

Prepregs and Laminates of Polyetherimide-Reinforced by a Thermotropic LCP

W. BU, A. I. ISAYEV

Institute of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301

Received 23 July 1996; accepted 31 December 1996

ABSTRACT: Unidirectional sheets (prepregs) of blends of polyetherimide (PEI) with a liquid crystalline polymer (LCP) are prepared. The mechanical properties of prepregs at directions of 0°, 45°, and 90° to the machine direction are investigated as a function of draw ratio and LCP concentration. The results show that drawing significantly increases the tensile strength and modulus of prepregs in the machine direction and only slightly decreases these properties in the transverse direction. An increase in the LCP content greatly enhances the tensile strength and modulus in the machine direction but decreases these properties in the 45° and 90° directions. The strain at break of prepregs decreases with LCP content in all directions tested. An abrupt drop in the tensile strength, modulus, and strain at break of prepregs occurs in the 45° and 90° directions when LCP content reaches 40%. Prepregs are used to manufacture unidirectional and quasi-isotropic laminates. Unidirectional laminates show mechanical properties close to those of the corresponding prepregs. The tensile modulus of quasi-isotropic laminates exhibits a continuous increase with increasing LCP content while the tensile strength increases with an LCP content up to 30%, then it decreases rapidly. The morphology of LCP in prepregs is observed to change from disperse to continuous at LCP contents of 40 and 50%. This effect is found to be responsible for the large decrease in tensile strength of prepregs in the 45° and 90° directions and quasi-isotropic laminates at higher LCP concentration. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 329–340, 1997

Key words: self-reinforced composites; prepregs; laminates; anisotropy; fibrillation

INTRODUCTION

Blending of polymers has become an important and attractive route for developing new and better materials. In the past decade, blends of thermotropic liquid crystalline polymers (TLCPs) with thermoplastics have attracted much attention.^{1–5} The ability to make high-performance materials and good process economics have made this so-called self-reinforced or *in situ* composite technology very promising. In the majority of investigations, extrusion and injection molding are

utilized. These processing methods are very convenient. However, there are still some limitations. In particular, the lack of high extensional flow does not allow LCP to form fibrils long enough to give a significant reinforcing effect in the final product. In applications where isotropic properties are desired, the high anisotropy of the mechanical properties of the molded product is a major deficiency of self-reinforced composites.

Recently, a new technology was proposed to improve the performance of these materials with respect to anisotropy.^{6,7} In this technology, LCP/thermoplastic prepregs are first made by extrusion followed by extension. In these prepregs, very large aspect ratio LCP fibrils can be achieved. Then, the prepregs are compression-molded into

Correspondence to: A. I. Isayev.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/020329-12

laminates with the required packing sequence. Unidirectional or quasi-isotropic laminates can be obtained very similar to conventional fiber-reinforced laminates. Obviously, the technology of making prepregs here is more convenient and economically viable than that of making conventional fiber-reinforcing prepregs.

Some articles have been published where this method was utilized. Dutta et al.^{7,8} studied the melt drawing of films of LCP/polycarbonate (PC) and LCP/fluoropolymer. They prepared unidirectional and cross-ply laminates using these films. The mechanical properties of these laminates were found to agree well with predictions from conventional composite lamination theory.⁹ Isayev and co-workers^{10,11} studied the systems of LCP/polypropylene (PP), LCP/poly(phenylene oxide) (PPO), and LCP/PPO–polystyrene (PS) alloy. The properties of both unidirectional and quasi-isotropic laminates were found to be dependent on the compression or the reduction ratio during lamination and the extension ratio of prepregs. Crevecoeur and Groeninckx¹² made unidirectional sheets with an LCP in a matrix of polyphenylene–ether (PPE) and PS. The effect of draw ratio, slit opening, and extruder throughput were investigated and related to the morphology and mechanical properties. In another study, Bassett and Yee¹³ spun LCP/PS blends into fibers and compression-molded these fibers directly into a composite. LCP fibrils were found to remain undisturbed by the molding process. Sabol et al.¹⁴ produced drawn strands of LCP/PP. Then, the drawn strands were cut and arranged uniaxially or randomly and compression-molded. Mechanical properties of the composites produced were found to increase with both draw ratio and strand length.

In the present article, a high-performance engineering plastic, polyetherimide (PEI), was blended with an LCP and prepregs and laminates were prepared. Systematic study of the mechanical properties of the prepregs, including the effect of draw ratio and LCP concentration, was carried out. Attention was also paid to the development of the microstructure of LCP within PEI in the prepregs. In addition, the mechanical properties of unidirectional and quasi-isotropic laminates were studied in relation to those of the prepregs.

EXPERIMENTAL

Materials

The PEI used was Ultem 1000 (GE Plastics). The LCP is a random copolyester of hydroxybenzoic

acid (HBA) and 2,6-hydroxynaphthoic acid (HNA) (Vectra A950, Hoechst-Celanese).

Preparation of Prepregs

Melt blending of LCP and PEI was conducted in a 1 inch Killion single-screw extruder, connected to a static mixer (Koch Industries), followed by a coat-hanger die and a take-up device. The die lip has a thickness of 2 mm and a width of 150 mm. Before extrusion, pellets of the materials were dried in a vacuum oven at 130°C for at least 24 h; then they were physically mixed. Five LCP/PEI compositions of 10/90, 20/80, 30/70, 40/60, 50/50 by weight were investigated. The following temperature profile of processing was used: in the extruder, 300, 340, 340, and 340°C; in the static mixer, 330, 330, and 330°C, and in the die, 330°C. The take-up device was used to uniaxially draw films. The cooling roll was positioned 15 cm below the die. The screw speed of the extruder was fixed at 50 rpm. The take-up speed was varied from 20 to 120 fpm to obtain different draw ratios. The draw ratio was defined as the ratio of the cross-sectional area of the die lip to that of the drawn film. It was not possible to obtain smooth and uniform films at each stretching condition. At a low take-up speed of 20 fpm, pure PEI and LCP/PEI 10/90 and 50/50 films solidified so fast that they could not be rolled and stretched. As the LCP content was increased to 50%, difficulty arose in getting good films at higher take-up speeds. Therefore, for LCP/PEI 50/50, the highest take-up speed was adjusted to 80 fpm. All the conditions and results are summarized in Table I.

Laminate Preparation from Prepregs

Compression molding of prepregs was carried out in a computer-controlled compression-molding press (Tetrahedron, MTP 24). A molding temperature of 260°C, force of 35.6 kN, and molding time of 5 min were used. Under these conditions, a good consolidation was achieved without delamination or excessive flow of materials. Both unidirectional and quasi-isotropic laminates were prepared. For each laminate, 8 or 12 sheets of prepregs were used depending on the thickness of the prepregs. In the case of quasi-isotropic laminates, prepregs were stacked in a sequence so that each subsequent layer was at an angle of 45° with respect to the previous one.

Table I Draw Ratios Used in Making Prepregs

Take-up Speed (fpm)	Composition (LCP/PEI w/w)					
	0/100	10/90	20/80	30/70	40/60	50/50
20			8.7	8.0	7.9	
40	17.4	17.6	17.4	15.9	15.7	11.9
60						17.8
80	34.8	35.2	34.8	31.8	31.4	26.7
120	52.2	52.8	52.2	47.7	47.1	

Mechanical Testing

The prepregs and laminates were cut into dumb-bell-shape specimens of the ASTM D638 type IV. Mechanical testing was performed in an Instron mechanical tester (Model 4204), controlled by a computer. A crosshead speed of 5 mm/min was used. The grip distance was set at 40 mm. Testing was conducted without an extensometer. Strain was calculated based on the crosshead speed and the grip distance. For each sample, at least five specimens were tested. The reported values are the average with standard deviation within 10% in most cases (except tensile strength of LCP/PEI 50/50 unidirectional laminates and strain at break, which were more dispersive, within 20%).

Morphological Characterization

The morphology of the LCP phase in prepregs was observed using a scanning electron microscope (SEM), ISI SX-40. For this purpose, PEI was extracted with chloroform. A piece of the film was immersed in chloroform for at least 12 h. Then, the solution was decanted and fresh solvent was filled. This process was repeated three times. The remaining dispersion was placed directly on an SEM sample holder. After the solvent was evaporated, the sample was coated with a gold-palladium alloy for observation.

RESULTS AND DISCUSSION

Mechanical Properties of the Prepregs

Figure 1(a) and (b) shows, respectively, the tensile strength and modulus in machine direction of LCP/PEI prepregs of various compositions, as a function of draw ratio. For comparison purposes, the properties of neat PEI film are also shown. It can be seen that the properties of pure PEI are

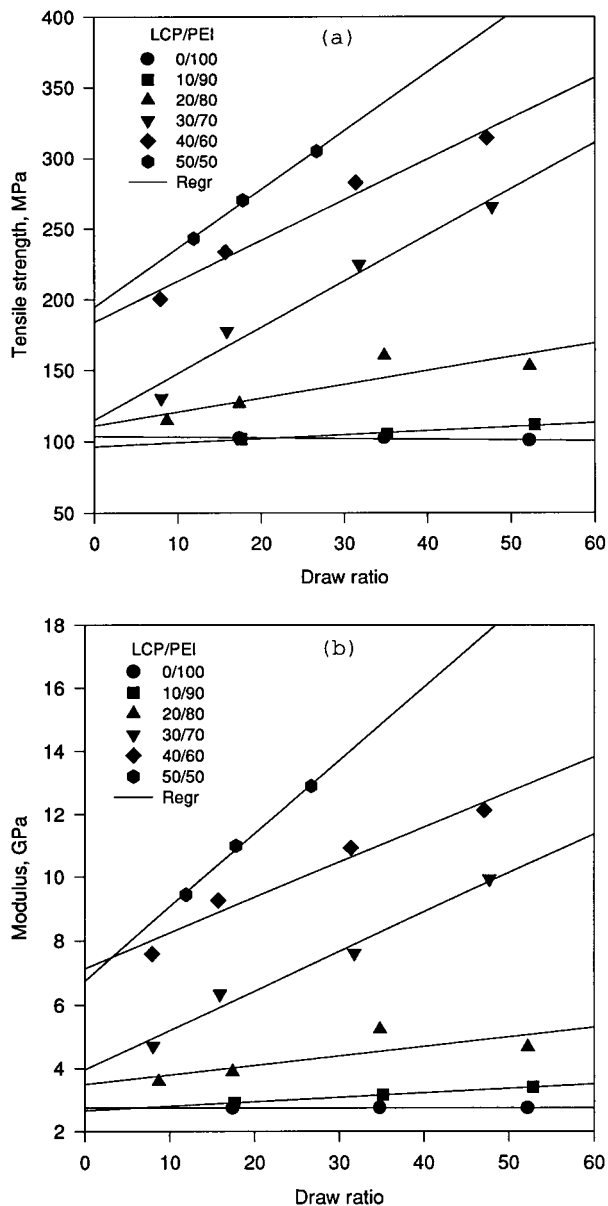


Figure 1 (a) Tensile strength and (b) modulus in the machine direction vs. draw ratio for prepregs at different LCP concentrations.

independent of the draw ratio, with a tensile strength of about 102 MPa and a modulus of 2.7 GPa, indicating that drawing has no effect on this amorphous polymer. The tensile strength and modulus of the blends show an almost linear increase with the draw ratio. The extent of this increase is stronger at higher LCP content. For LCP/PEI 10/90, the tensile strength increases from 102 to 112 MPa and the modulus from 2.9 to 3.4 GPa for the draw ratio variation from 17.4 to 52.2. While for LCP/PEI 30/70, at nearly the same draw ratio range from 15.9 to 47.7, tensile strength increases from 178 to 266 MPa, and the modulus, from 6.4 to 9.9 GPa.

The increase in the mechanical properties of prepregs with the draw ratio has been reported by many authors. However, in most studies, only one LCP concentration was considered.^{7,8,12,14} Here, one can see that the effect of the draw ratio is highly sensitive to the LCP content in the PEI matrix.

Since the properties of pure PEI are not affected by drawing, obviously, the increase in the tensile properties of LCP/PEI prepregs is caused by the change of structure and of the properties of LCP fibrils formed during drawing. It is known^{7,15} that during drawing both the molecular orientation of rigid LCP chains and the aspect ratio of LCP fibrils increase with the draw ratio. The increase in the aspect ratio of LCP fibrils is related to the deformation of the dispersed LCP phase, which depends on the viscosity ratio of LCP to PEI and the size of LCP particles. The larger the particle size, the larger deformation the particle can afford. So, at higher LCP concentrations, the LCP dispersed phase has a volume sufficient to be deformed into longer fibrils at larger draw ratios. Moreover, the substantially lower viscosity of the LCP melt in comparison with that of the PEI melt also assists in the elongation of the LCP dispersed phase.¹⁶

The effect of LCP content on the strength and modulus of prepregs in the machine direction at different draw ratios is shown in Figure 2(a) and (b). Since it is difficult to maintain a constant draw ratio for prepregs of various compositions, the data in Figure 1 are interpolated at constant draw ratios. Tensile strength and modulus at constant draw ratios of 16, 32, and 48 are thus obtained. Figure 2 clearly shows that both the tensile strength and modulus increase greatly with increase in LCP content. It is seen that no matter what draw ratio is used a significant increase in properties occurs only when the LCP content ex-

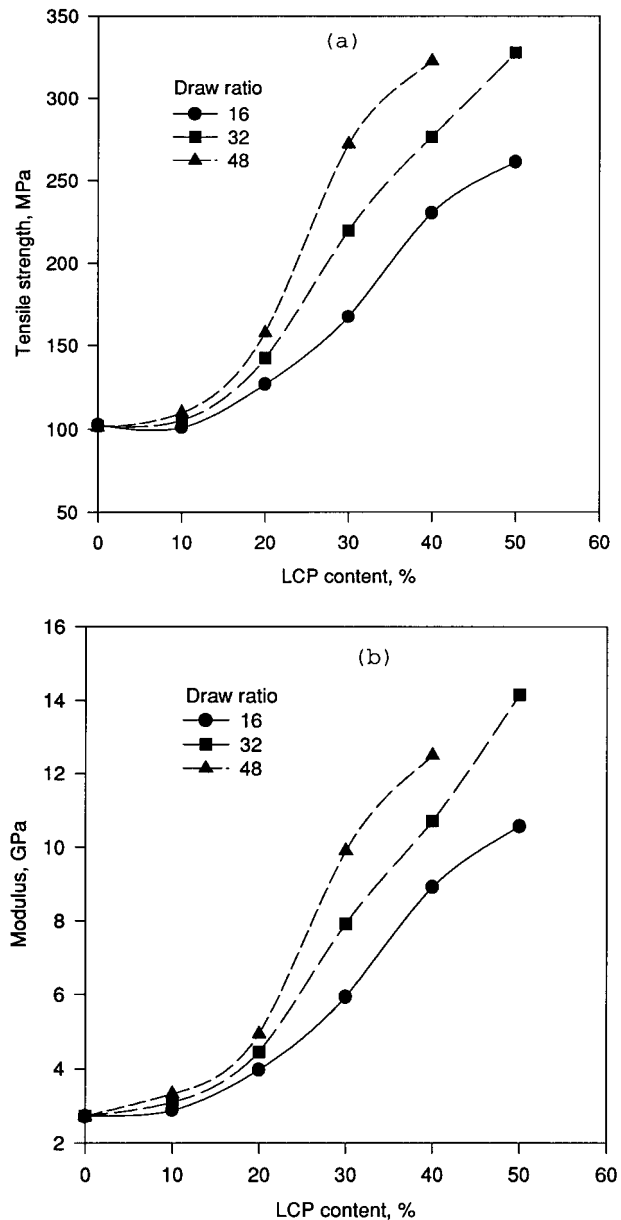


Figure 2 (a) Tensile strength and (b) modulus in the machine direction vs. LCP concentration for prepregs at different draw ratios.

ceeds 10%. At a draw ratio of 48, the tensile strength and modulus increases, respectively, from 101 MPa and 2.7 GPa of pure PEI to 110 MPa and 3.3 GPa for 10/90 LCP/PEI and to 323 MPa and 12.5 GPa for 40/60 LCP/PEI. At an LCP content higher than 40%, this increase in properties seems to slow down.

The effect of LCP concentration on the properties of drawn fibers and films of blends have been studied in many articles.^{8,11,15,17} Different tendencies were observed. In particular, in LCP/PC fi-

bers, Lin and Yee¹⁵ found a steady increase in both modulus and tensile strength with an increase in the LCP content from 10 to 80%. They attributed this tendency to the consistent generation of fibrillar morphology in this concentration range. On the other hand, for LCP/PET fibers, an abrupt increase in the mechanical properties between LCP content of 60 and 85% was observed by Li et al.¹⁷ as the result of the morphological changes of LCP from discontinuous fibrils to continuous fibrils. The effect here is similar to that reported by Li et al.; however, it occurs at a lower LCP content. From the morphological observation which will be shown later, one can see that at an LCP content of 10% the LCP particles are so small that they are only deformed to a certain extent, leading to fibrils with a small aspect ratio. So, these fibrils cannot generate a significant reinforcing effect. When the LCP content is increased from 10 to 40%, the aspect ratio of LCP fibrils is greatly increased during drawing—hence, the large increase of properties occurs in this concentration range. When the LCP content exceeds 50%, LCP fibrils tend to become continuous, and the effect of the aspect ratio on properties is reduced. In the latter case, the LCP content dominates the properties and their increase slows down.

Figure 3(a) and (b) gives, respectively, the tensile strength and modulus of preregs in the transverse direction as a function of the draw ratio at various concentrations of the LCP. It is noted that the draw ratio only slightly affects the properties of the prepreg in the transverse direction. In particular, for LCP/PEI 40/60, the modulus decreases from 2.2 to 2.1 GPa when the draw ratio increases from 7.9 to 47.1. Tensile strength is found to be almost constant at all the draw ratios examined, except in the case of LCP/PEI 50/50. The slight decrease in the modulus with the draw ratio was also observed by Dutta et al. in LCP/PC 10/90 preregs.⁷ But the large decrease in both tensile strength and modulus in LCP/PPO-PS preregs was reported by Isayev and Viswanathan.¹¹

In Figure 4(a) and (b), the transverse properties of preregs are plotted as a function of LCP concentration. It is clearly seen that both the strength and modulus in the transverse direction decrease significantly with increase in the LCP content, especially when the LCP content reaches 40 and 50%. Isayev and Viswanathan¹¹ observed the decrease in properties in the transverse direction with the LCP concentration in LCP/PPO-PS

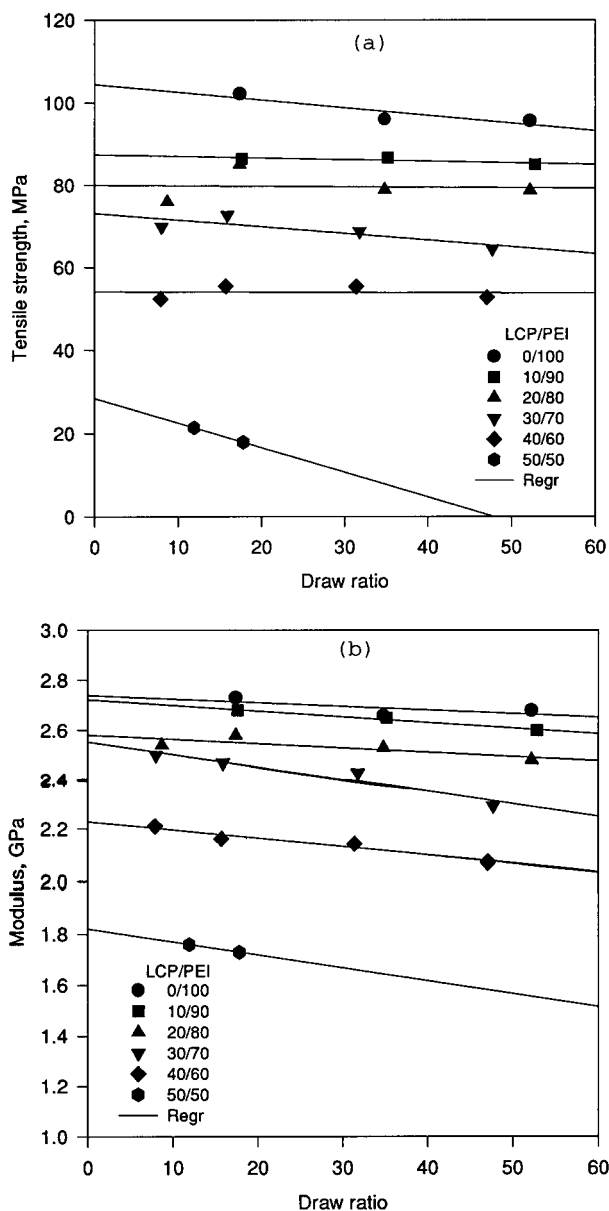


Figure 3 (a) Tensile strength and (b) modulus in the transverse direction vs. draw ratio for preregs at different LCP concentrations.

preregs. But Dutta et al.⁸ found a slight increase in the transverse modulus with increasing LCP content. In the case of conventional fiber-reinforced unidirectional composites, the transverse modulus increases with increase in fiber volume, while the transverse strength may decrease.¹⁸

Available literature gives little discussion concerning the properties of LCP/thermoplastics preregs in the transverse direction. There are two possible reasons for the reduction of the modulus, namely, the low transverse modulus of LCP fibrils

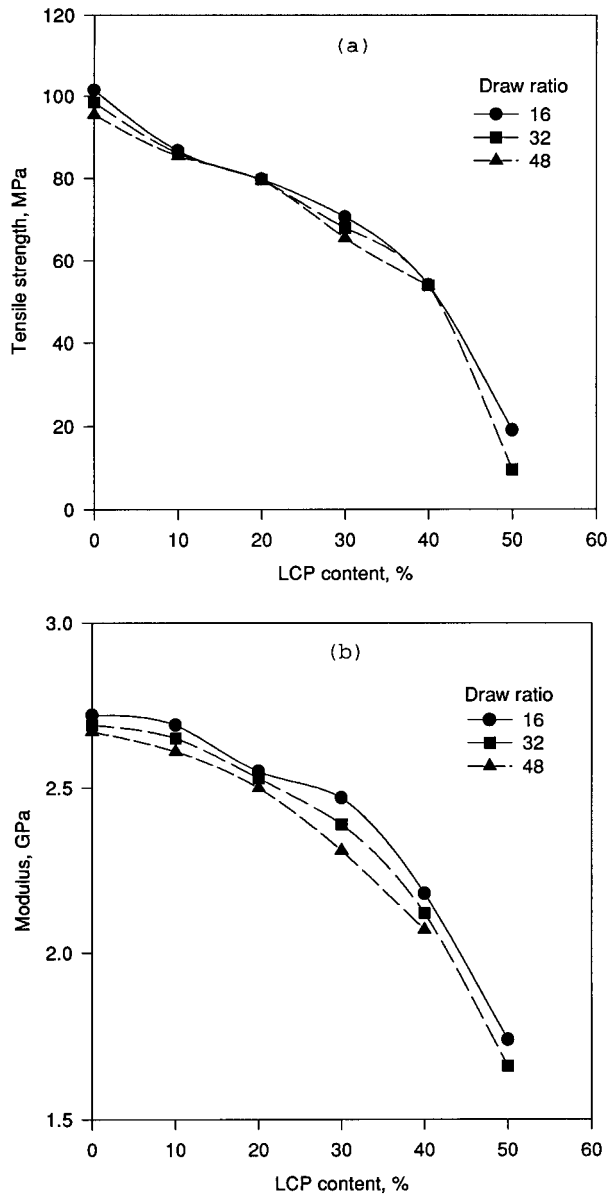


Figure 4 (a) Tensile strength and (b) modulus in the transverse direction vs. LCP concentration for prepreps at different draw ratios.

and the poor interface adhesion between LCP fibrils and matrix. According to the composite theory,¹⁸ the transverse modulus of the composite, E_c , can be given by

$$\frac{1}{E_c} = \frac{V_f}{E_f} + \frac{V_m}{E_m} \quad (1)$$

where E_f and E_m are the transverse modulus of the fiber and matrix, respectively, and V_f and V_m are the corresponding volume fractions. Usually,

in conventional fiber-reinforced unidirectional laminates, the transverse modulus of fibers such as glass or carbon is much higher than that of the matrix. So, one can assume that $E_c \approx E_m/V_m$. It means that the transverse modulus of a laminate is dominated by the transverse modulus of the matrix and its volume fraction. But LCP fiber properties are highly anisotropic with the transverse modulus being much lower than the longitu-

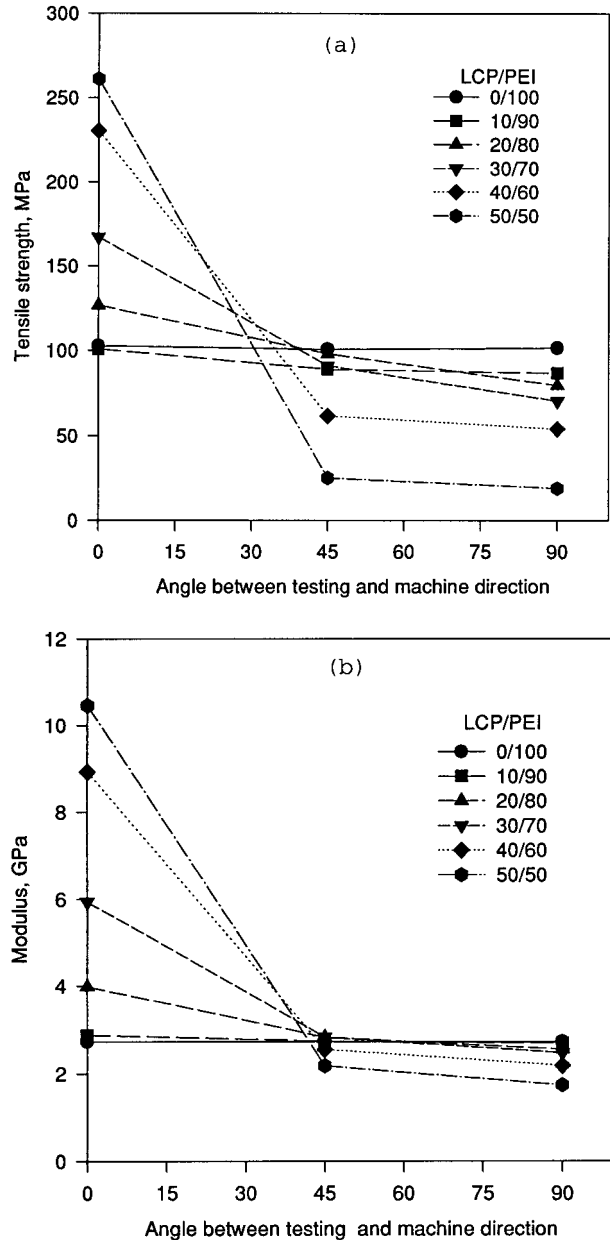


Figure 5 (a) Tensile strength and (b) modulus vs. the angle between the testing and machine direction for prepreps at different LCP concentrations and a draw ratio of 16.

Table II Strain at Break (%) of Prepregs in Different Testing Directions and Corresponding Quasi-isotropic Laminates at a Draw Ratio of 16

LCP/PEI (w/w)	Prepregs			Laminates
	0	45	90	
0/100	59.1	26.5	18.3	9.4
10/90	46.7	36.9	24.5	12.0
20/80	4.7	27.8	10.0	5.9
30/70	3.0	16.8	6.9	3.7
40/60	2.8	3.1	3.9	2.5
50/50	2.7	1.3	1.0	1.5

dinal modulus. Lin and Yee¹⁹ estimated that the transverse modulus of LCP fibers (Vectra B950) is 2.2 GPa. Using eq. (1) and experimental data for pure PEI and the prepreg of LCP/PEI 40/60, in which LCP fibrils are assumed to be continuous, one can calculate that the transverse modulus of LCP fibrils is only 1.5 GPa, which is lower than that of pure PEI. So, the transverse modulus of prepregs will decrease with increasing LCP content.

Equation (1) is based on the assumption that there is a perfect contact between fibers and matrix. But for LCP/thermoplastics system, the interface adhesion is usually very weak, which may further contribute to the reduction in the load-bearing capacity of prepregs in the transverse direction. This effect will increase with the LCP content since the interfacial area increases with LCP concentration. The most probable reason for the slight decrease in the transverse modulus with draw ratio is that drawing does not affect the transverse modulus of LCP fibrils significantly. Also, at a constant LCP content, the interfacial area between LCP fibrils and matrix is not affected greatly by drawing.

The large decrease in the transverse strength with LCP content is also related to the weak

transverse strength of LCP fibrils. For conventional fiber-reinforced unidirectional composites, failure in the transverse direction is initiated as a result of matrix or interface failure. In some cases, they may fail by fiber transverse failure, if the fibers are highly oriented and weak in the transverse direction.¹⁸ Similarly, in the case of LCP fibrils, one can expect the fiber transverse failure and interface failure to be more pronounced, since the splitting of LCP fibrils may easily occur. So, the higher the LCP content the prepreg has, the more significant is the decrease in transverse tensile strength. But when the draw ratio increases, LCP fibrils become longer and finer. Therefore, the ease of fiber splitting is reduced, and, hence, further drawing would affect slightly the tensile strength in the transverse direction.

Figure 5(a) and (b) gives the variation of tensile strength and modulus of the prepregs at a constant draw ratio of 16, with the angle between the testing and the machine direction. Properties are measured at 0°, 45°, and 90° to the machine direction. One can see that pure PEI shows isotropic properties for both the strength and modulus. For LCP content up to 30%, the properties in the machine direction are increased significantly

Table III State of LCP Phase After Extraction of PEI

LCP Content (%)	Sample Shape Before Extraction	Shape of Phase Remaining After Extraction	State of LCP Phase
10	Film	Particles	Dispersed
20	Film	Particles	Dispersed
30	Film	Particles	Dispersed
40	Film	Cottonlike	Partly continuous
50	Film	Loose film	Mostly continuous

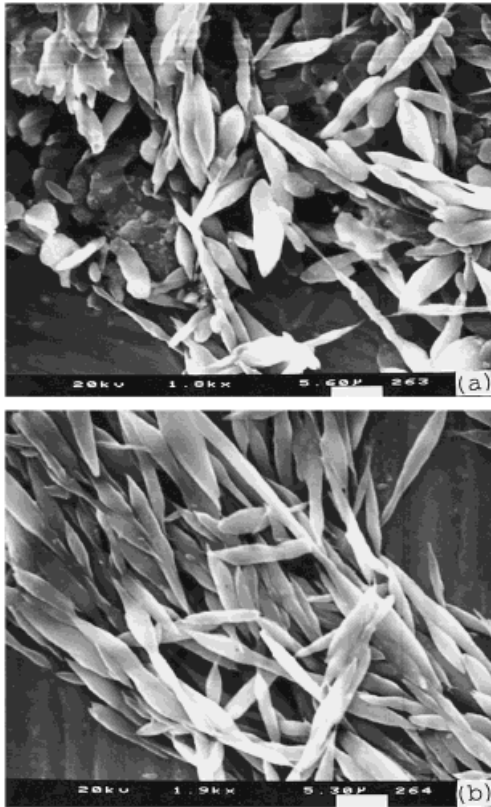


Figure 6 SEM microphotographs of LCP fibrils in LCP/PEI 10/90 prepregs after extraction of PEI at draw ratios of (a) 17.6 and (b) 52.8.

while the properties measured in the 45° direction are only slightly higher than those in the transverse direction, but still close to those of pure PEI. When the LCP content is increased to 40 and 50%, both the strength and modulus in the 45° direction drop significantly and are much lower than those of the prepregs with LCP content less than 40%. At these high LCP contents, properties in the 45° direction and the transverse direction are nearly the same.

Table II lists the strain at break of prepregs tested at 0°, 45°, and 90° to the machine direction and at a draw ratio of 16. It is noted that the strain at break in these three directions decreases with increase in LCP content. In the machine direction, the strain at break maintains its large value of 46.7% at an LCP content of 10%. It abruptly decreases to 4.7% when the LCP content increases to 20% and then stabilizes at higher LCP contents, reaching a value of 2.7% at an LCP content of 50%. At 45° and 90° to the machine direction, the strain at break for an LCP content of 30% is 16.8 and 6.9%, respectively. Yielding is

still observed during testing at this LCP content. When LCP content is increased to 40%, the strain at break at 45° and 90° to the machine direction drops to 3.1 and 3.9%, respectively, which is close to that in the machine direction. At an LCP content of 50%, the corresponding strain at break is only 1.3 and 1.0%, which is much lower than that in the machine direction. This change in strain at break correlates with the above-mentioned large decrease in the strength and modulus at 40 and 50% LCP content.

Microstructure of Prepreg

In this study, selective dissolution of PEI was used to observe the microstructure of prepregs. This observation reveals the size and shape of LCP fibrils and also gives information concerning whether LCP is the dispersed or continuous phase. Results obtained from the observation are summarized in Table III.

It is interesting to note that in the composition of 50/50 LCP becomes the continuous phase. After

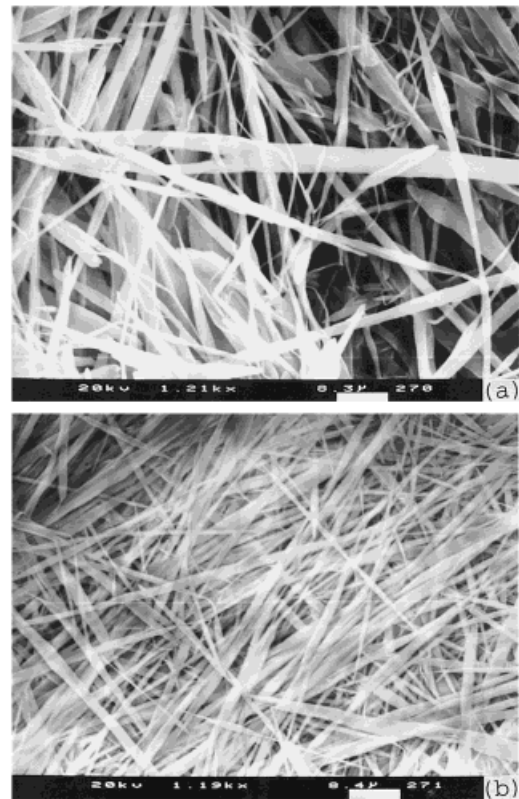


Figure 7 SEM microphotographs of LCP fibrils in LCP/PEI 20/80 prepregs after extraction of PEI at draw ratios of (a) 8.7 and (b) 52.2.

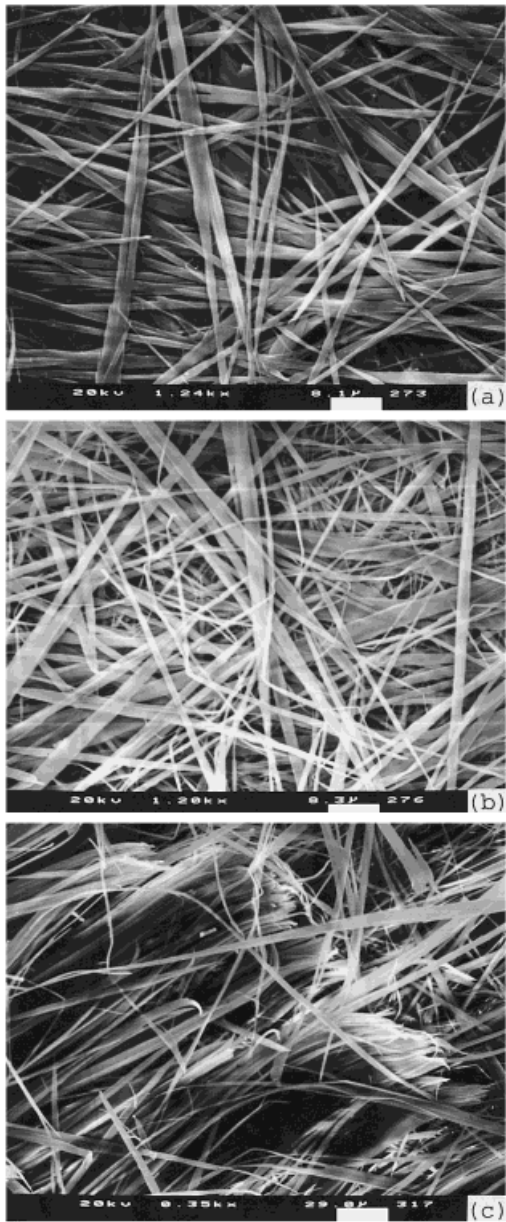


Figure 8 SEM microphotographs of LCP fibrils in LCP/PEI prepregs after extraction of PEI: (a) 30/70, draw ratio of 47.7; (b) 40/60, draw ratio of 47.1; (c) 50/50, draw ratio of 26.7.

extraction of PEI, the remaining film retains the shape of the original film although the compact structure is lost to some extent. For LCP/PEI 40/60, the remaining film is not capable of maintaining its shape. However, it looks like a pile of cotton and seems to be partially continuous.

In polymer blends, it is known that the phase of low viscosity has a tendency to become continuous even if it is a minor phase.²⁰ Bassett and Yee¹³ found that in LCP/PS fibers discrete LCP fibrils

were formed at an LCP concentration up to 40%. At 50% LCP content, LCP fibrils begin to form a continuous network. He et al.²¹ observed that phase inversion takes place at 50/50 composition in LCP/polyethersulfone extrudates. According to Ref. 16, at a shear rate of about 100 s^{-1} , the viscosity ratio of LCP to PEI is around 0.01. Therefore, in the LCP/PEI system, LCP could easily become the continuous phase when its concentration reaches 50%.

The SEM photomicrographs of the LCP phase after extraction of PEI are shown in Figures 6–8. At an LCP content of 10% and draw ratio of 17.6, the LCP phase appears as deformed or elongated particles [Fig. 6(a)]. When the draw ratio is increased to 52.8, a further elongation of the particles is observed, but the aspect ratio is still not large [Fig. 6(b)]. At an LCP content of 20%, the LCP forms very long and rigid fibrils even at a draw ratio as low as 8.7 [Fig. 7(a)]. An increase in the draw ratio to 52.2 leads to a reduction in the diameter of the fibrils with their diameter being more uniform [Fig. 7(b)]. The morphology of LCP at 30 and 40% is similar to that at 20%. At these concentrations, LCP forms almost continuous fibrils [Fig. 8(a) and (b)]. It is also noted that even at an LCP content of 40% the LCP seems to be isolated fibrils. But detailed observation shows that some thick LCP fibrils split into finer fibrils, indicating that they are partially interconnected. At an LCP/PEI content of 50/50 [Fig. 8(c)], LCP exists as an assembly of hierarchical structures of partially interconnected LCP fibrils. Obviously, due to the fact that LCP has molecular chains of high rigidity, they can orient easily in the highly extensional flow field. This leads to the high anisotropy of the continuous LCP phase. LCP is more continuous in the longitudinal direction and only partially connected in the transverse direction. This is the reason why the properties of pure LCP moldings in the transverse direction are so weak.²²

Accordingly, one can understand why the prepreg with LCP content of 40 and 50% indicates an abrupt reduction in properties in the 45° and transverse direction. For LCP content up to 30%, the LCP exists as isolated fibrils with PEI being the fully continuous phase, such that PEI dominates the properties of prepregs in the 45° and transverse direction. But when LCP content increases to 40 and 50%, the LCP starts to become the continuous phase and the transverse properties of prepregs are dominated by the LCP. Thus, the poor transverse properties of LCP cause lower

Table IV Comparison of Properties of Unidirectional Laminates and Corresponding Prepregs in Machine (0°) and Transverse (90°) Directions at Draw Ratio of 32

		LCP Content (%)				
		10	20	30	40	50
Tensile Strength (MPa)						
0°C	Prepreg	105	142	220	277	328
	Laminate	109	142	226	272	181
90°	Prepreg	86	80	68	54	
	Laminate	91	58	53	35	
Modulus (GPa)						
0°	Prepreg	3.1	4.5	7.9	10.7	14.2
	Laminate	3.1	4.6	7.2	10.0	12.8
90°	Prepreg	2.7	2.5	2.4	2.1	
	Laminate	2.6	2.6	2.5	2.3	

properties of prepregs at these contents. This phenomenon, as shown later, also affects the properties of quasi-isotropic laminates.

Mechanical Properties of Laminates

The tensile strength and modulus of unidirectional laminates, manufactured from prepregs obtained at a draw ratio of 32, in the fiber and transverse direction are listed in Table IV, along with the properties of corresponding prepregs. It is seen that the unidirectional laminates tested in the machine direction exhibit a tensile strength and modulus close to those of corresponding prepregs, except for the tensile strength of laminate with 50/50 composition. This indicates that the properties of the prepregs are retained in the laminates under the molding conditions used here. In the case of LCP content of 50%, breakage of the specimen is accompanied by the splitting of the laminate along the loading direction. This type of fracture is typical for pure LCP and their blends when the LCP phase is continuous.¹⁷ When tested in the transverse direction, the unidirectional laminates show somewhat lower tensile strength and higher modulus in comparison with those of the prepregs. Table IV also clearly shows that properties of unidirectional laminates as well as prepregs are highly anisotropic. This anisotropy increases with LCP content and is a major deficiency of LCP products. Thus, the quasi-isotropic laminates from these anisotropic prepregs are made. The tensile strength and modulus of quasi-isotropic laminates at various draw ratios as a function of LCP content are shown in Figure 9(a) and (b), respectively. It is seen that the modulus

of the quasi-isotropic laminates increases continuously with increasing LCP content [Fig. 9(b)]. At a draw ratio of 16, the modulus increases from 2.7 GPa for pure PEI to 5.0 GPa for an LCP content of 50%. Also, for each LCP concentration, the modulus of the laminates increases with draw ratio.

Since in the laminate each ply has the same in-plane strain,²³ the modulus of the laminates can be predicted from the modulus of each prepreg layer. For the quasi-isotropic laminates prepared in this work, the contribution of the modulus consists of one-fourth from the prepreg layers having a fiber direction parallel to the testing direction, one-fourth from those in the transverse direction, and two-fourths in the 45° direction. Therefore, the modulus of the quasi-isotropic laminates, E , can be calculated as follows:

$$E = \frac{1}{4}E_0 + \frac{1}{4}E_{90} + \frac{2}{4}E_{45} \quad (2)$$

where E_0 , E_{45} , and E_{90} are the moduli of prepregs tested at 0°, 45°, and 90° to the machine direction, respectively. For two-dimensional randomly oriented discontinuous fiber composites, the modulus can be predicted by the following approximate expression¹⁸:

$$E = \frac{3}{8}E_0 + \frac{5}{8}E_{90} \quad (3)$$

Using eqs. (2) and (3), the modulus of quasi-isotropic laminates made from prepregs at a draw ratio of 16 is calculated and compared with the experimental data. The results are listed in Table V. It is seen that the experimental data agrees

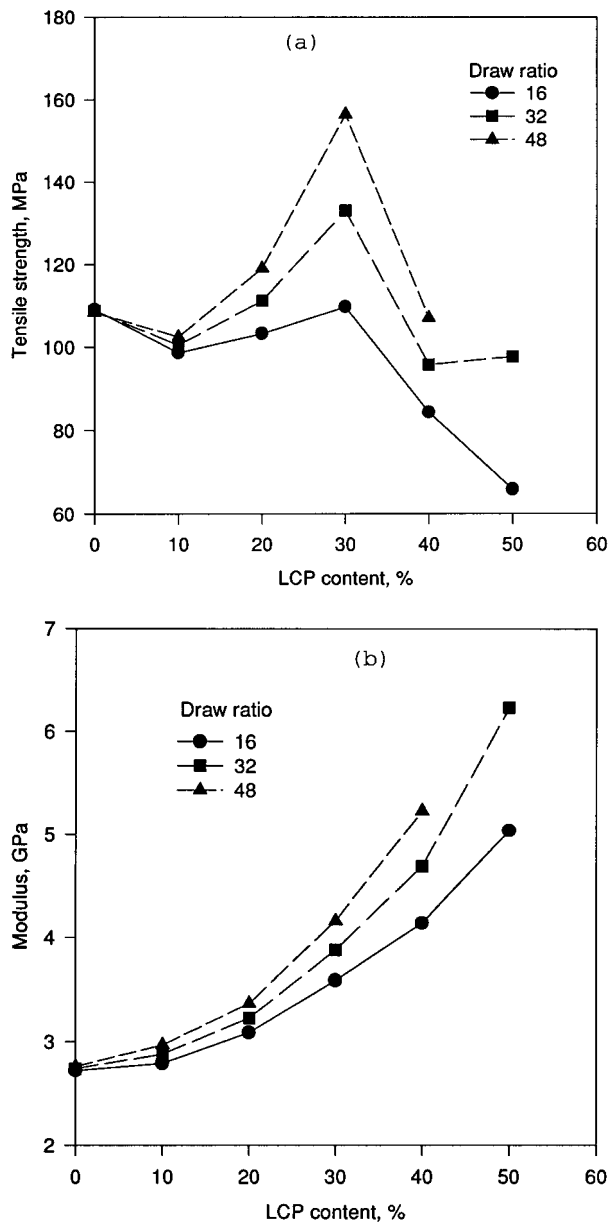


Figure 9 (a) Tensile strength and (b) modulus vs. LCP concentration for quasi-isotropic laminates at different draw ratios.

well with predictions of eq. (2) up to an LCP content of 40%. At an LCP content of 50%, the experimental modulus is higher than the calculated modulus. This may be because the low value of the modulus of the prepregs at the 45° and 90° directions is increased to some extent during lamination. Further, it is noted that the experimental data are also close to the values calculated according to eq. (3) for all LCP concentrations excluding 40%. At this LCP content, the unexpectedly low modulus of the prepregs in the 45° direc-

tion is obtained as indicated by Figure 5(b). In general, these results indicate that the quasi-isotropic laminates can be treated as random fiber-reinforced composites.

The behavior of the tensile strength of quasi-isotropic laminates with LCP concentration is very different from that of the modulus. As seen from Figure 9(a), tensile strength increases with LCP content up to 30%. Then, at an LCP content of 40 and 50%, it abruptly drops to a value even lower than that of PEI. So far, this unusual phenomenon has not been reported in the literature. In the case of LCP/PPO-PS blends, Isayev and Viswanathan¹¹ found that both the strength and modulus of quasi-isotropic laminates increase with increase in LCP content up to 80%. From the properties of prepregs discussed above and the lamination theory,¹⁸ one can understand why in the present case the drop in tensile strength occurs. From the lamination theory, it is known that the failure of a laminate occurs due to the initial breaking of the prepreg layer which has the lowest strain at break. When LCP content in prepregs is below 40%, the strain at break of the prepreg in the fiber direction is much lower than that in the 45° and 90° directions (see Table II). Therefore, upon application of load, the prepreg layers in which LCP fibrils are parallel to the direction of load are expected to fail first. Accordingly, the strength of the laminate in this case is dominated by the strength of these prepreg layers. When LCP content reaches 40%, at which the LCP phase starts to become continuous, the strain at break of prepregs in the 45° and 90° directions drops to values close to that in the fiber direction. At an LCP content of 50%, the strain at break of prepregs in the 45° and 90° directions is lower than that in the fiber direction. In these cases, the prepreg layers in these two directions may fail first. Thus, the laminate will break at a very low value of strain and, as a consequence, the prepreg layers having high strength in the fiber direction cannot fully contribute to the tensile strength of this laminate. This phenomenon is exactly reflected by the values of strain at break of laminates with LCP contents of 40 and 50% given in Table II.

CONCLUSION

Prepregs of PEI reinforced by highly oriented and almost continuous LCP fibrils were prepared through melt extrusion and subsequent stretch-

Table V Experimental and Calculated Modulus (GPa) of Quasi-isotropic Laminates

	Composition (LCP/PEI)				
	10/90	20/80	30/70	40/60	50/50
Experimental	2.8	3.1	3.6	4.1	5.0
Eq. (2)	2.8	3.1	3.5	4.1	4.1
Eq. (3)	2.8	3.1	3.8	4.7	5.0

ing. Using these prepregs, unidirectional and quasi-isotropic laminates were made. Quasi-isotropic laminates with an LCP content of 30% exhibit more than a 50% increase in tensile strength and modulus in comparison with those of pure PEI. The results indicate that the method used here provides a viable technique for preparation of self-reinforced laminates with improved isotropic mechanical properties. These laminates can be utilized for making products by thermoforming or other shaping techniques.

The investigation of properties of prepregs at 45° and 90° to the machine direction also shows the difference between this material and conventional fiber-reinforced composites. Since LCP fibrils in PEI are formed during flow, the low-viscosity LCP phase tends to become continuous at a concentration even less than 50%. In this case, the very weak transverse properties of pure LCP dominate the transverse properties of prepregs and led to the large decrease in the properties of prepregs in the 45° and transverse directions. The latter effect is responsible for the decrease in mechanical properties of quasi-isotropic laminates at higher LCP content. Such a behavior may limit a further improvement in the performance of *in situ* composites with a higher LCP content. However, since drawing significantly increases the mechanical properties of prepregs in the machine direction without decreasing their properties in the transverse direction, achieving the highest draw ratio can be an effective and economical way of manufacturing high-performance *in situ* composites.

REFERENCES

1. G. Kiss, *Polym. Eng. Sci.*, **27**, 410 (1987).
2. A. I. Isayev and M. Modic, *Polym. Compos.*, **8**, 158 (1987).
3. K. G. Blizard and D. G. Baird, *Polym. Eng. Sci.*, **27**, 653 (1987).
4. A. A. Handlos and D. G. Baird, *Macromol. Rev. Chem. Phys. C*, **35**, 183 (1995).
5. A. I. Isayev, in *Liquid Crystalline Polymer Systems: Technological Advances*, A. I. Isayev, T. Kyu, and S. Z. D. Cheng, Eds., *American Chemical Society*, Washington, DC, 1996, Vol. 632, pp. 1–21.
6. A. I. Isayev, Eur. Pat. Appl. WO 91/01879 (1991); U.S. Pat. 5,275,877 (1994); U.S. Pat. 5,238,638 (1993); U.S. Pat. 5,268,225 (1993).
7. D. Dutta, R. A. Weiss, and K. Kristal, *Polym. Compos.*, **13**, 394 (1992).
8. D. Dutta, R. A. Weiss, and K. Kristal, *Polym. Eng. Sci.*, **33**, 838 (1993).
9. J. C. Halpin, in *Primer on Composite Materials*, Technomic, Lancaster, PA, 1984.
10. A. I. Isayev, Y. Holdengreber, R. Viswanathan, and S. Akhtar, *Polym. Compos.*, **15**, 254 (1994).
11. A. I. Isayev and R. Viswanathan, *Polymer*, **36**, 1585 (1995).
12. G. Crevecoeur and G. Groeninckx, *Polym. Eng. Sci.*, **33**, 937 (1993).
13. B. R. Bassett and A. F. Yee, *Polym. Compos.*, **11**, 10 (1990).
14. E. A. Sabol, A. A. Handlos, and D. G. Baird, *Polym. Compos.*, **16**, 330 (1995).
15. Q. Lin and A. F. Yee, *Polymer*, **16**, 3463 (1994).
16. A. I. Isayev and S. Swaminathan, in *Advanced Composites III, Expanding Technology*, ASM International, Metals Park, OH, 1987, p. 259.
17. J. X. Li, M. S. Silverstein, A. Hiltner, and E. Baer, *J. Appl. Polym. Sci.*, **44**, 1531 (1992).
18. B. Z. Jang, *Advanced Polymer Composites*, ASM International, Metals Park, OH, 1994.
19. Q. Lin and A. F. Yee, *Polym. Compos.*, **15**, 156 (1994).
20. G. M. Jordhamo, J. A. Manson, and L. H. Sperling, *Polym. Eng. Sci.*, **26**, 517 (1986).
21. J. He, W. Bu, and H. Zhang, *Polym. Eng. Sci.*, **35**, 1695 (1995).
22. Z. Ophir and Y. Ide, *Polym. Eng. Sci.*, **23**, 792 (1983).
23. F. L. Matthews and R. D. Rawlings, *Composite Materials: Engineering and Science*, Chapman & Hall, London, 1994.