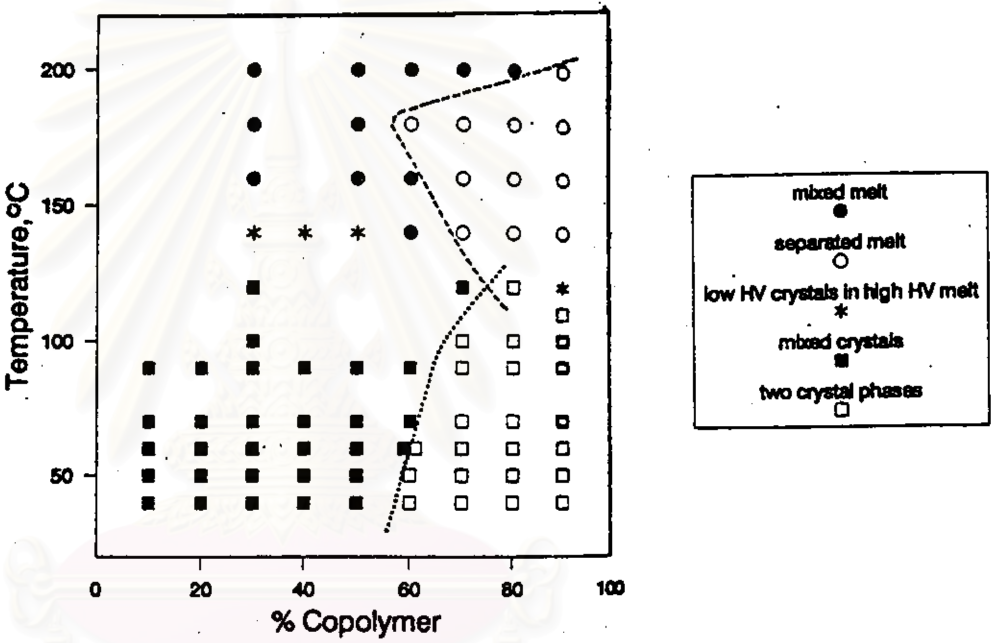

Figure 2-3 Summary of DSC results. The dashed curve (-----) shows approximate position of the boundary for liquid-liquid phase separation. The dotted curve (..........) shows the boundary between single-two phase crystallization [Organ and Barham, 1993].