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Processing of Liquid Crystal Polymer Reinforced Polyethylene Films

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Abstract

Blending liquid crystal polymer (LCP) of Vectra type into an extrusion-grade polyethylene matrix was examined as a possible route to obtain materials with suitable properties for thin film applications such as high performance film with desirable transport properties. This study was mainly concerned with enhancing PE film properties via in-situ formation of LCP fibers. Series of blends containing 5-50% LCP were studied. Cast and blown films containing 10% LCP showed a significant enhancement in modulus of ~400% over that of the neat PE matrix. LCP fibrils with high aspect ratios of ~100 or higher were developed in the presence of a strong elongational flow field. Apart from mechanical properties, these LCP/PE blend films showed a decrease in oxygen permeability of 40-50%. When extruded LCP/PE films were subsequently drawn (uniaxial and biaxial draw), films' yield stress properties were dramatically improved while unexpectedly higher oxygen permeability was observed in the samples. This paper describes the influence of some key process variables including temperature profile, number of extrusion cycles, degree of mixing and drawing ratio on LCP/PE blend film morphology, mechanical and transport properties.

Introduction

The art of blending polymers to obtain new superior materials with properties suitable for a variety of applications has been well recognized. This strategy is also applied in production of blends of liquid crystal polymer (LCP) with many different conventional thermoplastics. A primary incentive for development of the polymer blends containing LCP is to try and take advantage of LCP's outstanding properties that include its ability to form a fibrillar structure during processing giving rise to a self-reinforcing effect and correspondingly enhanced mechanical properties (Brown, *et al.* 1993; and Brostow, 1990). Another advantageous feature of LCP blends is reduction of overall blend viscosity because of shear response of LCP (Brown and Alder, 1993). However, critical drawback of LCPs and their blends can be their high degree of anisotropy and opacity (Chinsirikul, *et al.* 1996).

A number of studies on LCP blends with conventional thermoplastics such as polycarbonates, polyesters, polyamides, and polysulfones have been directed at determining optimal reinforcing effects of LCP domains. These studies primarily involved blend morphology, rheology and mechanical performances (Dutta, *et al.* 1990). However, few studies have addressed the anisotropy problem of LCP blends. (Blizard and Haghighat, 1993). Anisotropy in LCPs and their blends limits their success in a variety of applications under biaxial load condition as in electronic packaging, barrier films and structural component. As far as the barrier film is concerned, excellent gas barrier properties of LCP has been reported in a series of papers, nevertheless, limited attention has been paid on studying transport properties of the LCP blend systems (Flodberg and Hellman, 2000).

Previous work by the author and coworkers demonstrated a successful incorporation of LCP into the PE matrix (Chinsirikul, *et al.* 1996). By addition of a small amount of LCP (~10%) into PE, blown and cast films of these LCP/PE blends showed a modulus enhancement of ~400% over the parent PE matrix. However, since mechanical property of such films were highly anisotropic, another thrust in previous work also involved anisotropy minimization through a use of designed counter-rotating (C/R) die. High modulus blown film with nearly isotropic properties could be produced utilizing the C/R die. While produced LCP/PE films showed a dramatic improvement in modulus through reinforcing effect of LCP, yield stress of these films were surprisingly low. Similar findings on a slight increase in yield stress of LCP blends has also been reported for other LCP/thermoplastics systems. Thus, a practical means of improving yield stress in LCP/PE blend films was sought. Among several attempts at improving yield stress property in these blends, drawn films gave the most promising results. All these findings have led to a further examination of drawn film properties in terms of overall film stretchability associated with the presence of LCP fibers and resulting transport characteristics.

This current paper of LCP reinforced PE films consists of two major components: 1) Investigation of appropriate processing conditions under which the LCP phase forms fibrils having high aspect ratios (L/D) that can effectively reinforce the

PE matrix, and 2) Optimization of LCP/PE film properties through uniaxial and biaxial stretching. In addition to mechanical evaluation, additional study on transport property of extruded and drawn LCP/PE films has provided an interesting glimpse at their feasibility in several demanding applications in the polymer film industry such as packaging films and other engineering thin films.

Experimental

Materials and Preparation

LCP used was a copolyester (Vectra® type) resin supplied by Hoechst-Celanese and identified as RD-501. DSC results showed a melting endotherm of ~220°C and a crystallization exotherm at ~175°C upon cooling. PE used was commercially available extrusion grades (Dow chemical Co. and Thai Polyethylene Co.)

Pelletization and Cast film Extrusion

LCP was dried in a vacuum oven for 15 hours at ~110°C and mechanically blended with a blend of LLDPE and HDPE (2:1 by weight) to yield 10% weight fraction of LCP. The mixed materials were then extruded through a strand die, pelletized and again dried over night prior to being used for film fabrication. Extruded films were produced by extruding pelletized resin through a 15.3 cm wide, 0.6 mm die gap slit die. Beyond the die, extruded sheet was cooled, drawn and collected by a take-up assembly Figure 1.

Drawn films

Extruded films of PE matrix and LCP/PE blends were cold drawn on the Instron tester prior to testing. Film samples of ~5 inch wide and~4 inch long were grasped using a specially designed pneumatic clamps, and drawn at room temperature with a constant rate of 100 mm/min. Films with draw ratios ranging from 3 to 8 (3x to 8x) were produced. Biaxially drawn films were prepared using a common biaxial stretcher as known as T.M. Long device. Extruded films of PE and LCP/PE blends of 2x2 inch were used and stretched biaxially at a temperature of 120°C to achieve draw ratios ranging from 4x4 to 7x7.

Mechanical testing and Characterization

Measurement of tensile properties were performed on an Instron (model 4201), according to ASTM D882. The morphology and orientation of the blends were examined using an optical microscope and scanning electron microscope. Film samples were fractured in liquid nitrogen, mounted on sample stubs, and sputter coated with gold for enhanced surface conductivity.

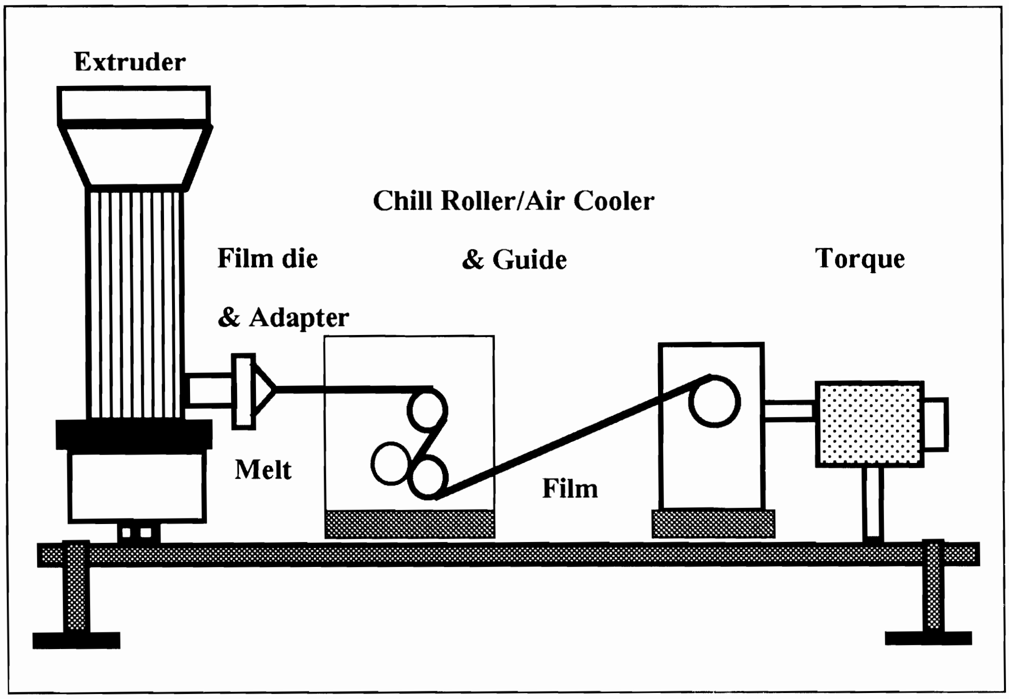


Figure 1 Schematic diagram of cast film line set-up

Results and Discussion

Development of LCP fibrillar structures could be achieved when processing LCP/PE blends under a strong elongational flow field and at appropriate temperatures. In general, the size, shape, and distribution of the LCP phase, as well as its reinforcement effect depended on a number of factors including composition, processing conditions, die geometry, degree of mixing, viscosity ratio of the component polymers, and the rheological property of the matrix. Influences of these process parameters on the LCP/PE blend morphologies during extrusion will be first reviewed. Process analysis was performed by determining the LCP/PE blend morphology at different locations throughout the extrusion process. Undrawn samples were collected at the end of each region Figure 1, and examined under an optical microscope.

Effects of process variables

Pelletization / Multi-pass process

All films containing 10% LCP content were produced using a two-pass process: pelletization followed by film extrusion. It was found that more uniform films with better surface finishes were normally obtained from two or three passes through the extruders, whereas "wood-grain" type films were formed when dry mixed polymer was given only a single pass through the extruder (Hsu, *et al.* 1994; and Hsu, *et al.* 1993). Films produced without pelletization were inhomogeneous and exhibited a wide range of thickness in the transverse (TD) direction. Furthermore, high toughness films have never been achieved from a single pass process. In contrast, films obtained from 2 passes, using 2 mixing elements, normally showed high toughness (>150 MPa) (Hsu, *et al.* 1994).

LCP content

PE blend cast films with varying LCP content from 5 to 50% were prepared using the extrusion set-up illustrated in Figure1. Cast films were produced based on the following temperature profile:

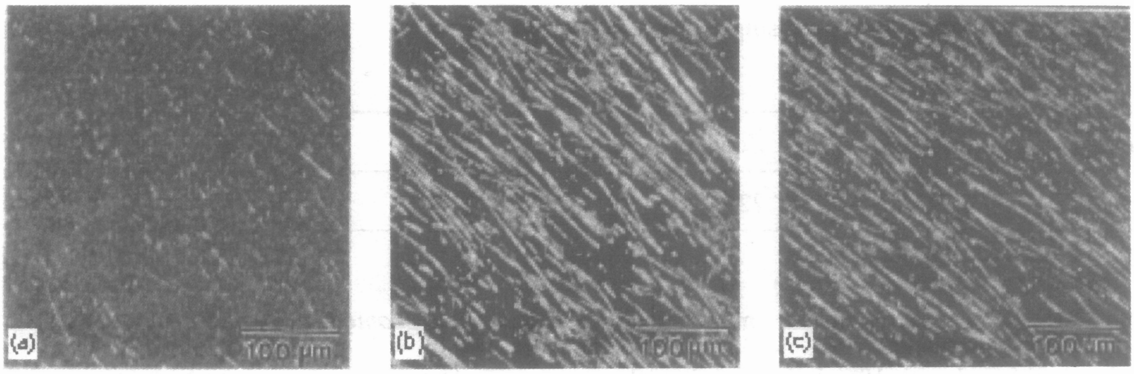
Extruder zone 1	Zone 2	Zone 3	15° adapter	Slit-die
188°C	200°C	225°C	215°C	215°C

Cast films having optimum mechanical properties were achieved with 10% LCP. In general, 5% LCP films had lower modulus and yield stress, compared with films containing ~10% LCP loading. Increasing the amount of LCP from 10% to 15% resulted in a dramatic decrease in film toughness even though an increase in modulus was also observed. In other words, PE blends with higher LCP content tended to be more brittle (Chinsirikul, 1996). Cast films with LCP concentration greater than 50% were difficult to make. The extrudate of such blends had poor melt strength under given extrusion conditions. Film surfaces were inhomogeneous and thickness varied grossly in TD.

Die adapter geometry and degree of mixing

The first region of the film line, as shown in Figure 1, included a 15° adapter with two mixing elements. These mixing elements were used as they provide a marked improvement in LCP dispersion and distribution (Hsu, *et al.* 1994). Adapters were placed between the extruder and the die to modify the flow pattern and/or the temperature profile. Results (Hsu and Harrison, 1993) showed that the 15° converging adapter was more effective in mixing and increasing fiber aspect ratio than the 30° and 90° adapters. Cast films of PE containing 10% LCP produced using the 15° adapter were uniform and had a high modulus in the range of 1000-1200 MPa.

The effect of the number of mixing elements on film properties was also investigated (Hsu, *et al.* 1994; and Hsu, *et al.* 1993). Film modulus increased on using 4 mixing elements versus 2 elements. However, films produced using a 15° adapter with 2 mixing elements showed higher toughness values and less thickness variation. It was also noticed that the extruder back pressure increased with increasing number of mixing elements, and was especially high for 4 mixing elements. Thus, based to some degree on practical considerations, the cast and blown film set-up used the 15° converging adapter with 2 mixing elements, and all films were produced from 2 passes.



(a) (b) (c)

Figure 2 Optical micrograph showing LCP morphologies of blends produced in cast film process.

(a) Sample collected in the extruder region

(b) Sample collected at the end of the adapter

(c) Cast film sample produced at the die temperature of ~ 215°C

Processing temperature profiles

<u>Extruder and 15° adapter region</u>

Temperature is one of the key factors governing LCP morphology as well as its distribution in the blends. Effects of different temperature profiles of the extruder and the adapter unit were studied (Chinsirikul, *et al.* 1996). A typical temperature profile was found to be 188°C, 200°C, 225°C in the extruder zones, and 215°C in the converging adapter. Figure 2(a) shows LCP droplets and short fibers in the extruder region. After passing the LCP/PE blends through the converging adapter, LCP fibrils with moderately high aspect ratios of 100 could be achieved (Figure 2(b)). Numerous fine LCP fibrils were uniformly distributed throughout the specimen. The development of these LCP fibrillar structures is presumably due to an extensional flow field introduced by the 15° converging adapter whose drawdown ratio is close to 64. However, microscopic examinations also suggest that fibril generation depends not only on the existing deformation field but also on processing temperature. Varying temperature profiles resulted in different rheological characteristics of the matrix and the LCP phase, and presumably the viscosity ratio of the system. It has been postulated that LCP should have an equal or lower viscosity than the matrix to ensure fiber formation (Chinsirikul, *et al.* 2000).

Die region

Figure 2(c) represents film morphology produced at die temperature of 215°C. In general, films produced at lower die temperatures (190-200°C) show extensive LCP fibrils with some LCP droplets (Chinsirikul, *et al.* 1996). However, as the die temperature increases to 215°C, the resulting film surfaces become even more uniform and their morphologies reveal numerous LCP fibrils with higher aspect ratios. In Figure 2(c), the observed LCP fibrils have diameters in a range of 1-3 μm, and lengths of 100-300 μm. Improvement in LCP fiber aspect ratios at a die temperature of 215°C is possibly attributable to more suitable viscosity ratios of the LCP component and the PE matrix. In addition, it should be noted that post-die drawing or deformation, as well as subsequent cooling, also influence LCP molecular structure, film uniformity, and film mechanical performances.

Property optimization through drawing process

Figures 3 (a) and (b) show property comparison of undrawn, uniaxially drawn and biaxially drawn films. As seen in Figure 3(a), film modulus is significantly improved by addition of 10% LCP. Comparing to the undrawn PE matrix, increases of modulus in uniaxially drawn LCP/PE films are ~300% and 30% for MD and TD, respectively. The increase in modulus of these blends is presumably due to self-reinforcement by LCP fibers formed in-situ during the extrusion process. LCP fibrils tend to be preferentially oriented in the extrusion or drawing direction, resulting in superior MD modulus versus TD modulus.

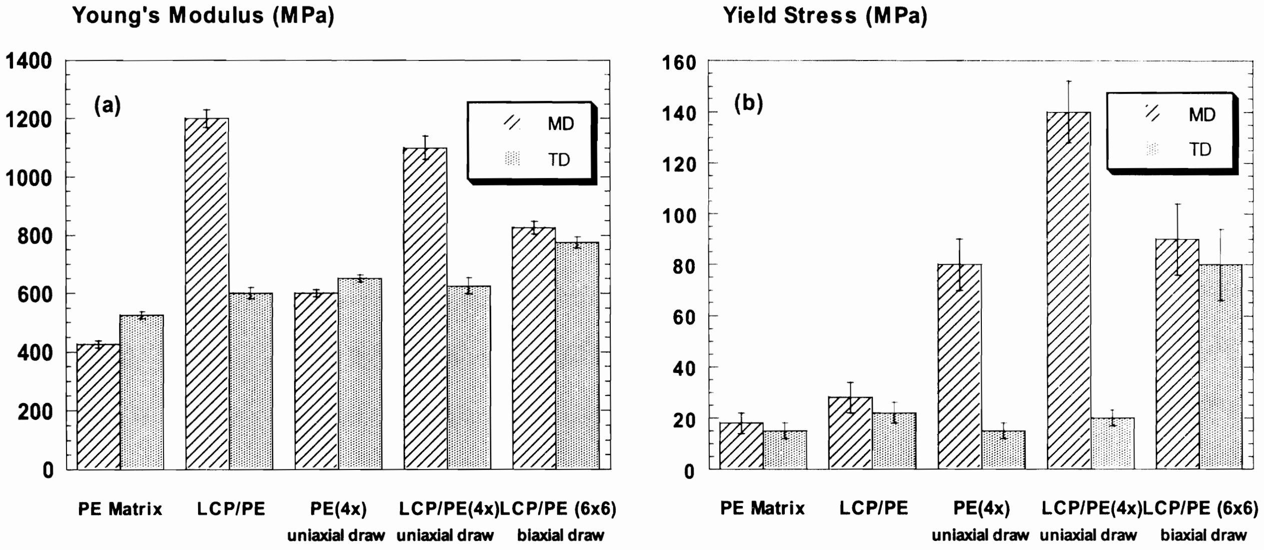


Figure 3 Property comparison of undrawn and drawn films

(a) Young's modulus

(b) Yield stress

While observing a dramatic increase in modulus, only a slight improvement in yield stress of the PE films containing LCP could be obtained. Another major effort was then made to improve yield stress property of the LCP/PE blends through drawing. From Figure 3(b), uniaxially drawn LCP/PE films (4x) exhibit a remarkable increase of ~600% in yield strength as compared to the base PE matrix. Measured yield stress value is nearly 140 MPa. In the case of drawn PE matrix, and increase of ~350% can be obtained (i.e., the resultant yield stress is approximately 80 MPa). Based on these observations, a portion of resultant yield strength increase in LCP/PE sample arises from the matrix. However, the final yield stress of drawn LCP/PE film significantly exceeds that of the drawn PE matrix, and is apparently the sum of contributions from both drawn PE matrix and LCP fibril component. Resulting properties of uniaxially drawn LCP/PE films (4x) are: modulus ~1100 MPa and yield stress ~140 MPa. It is noticeable that while yield stress increases with increasing draw ratio (from 1x to 4x), modulus tends to be retained at about the same value as that of the undrawn specimens (Figures. 3(a) and (b)). In the case of biaxial draw LCP/PE, films properties become more balanced in both MD and TD; modulus of ~800 MPa and relatively high yield stress of ~90 MPa could be produced.

Improved drawability of PE film containing LCP

Drawing ordinary PE specimens basically involves a necking process in which the stretched region must have a volume contraction corresponding to the increase in density resulting from crystallization and a denser packing of the microfibrils. In the case of LCP/PE, uniaxially drawn film (4x) has a more homogeneous deformation without any obvious necking formation during drawing. It is possible that the LCP fibrils existing in the PE matrix somehow hinder regular packing of the PE fibrils developed during drawing.

Differences in drawing behavior or drawability of the PE film and the LCP/PE films are apparent, especially when they are biaxially stretched. At a drawing temperature of ~120°C, LCP/PE blend films can be easily drawn to achieve a very high draw ratio of up to 7x7 whereas the PE films drawn at the same temperature shows limitation in drawability. PE films could only be stretched to a draw ratio of ~4x4, beyond which PE films start to break. Proposed explanation and mechanism for improved drawability of PE films associated with LCP fibrils was included in previous publication (La Mantia, *et al.* 1994). A similar findings to current study on improved stretchability of blends containing LCP has also been reported by Mantia, *et al.* (1994).

Drawn film morphology and permeability

The oxygen permeabilities of extruded PE, LCP/PE, uniaxially drawn LCP/PE (4x), and biaxially drawn LCP/PE (6x6) are included in Table 1. Extruded LCP/PE film shows a decrease in oxygen permeability of ~40 %, as compared to that of extruded PE matrix. Based on excellent gas barrier property of LCP, incorporation of LCP domain in a continuous PE phase can give rise to an improvement in gas barrier of the resulting blends. SEM micrograph also reveals the presence of continuous film of PE on the extruded blend surface. Similar results on improvement of gas barrier in PE blends with LCP was reported by Flodberg, *et al.* (2000). They observed a slight decrease in oxygen permeability of ~10% for compression molded PE containing 10% LCP (RD 501), and of 12.5% for LCP/PE blown films (with 1% compatibilizer content), respectively.

In the case of cold drawn LCP/PE samples (4x), films become more oxygen permeable than the undrawn films. High permeability in these drawn films could be attributed to pore or microvoid formation upon drawing process. As shown in Figure 4, pores or cavity are seen on the surface of cold drawn sample and pores tend to locate mostly at the LCP/PE interphase. For biaxially drawn LCP/PE films (6x6), preliminary results on oxygen permeability of these films show much greater permeability over those for the cold drawn samples. Further results on this particular aspect will be soon published.

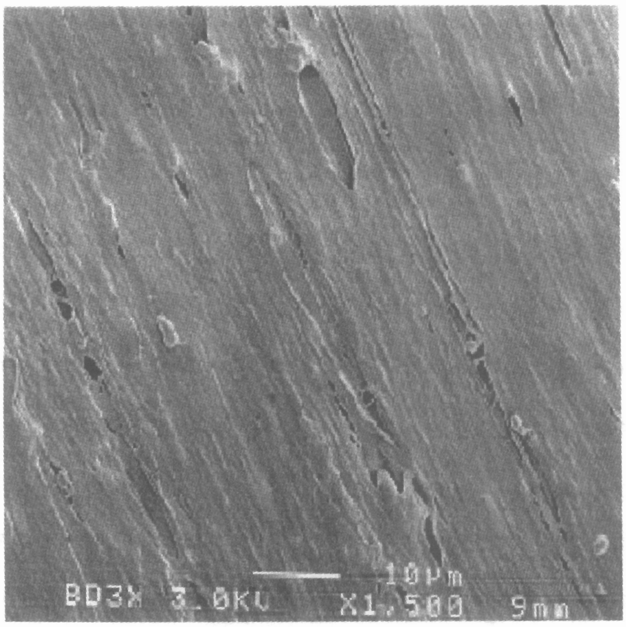


Figure 4 SEM micrograph of uniaxially drawn film surface, LCP/PE (4x)

Table 1 Oxygen permeability of PE and LCP/PE films

Film Type	**Oxygen permeability** $(cm^3\text{-mm})/m^2$ d atm @ 23 °C, 50% RH
Extruded PE matrix	66
Extruded LCP/PE	38
Uniaxially Drawn LCP/PE (4x)	50

Conclusion

Cast film extrusion of LCP/PE blends successfully demonstrated an in-situ formation of high aspect ratio LCP fibers which directly contributed to enhanced mechanical properties. Drawing appeared to be a practical method at improving yield stress of LCP/PE blends. PE containing LCP fibrils also exhibited enhanced drawability, as compared to the PE alone. Balanced LCP/PE film with excellent mechanical performance in both MD and TD was obtained through biaxial stretching. Improvement in oxygen barrier of ~40% could be observed in extruded PE films containing 10% LCP. With regard to future work, it would be interesting to further investigate if thin LCP/PE blend films with optimum properties (both mechanical and barrier characteristics), could be produced and controllable.

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