Polymer Blends Containing Liquid Crystals: A Review

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This paper reviews the literature of polymer blends containing low and high molar mass liquid crystals. Low molar mass liquid crystals have been used as plasticizers for thermoplastic polymers and in applications such as electro-optics, optical recording media, and membranes. High molar mass liquid crystalline polymers have been primarily used in polymer blends as processing aids and as an incipient reinforcing phase for "self-reinforced" materials. This review discusses the phase behavior, rheology, and mechanical properties of these blends.

INTRODUCTION

Polymer blends containing a liquid crystalline polymers have received considerable attention in the past decade, and there is now a substantial literature on this subject. Most recently, the topic that has been most widely investigated is the development of self-reinforcing blends in which a fibrillar morphology of a dispersed liquid crystalline polymer phase is sought. Other studies, however, have considered thermodynamic aspects of these blends, with particular emphasis on the assessment of theoretical predictions of the phase behavior of mixtures of rod-like and flexible molecules.

This review surveys the published literature concerned with liquid crystalline polymer blends. Also included are studies of blends of polymers and low molar mass liquid crystals, for which there are several interesting applications. The subject of molecular composites, though discussed is not covered rigorously in this article.

The article is divided into two major categories: 1) blends containing low molar mass liquid crystals (LC's) and 2) blends containing high molar mass liquid crystalline polymers (LCP's). Each topic is further subdivided in order to group studies that had similar objectives. In many cases, a single paper is referenced in more than one section.

BLENDS CONTAINING LOW MOLAR MASS LIQUID CRYSTALS (LC's)

Monomer liquid crystals (LC) have been known for over 100 years, and there are now a number of commercial applications based on these materials, such as electro-optical displays, thermometry, and radiation sensors (1). The earliest reference, however, to the addition of an LC to a polymer was by Gebhard, et al. (2) in 1977. They were interested in the large increase in the orientational birefringence of N-p-methoxy-benzylidene-p-butylaniline (MBBA) above its nematic to isotropic phase transition temperature when it was used to swell trans-1,5-poly-pentenamer. Since then, a number of other researchers have investigated LC/polymer blends. Most of the studies have involved the thermodynamics or phase behavior of the blends, though several have described applications.

Thermodynamics and Phase Behavior

Flory and coworkers (3-8) provided a theoretical framework for the thermodynamics of mixtures of rod-like molecules and polymers of varying flexibility. Considering only the shape anisotropy of the rod-like molecules, they derived expressions for the phase equilibria in mixtures of low molar mass mesogens with rod-like polymers, semi-rigid polymers, and flexible coil polymers. The main conclusion of their theory was that flexible and rigid-rod molecules have little tendency to mix.

Brochard (9) extended Flory’s theory to networks made of flexible chains, swollen in a nematogenic solvent. Above the nematic-to-isotropic transition temperature, $T_{ni}$, uniaxial stretching of the gel oriented the solvent and resulted in an increased orientational birefringence. Below $T_{ni}$, the gel could be maintained either by rapid cooling or if the gel were nematic.

Ballauf (10) extended the lattice theory of mixtures for blends of nematic LC’s and flexible polymers to include the effect of isotropic interactions between the components. The theory successfully described the main features of the phase diagram, Fig. 1, for mixtures of p-ethoxybenzylidene-bis-4-n-butylaniline (EBBA) and polystyrene (PS). At low polymer concentrations, a two phase region consisting of a nematic phase and an isotropic phase was observed upon cooling the mixture from the single phase isotropic region. Further cooling led to a triple point,
below which another nematic phase and a polymer-rich isotropic phase were in equilibrium. At higher polymer concentrations, cooling from an isotropic coexistence of a polymer-rich isotropic phase and a state led first to phase separation of two isotropic polymer-poor nematic phase.

The enthalpy change at the clearing point was proportional to the saturation concentration of the LC in the LCP. Cser, et al. (14) measured the heats of transition at a composition of about 77 weight percent LCP. Cser, et al. (14) measured the heats of transitions for a variety of LC’s and LCP’s using DSC. The enthalpy change at the clearing point was proportional to the polymer content in the mixture, while the enthalpy change at the solid-LC transition was proportional to the saturation concentration of the LC in the LCP.

George, et al. (15) constructed phase diagrams for blends of linear thermotropic liquid crystalline polymers with an LC of similar structure. The LC depressed the melting point of the polymer, and at elevated temperatures transesterification occurred. This lowered the melt viscosity and improved the thermal stability relative to that of either of the pure components.

Several groups have studied mixtures of side chain LCP’s and monomeric LC’s. Ringsdorf, et al. (16) studied the miscibility of mixtures of low and high molar mass nematic liquid crystals. Miscibility depended on the chemical structure of the component mesogens. Mixtures with unlike structures phase separated in the nematic state, while miscibility occurred when the mesogenic side group of the polymer was similar to the LC. In the latter case, the LC plasticized the LCP and the crystallization of the LC was depressed.

Achard, et al. (17) observed a biphasic region for mixtures of low molar mass nematic solvents and liquid crystalline polymethacrylates or polyacrylates. Miscibility in these systems depended on the chemical nature of the side chain and not on the backbone. That is, similarities between the polymer and monomer mesogens promoted miscibility. In general, the addition of a mesogenic solvent depressed \( T_N \) of the polymer.

Similar results were reported by Sigaud, et al. (18), who systematically studied the effect of chemical structure of LC’s on their miscibility with a side chain LCP based on poly(methyl siloxane) (PMS). Miscibility of the LCP in a nematic solvent depended on the length of the aliphatic tail of the solvent and the length of the flexible spacer and tail of the LCP side group. In some cases, blending also induced the formation of a smectic A phase.

Kroneberg and co-workers (19) studied the phase behavior of EBBA with PS and PEO. The width of the miscibility gap increased with increasing molar mass of the polymer, and hysteresis was observed in \( T_N \) between heating and cooling scans. Dubault, et al. (20) also constructed the phase diagrams of flexible polymers in low molar mass nematic solvents. They observed a biphasic region consisting of isotropic and nematic phases, and its width was increased as the polymer molar mass increased. A homogenous nematic phase was not observed when \( M_w \) of the polymer was greater than 10,000.

Belfiore and coworkers (21, 22) used UNIFAC-FV (Universal Quasi-Chemical Functional-Group Activity Coefficient including Free Volume Correction) group contribution thermodynamics to predict the phase behavior of blends of PEO, with \( p \)-hexyloxybenzoic acid (HOBA) and bisphenol-A-polycarbonate (PC) with \( p \)-pentoxyxcinnamic acid (POCA). Experimental results based on DSC and \(^{13}\)CNMR were used to construct the phase diagrams. Blends of PC/POCA were partially miscible, whereas PEG/HOBA were completely miscible.

Dormoy, et al. (23) found that the chain conformation of polystyrene in the isotropic phase of a nematic solvent, pentylyanobiphenyl, was perturbed due to coupling between the local orientational order of the solvent and the polymer. Lipatov, et al. (24) used a cobalt gun to irradiate phase-separated mixtures of cholesteric LC microdomains dispersed in a polyurethane matrix. Radiation doses varying from 5 to 50 Mrad improved the modulus and strength of the mixture. This was attributed to the formation of an additional network of microdomains as the polyurethane crosslink density increased. Optimum strength was achieved with a 20 Mrad dose.

Using ultrasonic impedometric techniques, Martinoty, et al. (25) measured the viscosity coefficients of dilute solutions of polystyrene in EBBA. Considerable increases in the LC viscosity were achieved by the addition of small amounts of PS. Moreover, the increase of the solution viscosity with decreasing temperature was more rapid than expected from a
classical Arrhenius dependence, which was satisfactory for describing the solution viscosity of PS in an isotropic solvent.

Applications

Huh and coworkers (26) used thermotropic LC's, EBBA and terephthal-bis-4-n-butylaniline (TBBA), as plasticizers for polystyrene. EBBA and TBBA were miscible in PS up to LC concentrations of 20 and 11 percent, respectively. Plasticization was demonstrated by decreases in the glass transition temperature, Fig. 2, and melt viscosity with increasing LC content up to the solubility limits of the LC's in the polymer. Above the solubility limit, the LC phase-separated and no further decreases in \( T_g \) or viscosity were observed. \( T_w \) of the LC's decreased as the PS concentration increased, Fig. 2.

Similarly, Buckley, et al. (27) used LC's to plasticize polyolefins and polyesters. The melt viscosities of blends were reduced by as much as 25 to 30 percent compared to the melt viscosities of the neat polymers.

Several research groups have described electro-optical display technology based on materials containing microdroplets of liquid crystals distributed in a polymer matrix, i.e., polymer dispersed liquid crystals (PDLC) (28–32). These materials have applications in optical displays, light valve, temperature sensors, and variable transmission windows. The principle of operation of such devices is based on the control of the refractive indices of the two phases, and hence the light scattering from a PDLC film, by application of an electric field. In one design, Fig. 3, in the absence of an electric field, the PDLC film appears opaque, due to the random orientation of the optic axes of LC droplets. This results in a mismatch in the refractive indices of the LC and the polymer, which is responsible for the scattering of the incident light. When an electric field is applied, the optic axes of the microdroplets align in a direction parallel to the electric field, matching the refractive indices, and the film becomes optically transparent.

A recent paper by West (33) described the following three ways to prepare PDLC materials: 1) the LC is dissolved in a polymer precursor and the dispersed LC-phase forms during polymerization, 2) the LC is dissolved in a polymer melt and phase separation of the droplets occurs during cooling of the melt, or 3) the LC and the polymer are dissolved in a common solvent followed by evaporation of the solvent, during which the LC precipitates as a microphase. The electro-optical properties are influenced by the droplet morphology. For example, the scattering efficiency of the PDLC is maximized when the droplet size is of the order of the wavelength of light. The size of the droplets, density, and electro-optical properties can be controlled by varying the cure temperature, rate of cooling, or rate of solvent removal, depending on the method used to prepare the PDLC material.

Fig. 2. (a) Phase diagrams for TBBA/PS composite. Reprinted with permission from (26). (b) Phase diagrams for EBBA/PS composite. Reprinted with permission from (26).

Fig. 3. Illustration of the principle of optoelectronic operation of the PDLC films. \( I_0 \) = incident light, \( I_s \) = scattered light, \( I_t \) = transmitted light, \( n_e \) = extraordinary refractive index, \( n_o \) = ordinary refractive index, \( n_p \) = polymer refractive index. Reprinted with permission from (33).
McIntyre and Soane (34) recently described a blend of EBBA and poly(methyl methacrylate) (PMMA) as a reversible optical storage medium. This blend exhibits an upper critical solution temperature, and therefore, when heated the two components become miscible. Since the blend is a glass at room temperature, the extent of phase separation that occurs when the blend is cooled from the one-phase region, can be controlled by varying the cooling rate—that is, phase growth is inhibited once the blend vitrifies. The device that these authors proposed involved a complicated process using three different incident light patterns to erase, write, and read the domain pattern. This system, however, has several potential advantages over the transition metal and rare earth element-based systems currently being developed in that they are less prone to oxidation and thermal expansion problems and can be more easily fabricated.

LC/polymer blends have also been shown to have unique transport properties. Kajiyama and coworkers (35–37) described the structure and permeation properties of membranes made from blends of EBBA with PVC or PC. The EBBA was molecularly dispersed in the composite membranes containing up to 30 weight percent LC. For membranes containing 60 percent EBBA, the morphology consisted of a 3-dimensional network of polymer fibrils in an LC continuous phase. The permeabilities of gases through the 60 percent EBBA composite membrane were enhanced in the vicinity of the crystalline to nematic transition of the EBBA, $T_{k_n}$. This was attributed to the onset of molecular motion in the membrane and/or an increase in pore formation. Permeation was principally governed by diffusion below $T_{k_n}$ and solubility above $T_{k_n}$.

Membranes were also prepared from blends of 4-cyano-4'-pentylibiphenyl with PC (38). The application of an electric field increased the gas permeability through the membrane, which was attributed to a preferential orientation of the LC molecules parallel to the field. The gas permeability was directly proportional to the magnitude of the applied voltage.

Shinkai, et al. (39), prepared ternary blend composite membranes composed of EBBA, PC, and amphiphilic crown ethers. The ion permeability was affected by molecular motions of the LC phase. That is, below $T_{k_n}$ permeability was low, but it increased significantly above $T_{k_n}$. This phenomenon was found to be thermally reversible and has the potential as a temperature-switchable permselective membrane.

**BLENDS CONTAINING LIQUID CRYSTALLINE POLYMERS (LCP)**

The literature dealing with polymer/polymer blends containing liquid crystalline polymers (LCP's) is divided below into three main categories: 1) phase behavior and thermal studies, 2) rheology and processing, and 3) mechanical properties and morphology. Each of these categories is further subdivided.

**Phase Behavior and Thermal Studies**

**Crystallization Phenomena**

Various investigators have reported that the rate and degree of crystallization of flexible-coil polymers was increased by the addition of an LCP (40–44). Joseph, et al. (40, 41) studied the thermal behavior of blends of poly(ethylene terephthalate) (PET) and a liquid crystalline copolyester based on 60 mole percent parahydroxy benzoic acid (PHB) and 40 mole percent PET (40 PET/60 PHB). The rate of crystallization increased as the LCP content increased in the blend, which was attributed to nucleation of the PET crystallization by the LCP. The degree of crystallinity also increased with the addition of the LCP (Fig. 4). Similarly, Misra and co-workers (42–43) studied blends of PET with 2 different LCPs: one, a commercial LCP, based on 6-hydroxy-2-naphthanoic acid (HNA) and PHB, and the other, a copolymer of PET and PHB. Like Joseph and coworkers, they also found that the crystallization rates for the blends were higher than that of pure PET. Takayanagi, et al. (44) studied blends of wholly aromatic polyamides with aliphatic polyamides, and they suggested that the surface of the rigid polyamide acted as a nucleating agent for the crystallization of the matrix polymer.

Isothermal crystallization kinetics studies of nematic and smectic liquid crystalline polyesters containing polymethylene flexible spacers in the main chain and their blends were reported by Yoo and Kim (45). They used differential scanning calorimetry (DSC) and microscopy and found that regardless of crystallization temperature, the crystallization kinetics followed the Avrami equation up to a high degree of crystallization. Blends of nematic and smectic

![Fig. 4. Effect of LCP content on heat of crystallization of PET. Reprinted with permission from (40).](image-url)
LCPs showed that the crystallization rate of one component was significantly affected by the presence of the second component.

A theoretical analysis of the effect of adding a non-rigid crystalline solute to a main chain LCP was done by Dowel (46) using the localized mean-field, simple cubic lattice theory. The results predicted a mixture of two phases in which the anisotropic and isotropic phases coexist, and the addition of the flexible solute causes the disruption of orientational order of the LCP. This results in a lowering of $T_{\text{N} \cdot}$.

**Miscibility of LCP Blends**

The miscibility behavior of blends containing an LCP have been widely investigated (47-68), using DSC, scanning electron microscopy (SEM), and X-ray diffraction (XRD). A great deal of this literature involves the miscibility of the liquid crystalline copolyesters of PET and PHB with other, flexible-chain polymers (47, 51, 58-62). Kimura and Porter (47) studied the phase behavior of blends of PET/PHB with poly(butylene terephthalate), PBT, using DSC. Their studies showed that the PET-rich phase of the copolyester was miscible with PBT whereas the PHB-rich phase was not. PET/PHB itself exhibited two phases: a PHB-rich phase and a PET-rich phase. When PC was used instead of PBT, it also was partially miscible with the PET-rich phase of the copolyester (69). According to Luise (50), miscibility of melt blends of thermotropic polyesters with isotropic polyesters is governed primarily by polymer asymmetry.

Blends of various PET/PHB copolymers containing 30, 60, and 80 percent PHB with thermoplastic polymers such as polystyrene (PS), polycarbonate (PC), and PET were investigated by Zhuang, et al. (51). While PS blends were found to be completely immiscible, the PC and PET blends were partially miscible. Immiscibility of 40 PET/60 PHB with PC was also reported by Noble, et al. (58). Hess and co-workers (60-62) however, reported that annealing the LCP/PC blend in the melt caused transesterification reactions that resulted in a miscible blend as evidenced by a single $T_g$, Fig. 5. Although annealing a blend of PET/PHB with PET in the melt had no effect on either of the $T_g$'s, it did reduce the melting temperature of the PET in the blend by 42°C.

The phase behavior of solvent cast films of blends of 40 PET/60 PHB with PET or PC were studied by Nakai, et al. (58) and Kyu and Zhuang (59). The films of PET and the copolyester were prepared by dissolving the polymers in o-chlorophenol and removing the insoluble part by filtration (59). The as-cast films were optically clear and homogeneous. They phase separated, however, into an anisotropic phase and an isotropic phase when heated above the melting temperature of the PET. Similarly, solvent-cast films prepared from the LCP and PC were optically transparent (59). A cloud point curve characteristic of a lower critical solution temperature was determined by annealing the film at elevated temperatures and identifying the temperature at which phase separation occurred, Fig. 6. Phase separation appeared to occur via a spinodal decomposition mechanism.

A similar phase separation phenomenon was observed by Chuah, et al. (57) in films of rigid rod molecular composites of poly(p-phenylene benzobis-thiazole), (PPBT), and Nylon 66. Microscopic studies showed that the processed films were optically clear and homogeneous. However, the molecular composite was phase-separated above the melting temperature of the polyamide.

Transesterification reactions increase the miscibility of a liquid crystalline co-polyesters with isotropic polyesters (62-64). Zhou, et al. (63) found that blends of PET and a copolyester of PHB, bisphenol A and terephthalic acid (TA) exhibited one-phase behavior after transesterification. Paci, et al. (64) reported that blends of PBT and a liquid crystalline poly(biphenyl-4,4’-xylene sebacate) (PB8) were miscible in the isotropic state and phase separation depended on the rate of cooling. The degree of PBT crystallinity first increased with the addition of as little as 5 weight percent PB8 and then decreased with increasing LCP. The authors attributed this to

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**Fig. 5.** Effect of annealing time on miscibility of PC/PET-PHB blend. Reprinted with permission from (60).

**Fig. 6.** Cloud point phase diagram of PC/PHB-PET blends obtained at 2°C/min. Reprinted with permission from (59).
a cybotactic structure observed in the quenched blends of PBT and the polyarylate that favored the cold crystallization of PBT. Transesterification reactions between the two polyesters improved their miscibility. In contrast, blends of a PHB-based thermotropic polyester and Nylon 12 were immiscible (48, 49).

Miscibility studies on blends of PHB/HNA liquid crystalline copolymers differing in comonomer ratios were reported by DeMeuse and Jaffe (52). Using XRD and DSC results, the authors showed that the blends were miscible in the solid state.

Weiss, et al. (67) prepared blends of PS and a thermotropic polylkanoate of 4,4'-dihydroxy-a,a'-dimethylbenzalazine using a two roll mill. DSC studies indicated that the blends were in general miscible, though there may have been some marginal miscibility of the LCP in PS of about 1 percent.

Pracella, et al. (65, 66) characterized blends of PET and poly(decamethylene 4,4'-terephthaloyl dioxy dibenzoate) (HTH10). The phase behavior of the blends depended on composition and thermal history. The DSC thermograms of the blends showed a double melting peak on second heating. The higher melting peak was attributed to reorganization of the PBT crystals on heating and its temperature was almost independent of the composition of the blend. The temperature of the lower melting peak, however, decreased with increasing HTH10 content, indicating that HTH10 plasticized the PBT. For blends containing more than 30 weight percent HTH10, coexistence of the crystal phases of the PBT and HTH10 was observed. Blends quenched from the isotropic melt showed one Tg that was intermediate between the neat polymers, which led the authors to conclude that PBT and the HTH10 were miscible in the amorphous phase. The presence of HTH10 in the blend depressed the primary heterogeneous nucleation and growth rate of the PBT spherulites and caused a decrease in the crystallization rate of the PBT.

Seurin, et al. (53) used polarized microscopy to construct a phase diagram of mixtures of a semi-rigid polymer, hydroxypropyl cellulose (HPC), and a flexible polymer, polyethylene glycol (PEG). The PEG had no effect on the orientation of the LCP. Low molar mass PEG was miscible with HPC, which was attributed to intermolecular interactions between the two polymers. As the molar mass of the PEG increased, the intermolecular interactions weakened and eventually phase separation occurred. Increasing the molar mass of the HPC simply shifted the mesophase to isotopic transition to higher temperatures. Billard, et al. (54) also used polarized microscopy to construct the phase diagrams of mixtures of cholesteric and nematic thermotropic LCP's. The mesophases were identified by the contact method, and the sign of the twist of the cholesteric phase was determined from the displacement of the isoschomatic lines (55).

The phase behavior of blends containing side chain liquid crystalline polymers have also been investigated using DSC, hot-stage microscopy and XRD (56).
the solution became biphasic. The anisotropic phase consisted only of the high molar mass fraction rod-like polymer, and the isotropic phase contained a low molar mass fraction of the rigid polymer in addition to the flexible polymer. Hwang, et al. (76, 77) who studied systems of a rigid rod poly-p-phenylene benzobisthioazole (PPBT) and a flexible coil polymer in a solvent also reported similar behavior. Their flexible polymers exhibited cholesteric mesophases. Four zones in the phase diagrams were identified: zone I was an isotropic single phase, zone II was an isotropic-isotropic biphase, zone III had an isotropic-anisotropic and an anisotropic-anisotropic biphases, and zone IV was an anisotropic monophase. By changing the polymer concentration in zone III they were able to control the texture of each phase, and droplets of either phase could be easily deformed by moving one of the slides.

Wiff, et al. (82) prepared films of PPBT and Nylon 66 by casting the mixture from a common solvent, methane sulfonic acid. DSC studies indicated that PPBT and Nylon 66 formed a two-phase system. TGA studies indicated that the addition of PPBT enhanced the thermal stability of Nylon 66.

**RHEOLOGY AND PROCESSING**

One of the major advantages of blending LCP's with thermoplastic polymers is that the LCP acts as a processing aid. A number of studies (48, 49, 51, 67, 68, 83–98) have shown that extensional flows, such as is encountered in the entrance of a capillary, can preferentially orient the LCP domains in the direction of flow. The oriented LCP domains smoothly glide past each other, thus lubricating the polymer melt and lowering the melt viscosity of the blend. Rheological characterization of LCP/polymers blends have been done mainly by capillary viscometry, though some researchers have used cone and plate or parallel plate rheometers.

An important parameter in utilizing the LCP as a processing aid for a conventional thermoplastic is the temperature at which the blend is melt processed. Cogswell, et al. (83–85) concluded that the temperature range at which conventional polymers are melt processed should overlap with the temperature range in which the LCP forms an anisotropic melt. The viscosity of such melts were found to be much lower than that of the thermoplastic polymer alone and the processing temperatures could be reduced. The advantages of this reduction in processing temperatures are reduced energy consumption and less degradation of polymers that are sensitive to higher temperatures. Moreover, lowering the viscosity facilitates the filling of large or complex molds.

Polymer blends using 40 PET/60 PHB have been studied by a number of research groups (51, 68, 92, interactions and to deviations from a rod-like conformation.

Russo and Cao (78) determined the ternary phase diagram for poly-(γ-benzyl-α,L-glutamate)/Nylon 6/m-cresol using optical microscopy. The isotropic phase excluded the rod-like polymer, and the phase diagrams were significantly different from those predicted by the Flory theory. The deviations from theory were attributed to hydrogen-bonding interactions between the three components.

Ambrosino, et al. (79) constructed ternary phase diagram of HPC, ethyl-cellulose (EC), and acetic acid (AA) using polarized microscopy. The cellulosic polymers exhibited cholesteric mesophases. Four zones in the phase diagrams were identified: zone I was an isotropic single phase, zone II was an isotropic-isotropic biphase, zone III had an isotropic-anisotropic and an anisotropic-anisotropic biphases, and zone IV was an anisotropic monophase. By changing the polymer concentration in zone III they were able to control the texture of each phase, and droplets of either phase could be easily deformed by moving one of the slides.

Polymers and LCPs are often used together to improve the properties of the blend. The LCP can act as a processing aid to reduce the melt viscosity of the blend, allowing for easier processing and lower energy consumption.
Blizard and Baird (92) studied the rheological property of blends of this LCP with PC and Nylon 66. The measurements were made with a cone and plate rheometer at low shear rates and with a capillary rheometer at higher shear rates. Dynamic oscillatory and steady shear data showed a significant reduction in the viscosity of the blends by the addition of the LCP, Fig. 9. Similar results were reported by Zuang, et al. (68) who studied the blends of this LCP with PS, PC, and PET. Studies by Acierno, et al. (93) on blends of 40 PET/60 PHB with PC also showed a decrease in viscosity with the addition of the LCP. In contrast to these studies, however, Nobile, et al. (68) reported that at low shear rates (below 0.3/s) the complex viscosity $\eta^*$ increased with increasing LCP content for blends of 40 PET/60 PHB and PC. At higher shear rates $\eta^*$ decreased with increasing LCP concentration.

A reduction in the melt viscosity of blends of this LCP with chlorinated poly(vinyl chloride) was observed by Lee (98). These blends also showed a decrease in the extrudate swell and an increase in the spiral mold flow at low LCP concentrations.

The viscoelastic behavior of blends of 40 PET/60 PHB with a styrene-butadiene copolymer was reported by Lorenzo, et al. (99). They found that the barrel temperature had a significant effect on the melt flow index (MFI) and $\eta^*$ of the blends. For example, when the blends were extruded below the melting temperature of the LCP, $\eta^*$ was independent of LCP concentration. However, when the extrusion was done above the melting point of the LCP, both the MFI and $\eta^*$ exhibited a minima at 10 percent LCP concentration.

Another liquid crystalline co-polyester that has been widely used in blends is the copolyester of 6-hydroxy-2-naphthanoic acid (HNA) and PHB (57, 86–88, 97, 98, 100–102). Several grades of this type of LCP have been commercialized by Hoechst-Celanese Corp. under the trade name Vectra and by Imperial Chemical Industries, Ltd. under the trade name Vitrex. Some of these LCP compositions also incorporate aromatic ester groups derived from monomers such as terephthalic acid (TA) and hydroquinone (HQ).

Siegmann and co-workers (86) studied the rheological behavior of blends of an HNA/PHB LCP with an amorphous polyamide using a capillary rheometer. All the melts exhibited non-Newtonian flow behavior, which could be described by a power-law constitutive equation over a limited shear rate range. The viscosities of the blends were much lower than those of the thermoplastic polymer. The addition of as little as 5 weight percent LCP resulted in a large reduction in viscosity from that of the pure polyamide.

Swaminathan and Isayev (88) reported similar results for blends of an HNA/PHB copolyester with poly(ether amide). A reduction in viscosity of poly(ether sulfone) (PES) by the addition of an HNA/PHB LCP was reported by James, et al. (90) and Froix, et al. (91). James and coworkers (90) characterized the rheological behavior of the blends by plotting dynamic viscosity vs. shear rate. About a four fold drop in viscosity was observed with the addition of only 2 weight percent LCP. The shape of the flow curves for blends with up to 20 weight percent LCP resembled that of pure PES, and they were Newtonian until about 16 s$^{-1}$. The viscosity curve of the 50 percent LCP blend showed shear thinning behavior and was similar to that of the pure LCP. Chung (48–49) found a minimum in viscosity at a concentration of 10 weight percent LCP and a maximum at 20 percent LCP for blends of HNA/PHB and Nylon 12. According to Chung, below 10 percent LCP the LCP domains were well dispersed in the Nylon 12 matrix and acted as a lubricant, thereby reducing viscosity. At 20 weight percent LCP, however, an interlocking morphology developed which resulted in a sharp increase in viscosity.

Several research groups have studied blends of HNA/PHB type copolyesters with PC. Isayev and Modic (87) observed a crossover point in the flow curves of the PC and the LCP melts, and this crossover point had a special significance in that maximum fibrillation of a blend occurred at this point during flow. Malik, et al. (101) studied similar blends and found that the melt viscosities were similar to that of the unblended PC, but more shear thinning and less viscous. They also investigated time-dependent behavior of the blends by solid-state relaxation measurements and found that the relaxation modulus increased with the addition of the LCP.

Kohli, et al. (102) studied blends of PC and a lower melting point LCP based on HNA/PHB/TA/HQ and found that the addition of about 5 percent LCP resulted in a 68 percent drop in viscosity. Moreover, the viscosity decreased monotonically with increas-
fig LCP content over the entire range of blend composition. They observed that the general shape of the viscosity vs. shear rate curve was dominated by the continuous phase of the blend, Fig. 10. At low LCP concentrations, the PC constituted the continuous phase. Here, the flow curves were similar to that of PC, except that shear thinning occurred at lower shear rates as the LCP concentration increased. A phase inversion occurred at about 40 to 50 percent LCP content and above this composition the flow curves were more like that of the LCP. No Newtonian region was observed and the viscosities were strongly shear thinning.

Most investigators have reported a decrease in viscosity of blends with the addition of an LCP. Weiss, et al. [67, 94–97], however, reported that the addition of a thermotropic LCP based on 4,4'-dihydroxy,a,a'-dimethylbenzalazine to PS raised both the steady shear and dynamic viscosities at low shear rates (1 s⁻¹) or frequencies. This increase in viscosity was attributed to tumbling and rotation of phase-separated LCP domains. At higher shear rates, however, the viscosity decreased with increased LCP content. For example, a composition of 10 weight percent LCP resulted in about a 40 percent reduction in viscosity.

The lowering of viscosity at high shear rates was explained by an extensional deformation of the LCP domains during flow in the entrance region of the capillary viscosometer. An important point in this research was that the lower shear rate data were obtained with a cone and plate rheometer and, therefore, the blends experienced only simple shear flow. The increase in viscosity under these conditions was consistent with the theoretical predictions for the simple shear flow of two-phase fluids. The higher viscosity data required the use of a capillary viscometer, and in this case, the simple shear flow in the capillary is preceded by an extensional flow in the entrance region. The extensional flow can align and deform the LCP domains in the flow direction, and it is this change in the melt morphology that is largely responsible for the decrease in the blend viscosity.

Most studies of LCP-containing polymer blends have used a thermotropic LCP together with a flexible, thermoplastic polymer. In contrast, DeMeuse and Jaffe (52) studied blends in which both the components were LCP copolyesters based on PHB and HNA. The rheological behavior of the blends depended on the composition of the individual copolymers. For example, when the compositions of the copolymers were similar, the viscosity of the blend followed a rule of mixtures relation similar to that for a miscible blend,

\[ \ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 \] (1)

where \( \eta \) is the viscosity of the blend, \( w_1 \) and \( w_2 \) are the mass fractions of the two polymers, and \( \eta_1 \) and \( \eta_2 \) are the viscosities of the individual components in the blend. When the difference in the composition of the copolymers was significant, the viscosity of the blend followed an inverse rule of mixtures expression formulated for immiscible blends,

\[ \frac{1}{\eta} = \frac{w_1}{\eta_1} + \frac{w_2}{\eta_2} \] (2)

The rheology of blends of rod-like and flexible polymers was modeled by Kim, et al. (103). They studied the blends below a critical concentration that was defined as the concentration above which phase separation occurred. The rheological behavior of these blends could be represented by a single integral constitutive equation of the BKN type.

MECHANICAL PROPERTIES AND MORPHOLOGY

One of the primary objectives of blending LCPs with thermoplastic polymers has been to use the LCP as a reinforcement for flexible thermoplastic polymers. Mechanical properties of blends have been reported in a number of studies (48, 49, 67, 86–89, 92, 93–97, 102, 104–109). Most of these researchers have attempted to explain the changes in mechanical properties in terms of the morphology of the LCP domains in the blends. The most widely used technique to study the morphology has been scanning electron microscopy, (SEM), though XRD and SAXS have also been employed (68, 100, 110, 111) to find the degree of order of the LCP phase in the blend.

In nearly all the studies of LCP/polymer blends, the two component polymers were immiscible. The size, shape, and distribution of the LCP phase depended on many factors such as composition, processing conditions, viscosity ratio of the component polymers, and the rheological characteristics of the matrix polymer (i.e., viscoelastic, pseudoplastic, or Newtonian). For example, Acerio, et al. (93) found that for a blend of 60 PHB/40 PET and PC containing 10 percent LCP, extrudates at 260°C contained spherical LCP domains dispersed in the PC matrix. This was true even for drawn blends. But blends drawn at 210°C had fibrillar LCP domains oriented in the direction of flow. The difference in the mor-

Fig. 10. Viscosity vs. shear rate data for LCP/PC blends at 270°C. (□) 0, (•) 5, (□) 10, (○) 20, (□) 40, (△) 60, (●) 80, (V) 100% LCP). Reprinted with permission from (102).
phologies was due to different viscosity ratios at the two temperatures. Similar results were also obtained by Nobile, et al. (68) with the same system. They reported that although the tensile modulus increased with draw ratio for fibers drawn at 220°C, there was very little effect of draw ratio for fibers drawn at 260°C. In general, drawing or stretching a blend extrudate results in the formation of LCP microfibrils that are highly oriented in the direction of stretch (67, 84, 97, 102, 109, 112), Fig. 11. Ramanathan, et al. (113), however, studied blends of poly(phenylene sulfide) and a variety of LC copolymers and found that the shape of the LCP domains (i.e. droplets vs. fibrils) in an extrudate depended on the composition of the LCP and not on draw ratio.

Increased orientation of the dispersed LCP microfibrils formed by drawing can result in greatly improved mechanical properties of the blend (68, 101, 102, 104, 109, 112, 114, 115). Malik, et al. (101) studied blends of HNA/PHB and PC and found that the modulus of the pure LCP extruded from a capillary viscometer increased up to shear rate of 150 s⁻¹, but then decreased above this deformation rate.

Wellman, et al. (104) investigated the reinforcement of the flexible coil-like, amorphous polymer, ABPBI, with the rod-like polymer, PPBT. Stretching a blend film resulted in an increase in the modulus. Blends containing up to 30 percent PBT had saucer-shaped domains, which the authors concluded were undesirable. In an attempt to remove the LCP aggregates, a blend containing 60 percent PPBT was made. The modulus in this case did not change much upon stretching. The high LCP content made it difficult to control the morphology and failed to improve the orientation of the domains. Similar studies (114, 115) were carried out by blends containing a variety of rod-like aromatic heterocyclic polymers and a flexible coil-like amorphous polymer. Thin films were obtained by vacuum casting and by precipitation from dilute solutions. The modulus increased on stretching when the rod-like polymer was present as a minor component in the blend.

Weiss, et al. (109) observed an order of magnitude increase in modulus as the draw ratio was increased from 1 to 1000 for fibers extruded from blends of an HNA/PHB/HQ/TA LCP with PC, Fig. 12. The enhancement of the modulus due to melt drawing was a result of improved orientation and fibrillation of the dispersed LCP domains. They also found that the LCP chains within the domains were highly oriented in the direction of flow (109).

Sun, et al. (112) extruded sheets of PPS and 40 PET/60 PHB and 20 percent PET/80 percent PHB copolyester and PEI/Thermoplastic polyimide and HNA/PHB LCPs and found that the modulus increased with drawing. SEM micrographs revealed fibrillar morphologies of the LCP domains. A high degree of molecular orientation within the LCP was also confirmed by XRD.

A number of studies have considered the effect of LCP concentration on the mechanical properties and morphology of blends (43, 51, 66, 68, 86, 87, 100, 101, 108, 113, 116, 117). Ko and Wilkes (100) reported that the modulus of blends of HNA/PHB and PET increased only at high LCP content (80 percent LCP). When this same LCP was blended with an amorphous polyamide, however, the mechanical properties increased monotonically with increasing LCP content (86), Fig. 13. For blends of 40 PET/60 PHB and PET, Bhattacharya, et al. (43) found that the initial modulus and tenacity of melt spun fibers increased with increasing LCP content, while elongation to break decreased. As the LCP content was increased, the mode of failure changed from brittle to ductile.

Zhuang, et al. (51) found that adding small amounts of 40 PET/60 PHB to PET, PC, or PS increased the modulus and tensile strength of compression molded films, extrudates, and melt spun filaments. Similarly, Froix and Park (116) showed that the mechanical properties of PC were improved by incorporating melt processible, wholly aromatic liquid crystalline polyesters. Amano and Nakagawa (108) investigated the drawing behavior of blends of PET and a 40 PET/60 PHB copolyester using conventional and microwave heating. The optimum drawing tension, drawing temperature, and draw ratio necessary for attaining an optimum modulus decreased with increasing LCP concentration.
Polymer Blends Containing Liquid Crystals: A Review

Isayev and Modic (87) reported that injection molded and extruded blends of an HBA/HNA and PC containing greater than 25 weight percent LCP had spherical LCP domains dispersed in the PC matrix. Blends with 10 percent LCP content, however, had a fibrillar LCP morphology. A similar observation was also reported by Pracella, et al. (66), who examined the morphology of blends of PBT and a liquid crystalline polyester, decamethylene 4,4'-terephthaloyl-dioxoy dibenzoate, quenched from melt. The fracture surfaces of blends containing up to 50 weight percent LCP revealed the presence of rod-like structures of the LCP component oriented perpendicular to the fracture plane. For blends containing more than 50 weight percent LCP, the morphology was homogeneous and LCP domains were not observed.

Skin-core morphologies are common in blends of LCP's and thermoplastic polymers (48, 49, 67, 86, 88, 90, 92, 97, 107, 114, 118), and they play an important role in determining the properties of extruded and injection molded samples. Normally, LCP's in the skin have a higher degree of orientation than in the core when the blends are extruded or injection molded (86, 90, 106). Baird and coworkers (92, 107) observed a skin-core morphology in blends of Nylon 66 with HBA/HNA and 40 PET/60 PHB and 20 percent PET/80 percent PHB copolymers. In both systems more LCP fibers were present in the skin than in the core. Swaminathan and Isayev (88) also observed a shell-core structure in the fracture surfaces of injection molded blends of an HNA/PHB liquid crystalline copolyester and poly(etherimide).

Weiss, et al. (67, 97), however, found a higher concentration of LCP microfibrils near the core in blends of PS and LCP based on 4,4'-dihydroxy-a,a'-dimethylbenzalazine. They attributed this behavior to a two way migration effect in which drops initially at the center of the tube migrated towards the wall and drops initially at the walls migrated towards the tube axis. With increasing shear rates, the inward migration dominated and the equilibrium position shifted towards the tube axis. A similar phenomenon was observed by Chung (48, 49) in his studies of blends of copolymers and Nylon 12. For melt drawn blends of this LCP with PES, however, an LCP phase oriented in the draw direction was found in the skin region (90).

The fact that LCPs can act as a reinforcing agent in a blend has led some investigators to model the mechanical behavior of the blends according to composite theories (87, 102). Isayev and Modic (87) based their calculations on the assumption that blends of PHB/HNA and PC could be treated as unidirectional fiber-reinforced composites. Their experimental data approached the calculated properties. Kohli, et al. (102) in their studies on blends of PHB/HNA/HQ/TA and PC showed that the moduli of highly drawn melts could be modeled effectively by the simple rule of mixtures:

$$E_c = E_1V_1 + E_2V_2$$  \[(3)\]

where $E_c$ is the composite modulus, $E_1$ and $E_2$ are the moduli of the reinforcing LCP and the matrix, respectively, and $V_1$ and $V_2$ are their volume fractions. Fig. 14. A major reason for the good agreement in this study between the data and the model was the high alignment of the LCP microfibrils LCP in the draw direction and their high aspect ratios. They also
modeled the modulus of compression molded samples where the LCP phase was spherical according to the inverse rule of mixtures:

\[ \frac{1}{E_c} = \frac{V_1}{E_1} + \frac{V_2}{E_2} \]  

(4)

Takayanaki, et al. (38, 44, 119, 120) investigated blends of rigid, wholly aromatic polyamides such as poly[p-phenylene terephthalamide] (PPTA), poly-p-benzamide (PBA) with aliphatic nylons, PVC, NBR, and ABS. The Young’s modulus and yield stress increased when the rigid polyaramides were dispersed in the aliphatic polyamides (38). The modulus and yield stress increased with increasing molar mass of the polyaramide, but the elongation to break decreased. This was due to the formation of more perfect and stronger microfibrils with increasing molar mass which restrained the ductile deformation of the blend. In an attempt to improve the ultimate elongation block copolymers of a wholly aromatic polyamide and an aliphatic polyamide were blended with the aliphatic polyamide. The elongation to break increased while the high modulus and strength were retained. PPTA and ABS blends had superior mechanical properties than the ABS alone (119). Outstanding reinforcement at concentrations less than 5 percent of the rigid component was obtained. This was due to the formation of a microfibrillar network. The properties of the network were anisotropic, and a quasi-three-dimensional lattice model was proposed by Takayanagi (120) to explain the anisotropy.

One of the drawbacks of using LCP’s as reinforcements is their poor adhesion to the matrix. To overcome this problem Akkapeddi, et al. (121) described a process of blending thermotropic oligomers and isotropic polymers in the presence of a particulate material such as talc, silica, carbon black, and quartz. The particulate material served two purposes: 1) it reduced phase separation between the thermotropic oligomer and the polymer and 2) it helped improve the dispersion of the oligomer in the polymer. The resulting blends had increased tensile modulus, tensile strength, and abrasion resistance than when the particulate was not used.

**CONCLUSIONS**

LCP/polymer blends may represent a feasible method for exploiting some of the desirable features of LCPs, but at a reduced cost. The addition of small amounts of an LCP to a thermoplastic polymer can result in significant improvements in processability. At the same time, a suitable processing history, i.e., one that includes extensional flow, can yield a reinforcing, microfibrillar morphology of the dispersed LCP-phase. Moduli similar to those of short glass fiber-reinforced plastics have been achieved. One deficiency of these blends is the poor interphase adhesion, which limits the strength of the material. It is also difficult to prepare samples that contain other than a unidirectional microfibril orientation. This limits the applications to those requiring high mechanical anisotropy. Future research is expected to be focused at improving these deficiencies.

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>ABPBI</td>
<td>Poly(2,5(6))-benzimidazole.</td>
</tr>
<tr>
<td>ABS</td>
<td>Acrylonitrile-butadiene-styrene.</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate.</td>
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<tr>
<td>DMAC</td>
<td>N,N-dimethyl acetamide.</td>
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<tr>
<td>EBBBA</td>
<td>P-ethoxy benzylidene-bis-4-n-butylaniline.</td>
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<tr>
<td>HNA</td>
<td>6-hydroxy-2-naphthoic acid.</td>
</tr>
<tr>
<td>HPC</td>
<td>Hydroxy propyl cellulose.</td>
</tr>
<tr>
<td>HOBA</td>
<td>P-hexyloxybenzoic acid.</td>
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<tr>
<td>HQ</td>
<td>Hydroquinone.</td>
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<tr>
<td>MF1</td>
<td>Melt flow index.</td>
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<tr>
<td>NBR</td>
<td>Acrylonitrile-butadiene rubber.</td>
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<tr>
<td>PC</td>
<td>Polycarbonate.</td>
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<tr>
<td>PEI</td>
<td>Polyetherimide.</td>
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<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate).</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly(ethylene glycol).</td>
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<td>PMMA</td>
<td>Poly(methyl methacrylate).</td>
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<tr>
<td>PAN</td>
<td>Polyacrylonitrile.</td>
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<tr>
<td>PPTA</td>
<td>Poly(p-phenylene terephthalamide).</td>
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<td>PPBT</td>
<td>Poly-p-phenylenobenzobisthiazole.</td>
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<tr>
<td>POCA</td>
<td>P-pentyloxy cinnamic acid.</td>
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<tr>
<td>PS</td>
<td>Polystyrene.</td>
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<tr>
<td>PVC</td>
<td>Poly(vinyl chloride).</td>
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<tr>
<td>TA</td>
<td>Terephthalic acid.</td>
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<td>TGA</td>
<td>Thermogravimetric analysis.</td>
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<tr>
<td>(T_{K,N})</td>
<td>Crystal to nematic transition temperature.</td>
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<tr>
<td>(T_{N,I})</td>
<td>Nematic to isotropic transition temperature.</td>
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<tr>
<td>(\eta^*)</td>
<td>Complex viscosity.</td>
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</table>

**REFERENCES**

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