

Energy-Based Predictive Criterion for LCP Fibrillation in LCP/Thermoplastic Polymer Blends Under Shear

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ABSTRACT: This article relates the fibrillation of liquid crystalline polymer (LCP) under shear in its blend with a thermoplastic polymer (TP) to the relative rate of energy utilization in the LCP and TP phases. The development of a criterion based on the energy relationship for predicting LCP fibrillation in the blend is discussed. The formation of LCP fibers in the blends of LCP with polycarbonate (PC), polyethylene naphthalate (PEN), high-density polyethylene (HDPE), polypropylene (PP), and silica-filled polypropylene (PP) was studied to validate the criterion and to demonstrate its applicability. For all the blends, viscosity data were obtained by using a capillary rheometer, which was subse-

quently used to estimate the rate of energy utilization in the LCP and the matrix phases. The predictions based on the proposed criterion were verified through the morphological investigations carried out on the extrudates obtained from the same capillary experiments. The energy-based criterion was easy to implement, could account for the effect of variable LCP concentration and fillers in the blend, and could provide reliable predictions for a variety of LCP/TP blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3314–3324, 2003

Key words: liquid crystalline polymers; shear deformation; viscosity

INTRODUCTION

Blending of liquid crystalline polymer (LCP) with conventional thermoplastics (TP) is considered a promising option for developing high-performance, self-reinforced polymer composites. An LCP, when used as a minor phase in a polymer melt and subjected to elongational shear, orients itself to form a fibrillar structure that reinforces the blend.

Morphology of LCP phase is reported to be dependent on thermal characteristics of the component polymers and their compatibility, blend composition, viscosity ratio, shear rate, interfacial tension, melt temperature, flow modes (shear or extensional), etc.^{1–4}

Among all these parameters, the ratio of viscosity of dispersed (LCP) phase to continuous (matrix) phase (η_d/η_m) has been used by many researchers as a criterion to predict LCP fibrillation. The majority of the investigations indicate that LCP fibrillation is enhanced when the viscosity ratio is less than unity.^{2,3,5} However, contradictions to this rule were observed in some cases,^{1,2,4,6,7} indicating that other parameters are important in deciding the nature of the fibrillation process. One major shortcoming of this criterion is that it has no consideration for the effect of LCP concentration in the blend on fiber formation.

Following Taylor's work on the breakup of a single Newtonian drop in a simple shear, researchers combined the capillary number (the ratio of viscous force to interfacial force)^{8,9}

$$C_a = \frac{\dot{\gamma}\eta_m D}{2\sigma} \quad (1)$$

with the Taylor's theory. The resultant parameter⁹

$$C_a^T = \frac{\dot{\gamma}\eta_m D}{2\sigma} \left[\frac{16\lambda + 16}{19\lambda + 16} \right] [1 - (4\phi_d\phi_m)^{0.8}] \quad (2)$$

explains various factors that govern *in situ* LCP fiber formation in an LCP/TP blend. In the above equations, subscripts *m* and *d* represent the matrix and dispersed phases, respectively. η denotes the viscosity, $\lambda = (\eta_d/\eta_m)$, $\dot{\gamma}$ is the shear rate, σ is the interfacial tension, D is the diameter of a LCP droplet, and ϕ is the volume fraction. This can be considered a more comprehensive criterion because it combines the effect of various parameters responsible for fibrillation. However, the values of σ are not easily obtainable for LCP/TP blends.² Thus, the available information concerning σ and its effect on the morphology of the LCP phase is not reliable and conclusive.

Recently, slip at polymer–polymer melt interfaces was analyzed and verified experimentally.^{10–13} In particular, some members of the present team studied layered blends of LCP/PC subjected to in-plane shear and developed an energy-based model for predicting

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the interfacial slip in the blend.¹² This model assumed a layered construction of the individual polymers and an interfacial layer between them. The viscosity of the blend and the individual polymers were used to determine the proportion of energy consumed in LCP and PC phases. This information was used to calculate energy factor parameter, β , for quantifying the interfacial slip. The effects of the parameters such as viscosity, LCP concentration, interfacial slip, etc., which have significant effect on the blend behavior, were thus combined into and expressed in terms of a single parameter β . The concept was extended further and shown that the value of β could be used to identify the conditions that favor LCP fiber formation.¹³ It was demonstrated that the higher the value of β , the better was the LCP fibrillation. However, no definite limits were specified for β to be used as a generalized criterion for predicting *in situ* LCP fibrillation. Moreover, the studies were limited to LCP/PC blends processed under low-shear-rate conditions.

In the present investigation, the same energy concept was investigated from a different perspective to propose a more specific criterion that can be used in a variety of situations. The criterion is based on the relative rate of energy utilization in the two constituent phases of a LCP/TP blend. The proposed concept and the development of the predictive criterion are discussed. The fiber formation in the blends of LCP with polycarbonate (PC), polypropylene (PP), silica-filled polypropylene (PP), polyethylene naphthalate (PEN), and high-density polyethylene (HDPE) was studied to validate the proposed criterion. A capillary rheometer was used to obtain the viscosity data for the constituent polymers as well as for the blends with different concentrations of LCP and fillers under a variety of processing conditions. The data were employed to estimate the relative shear energy utilized in the LCP and the matrix phases during extrusion of the blend through the capillary. Morphological investigations were carried out on the same extrudates to examine LCP fibrillation. The reliability of the proposed criterion was assessed by comparing the predictions with the conventional criterion based on viscosity ratio and the morphological observations.

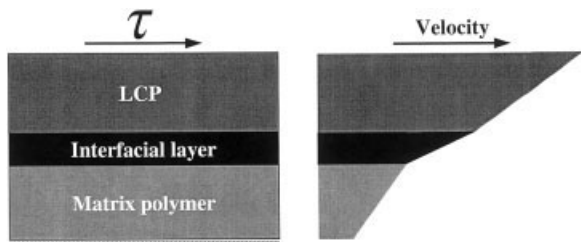


Figure 1 Layered structure representing TP-LCP interaction in a blend and its deformation under elongational shear.

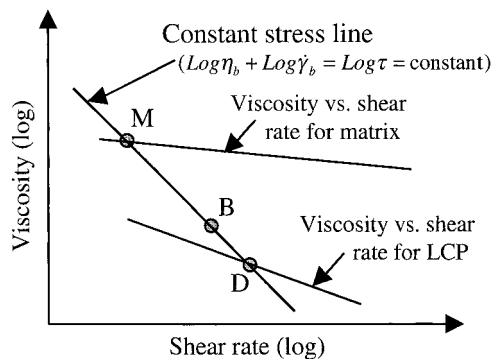


Figure 2 Use of constant shear stress condition for the calculation of $\dot{\gamma}_m$ and $\dot{\gamma}_d$.

THE ENERGY IN A LCP/TP BLEND

In the present studies, the approach by Lyngaae-Jorgensen¹⁴ for a layered model of a LCP/TP blend was employed to derive the energy utilized under shear by the individual blend components. A simple three-layer construction, as shown in Figure 1, consisting of LCP, TP, and the interfacial layers, is taken as a representative model of a LCP/TP blend.

When such a layered blend is subjected to shear, considering force equilibrium, all the layers will experience the same shear stress, such that

$$\tau = \eta_b \dot{\gamma}_b = \eta_m \dot{\gamma}_m = \eta_d \dot{\gamma}_d \tag{3}$$

where subscript *b* refers to the blend. Under the action of τ , depending upon the individual viscosity, different layers experience different deformation (see Fig. 1). The rates of energy utilization per unit volume of the blend in the LCP and thermoplastic layers (\dot{E}_d and \dot{E}_m) may then be calculated as:

$$\dot{E}_m = \frac{\tau \dot{\gamma}_m v_m}{v_b} = \tau \dot{\gamma}_m \phi_m \tag{4}$$

$$\dot{E}_d = \frac{\tau \dot{\gamma}_d v_d}{v_b} = \tau \dot{\gamma}_d \phi_d \tag{5}$$

where *v* represents the corresponding volume. Substituting from eq. (3), eqs. (4) and (5) can be rewritten as:

$$\dot{E}_m = (\eta_b \dot{\gamma}_b) \dot{\gamma}_m \phi_m = (\eta_b \dot{\gamma}_b)^2 \phi_m / \eta_m \tag{6}$$

$$\dot{E}_d = (\eta_b \dot{\gamma}_b) \dot{\gamma}_d \phi_d = (\eta_b \dot{\gamma}_b)^2 \phi_d / \eta_d \tag{7}$$

At any given temperature, η_b as a function of $\dot{\gamma}_b$ can be obtained by conducting rheological tests on a blend. Although $\dot{\gamma}_m$ and $\dot{\gamma}_d$ cannot be measured directly for a blend, they can be determined by using viscosity data for the individual blend components and the blend. When a polymer blend is subjected to a constant shear

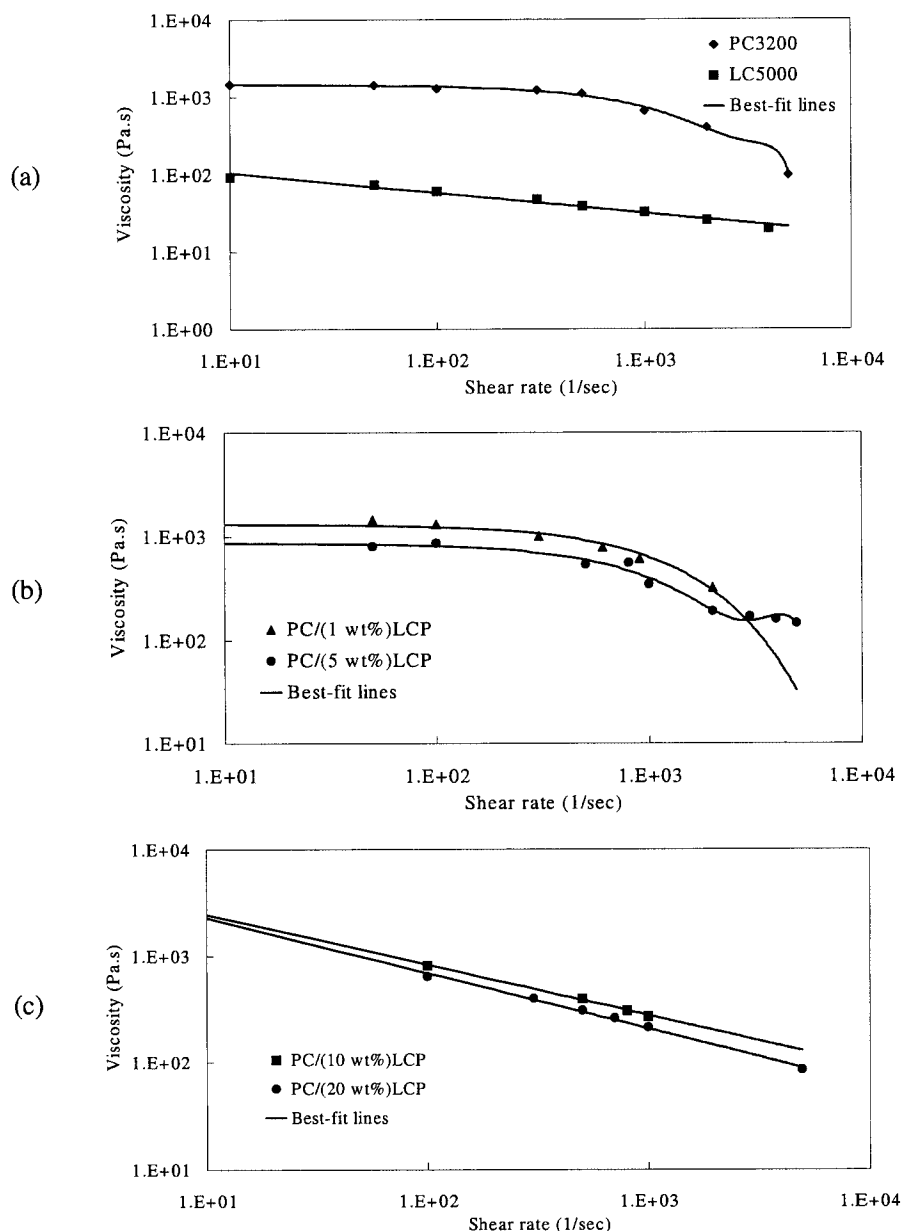


Figure 3 Viscosity measurements for the PC, LCP, and PC/LCP blends.

stress, at any given shear rate, a constant shear-stress line can be drawn on a log-log scale ($\log \eta_b + \log \dot{\gamma}_b = \log \tau = \text{constant}$). At any given shear rate, there can be only one constant-shear-stress line. This line will intercept the viscosity profiles for each of the individual blend components drawn on the same scale as shown in Figure 2. The shear rate and viscosity of individual components at those intercepting points (i.e., at point D for LCP and at point M for matrix polymer) can be subsequently determined.

In general, LCP concentration in a blend is based on weight measurements. Assuming that the interfacial layer is very thin, ϕ_d may be calculated from weight fraction and density as

$$\phi_d = \frac{(w_d/\rho_d)}{(w_d/\rho_d + w_m/\rho_m)} \quad (8)$$

ϕ_m will be then equal to $(1 - \phi_d)$. Having been able to calculate all the parameters for eqs. (6) and (7), \dot{E}_m and \dot{E}_d can be determined at any particular value of $\dot{\gamma}_b$.

PREDICTIVE CRITERION FOR LCP FIBRILLATION

Because an LCP/TP blend consists of two distinct polymer phases, it is likely that the characteristics of the blend are decided by the relative rate of energy

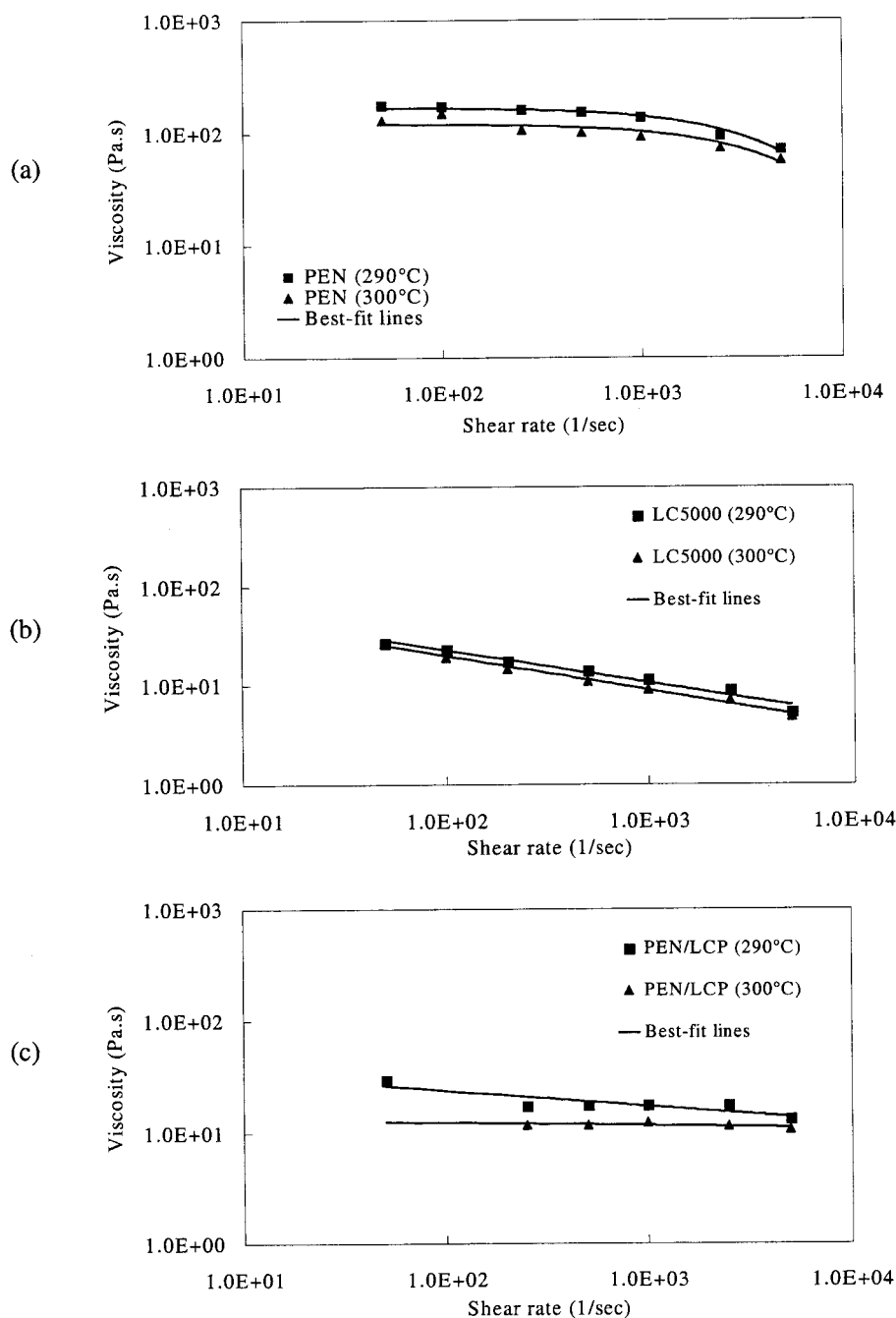


Figure 4 Viscosity measurements for the PEN, LCP, and PEN/LCP blends.

consumption in those two constituent phases. As may be seen from eqs. (6) and (7) that when the energy consumption is higher in the LCP phase than the matrix phase, the LCP phase experiences a relatively higher shear rate. Under such conditions, the chances of near-spherical LCP droplets getting sheared and changed to a cylindrical geometry to form fibers are higher.

Thus, when $\dot{E}_m/\dot{E}_d < 1.0$ for a LCP/TP blend, better LCP fibrillation will occur. The criterion can be written in an equation form as the ratio of eqs. (6) and (7) as:

$$\frac{\dot{E}_m}{\dot{E}_d} = \frac{\dot{\gamma}_m \phi_m}{\dot{\gamma}_d \phi_d} = \frac{\eta_d \phi_m}{\eta_m \phi_d} < 1.0 \quad (9)$$

This energy-based criterion differs from the conventional viscosity ratio criterion, $\eta_d/\eta_m \leq 1.0$, in the following important aspects:

1. It includes the volume fraction terms that can take care of different LCP concentrations in the blend, and

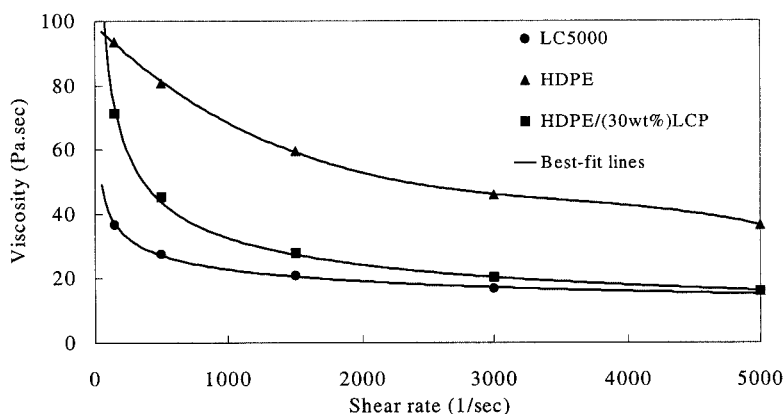


Figure 5 Viscosity measurements for the HDPE, LCP, and HDPE/LCP blends.

2. it accounts for the effect of other parameters on fiber formation.

It was observed that at a given shear rate, the viscosity of a LCP/TP blend is governed not only by the viscosity of the LCP and TP but also by the interaction between those two constituents.¹¹ Because the energy-ratio criterion uses η_b versus $\dot{\gamma}_b$ relationship for a blend as its basis, the effect of various parameters (such as interfacial slip, processing conditions, etc.) that influence this relationship is implicitly taken care of. In addition, as depicted in eq. (9) and its derivation, the interaction between parameters such as η_{br} , η_{mv} , η_{dv} , $\dot{\gamma}_{br}$, $\dot{\gamma}_{mv}$, $\dot{\gamma}_{dv}$, ϕ_m and ϕ_d is explicitly considered.

EXPERIMENTAL

Viscosity measurements for various polymers and their blends with LCP at various shear rates were carried out by using a capillary rheometer. The experimental data were used to determine \dot{E}_d and \dot{E}_m and subsequently test the proposed criterion. The melt-extrudates from the same capillary experiments were used to examine the blend morphology for corroborating the predictions.

It was expected that at low-to-medium shear rates, effects of extensional flow experienced at the entrance of a capillary would be minimal and shear flow would dominate formation of LCP fibers and retention of their geometry. Any fibers formed at the entrance of a reasonably long capillary would relax and contract unless sustained under the action of the applied shear.

LCP/TP blends

Five types of blend systems with different LCP and filler contents, and test temperatures were considered for the investigation:

1. PC3200 with 1, 5, 10, and 20 wt % of Rodrun LC5000 at 280°C,
2. PEN with 20 wt % Rodrun LC5000 at 290 and 300°C,
3. HDPE with 30 wt % of Rodrun LC5000 at 280°C,
4. PP without any filler with 30 wt % Rodrun LC5000 at 280°C, and
5. PP with 5, 10, and 15 wt % hydrophobic silica (with average particle diameter of 12 nm) fillers and 30 wt % Rodrun LC5000 at 280°C.

Reinforced PCs, because of a good combination of properties and processing flexibility offered by PC, have been of interest for replacing metal parts in various applications. Solubility of PC in various solvents, which allows its extraction for morphological observation, offered an added advantage for the present studies. PEN is a newly commercialized TP and offers a large temperature window of 250–350°C for processing. This made it easy to study the characteristics of its blends at different temperatures. HDPE and PP belong to the polyolefins category and are lighter polymers (density < 1 g/cm³). This made them interesting candidates for studying fiber formation by using a capillary of different lengths. PP being a common commodity plastic, its blend with silica fillers has a commercial interest, and therefore, is considered for the present analysis.

The densities of LC5000, PC3200, PEN, HDPE, PP, and the silica were 1.4, 1.2, 1.36, 0.95, 0.85, and 2.0 g/cm³, respectively. A rule of mixture based on volume fractions was used to calculate density of the silica-filled PP. The respective values were 0.87, 0.902, and 0.93 g/cm³ for the 5, 10, and 15 wt % silica filler.

TABLE I
Rheological Data for the PP, LCP, and PP/LCP Blends

Description	Viscosity η (Pa s)				
	$\dot{\gamma} = 50 \text{ s}^{-1}$	$\dot{\gamma} = 200 \text{ s}^{-1}$	$\dot{\gamma} = 500 \text{ s}^{-1}$	$\dot{\gamma} = 1000 \text{ s}^{-1}$	$\dot{\gamma} = 3000 \text{ s}^{-1}$
PP	114	66.7	47.1	30.8	17.1
PP (with 5 wt % silica)	354.4	135	88.7	60.5	35.5
PP (with 10 wt % silica)	384	145	92.7	68.9	—
PP (with 15 wt % silica)	368	172	105	—	51.8
LC5000	64.9	36.6	27.1	21.2	16.6
PP/LCP (30 wt %)	122.1	88.6	52.5	36	19.1
PP (5 wt % silica)/LCP (30 wt %)	148	48.9	31.8	22	13.2
PP (10 wt % silica)/LCP (30 wt %)	162	58	39.1	24.4	14.7
PP (15 wt % silica)/LCP (30 wt %)	171	76.3	50.1	35.4	20.2

Note that the LCP concentration in all the blends was maintained at 30 wt % or less to minimize the possibility of coalescence of the dispersed phase.

Sample preparation

The PC and LCP were vacuum-dried at 120°C for at least 12 h prior to use. The PC and LCP were subsequently melt-blended by using a Haake twin-screw extruder at 270°C and 15 rpm. As extrusion is the first step in the processing of the blend, higher temperatures were not used to avoid degradation in further stages of processing. The extrudates were quenched and pelletized. The pellets were then dried at 120°C under vacuum for 12 h before further processing. The

same procedure was used for the PEN/LCP and HDPE/LCP blends.

The preparation of the silica-filled PP/LCP blends involved the extruding of PP with silica first followed by the filled PP with LCP. The silica and PP were first blended in an extruder at a die temperature of 200°C, followed by the PP-LCP blending at about 280°C. The hopper temperature was maintained at 180°C. The blending of PP and silica was not required in the case of unfilled PP/LCP blends.

Rheological tests

All the dried blends were extruded at controlled shear rates ($\dot{\gamma}$) by using a Gottfert capillary rheometer, Rheo-

TABLE II
Equations of the Best-Fit Curves for Viscosity Measurements for Various Material Systems

Material system	Equation of the best-fit curve
LC5000 (Rodrun)	$\eta = 190.02\dot{\gamma}^{(-0.2597)}$ (batch for the PC/LCP blends) $\eta = 103.01\dot{\gamma}^{(-0.3292)}$ (batch for the PEN/LCP blends at 290°C) $\eta = 97.823\dot{\gamma}^{(-0.3468)}$ (batch for the PEN/LCP blends at 300°C) $\eta = 133.19\dot{\gamma}^{(-0.2555)}$ (batch for the HDPE/LCP blends) $\eta = 227.72\dot{\gamma}^{(-0.3364)}$ (batch for the PP/LCP blends)
PC3200	$\eta = -3 \times 10^{-8} \dot{\gamma}^3 + 3 \times 10^{-4} \dot{\gamma}^2 - 0.9731\dot{\gamma} + 1453.2$
PEN	$\eta = 168.43e^{(-0.0002\dot{\gamma})}$ (at 290°C) $\eta = 120.95e^{(-0.0002\dot{\gamma})}$ (at 300°C)
HDPE	$\eta = -1 \times 10^{-9} \dot{\gamma}^3 + 1 \times 10^{-5} \dot{\gamma}^2 - 0.0396\dot{\gamma} + 98.834$
PP	$\eta = 747.26\dot{\gamma}^{(-0.4624)}$
PP (with 5 wt% silica)	$\eta = 2862.9\dot{\gamma}^{(-0.5559)}$
PP (with 10 wt% silica)	$\eta = 3423.1\dot{\gamma}^{(-0.576)}$
PP (with 15 wt% silica)	$\eta = 2251.3\dot{\gamma}^{(-0.4789)}$
PC/LCP (1 wt%)	$\eta = 1332.2e^{(-0.0007\dot{\gamma})}$
PC/LCP (5 wt%)	$\eta = -2 \times 10^{-8} \dot{\gamma}^3 + 2 \times 10^{-4} \dot{\gamma}^2 - 0.646\dot{\gamma} + 873.93$
PC/LCP (10 wt %)	$\eta = 7301.1\dot{\gamma}^{(-0.4735)}$
PC/LCP (20 wt %)	$\eta = 7543.3\dot{\gamma}^{(-0.5202)}$
PEN/LCP (30 wt %)	$\eta = 45.019\dot{\gamma}^{(-0.1388)}$ (at 290°C) $\eta = 13.91\dot{\gamma}^{(-0.0262)}$ (at 300°C)
HDPE/LCP (30 wt %)	$\eta = 622.58\dot{\gamma}^{(-0.4272)}$
PP/LCP (30 wt %)	$\eta = 864.45\dot{\gamma}^{(-0.4623)}$
PP (5 wt % silica)/LCP	$\eta = 1251.8\dot{\gamma}^{(-0.5816)}$
PP (10 wt % silica)/LCP	$\eta = 1442.2\dot{\gamma}^{(-0.5826)}$
PP (15 wt % silica)/LCP	$\eta = 1247.6\dot{\gamma}^{(-0.517)}$

TABLE III
Aspect Ratio Measurements of LCP Fibrillation for the PC/LCP Blends

$\dot{\gamma}$ (s^{-1})	LCP (1 wt %)	LCP (5 wt %)	LCP (10 wt %)	LCP (20 wt %)
50	1.4	2.3	2.5	3.9
100	~ 1.3	3.7	2.6	5.9
500	~ 1.3	8.2	3.3	>20
800	~ 1.3	6.7	8.6	>20
1000	~ 1.3	7.5	10.1	>20
2000	~ 1.3	9.2	7.1	>20
3000	~ 1.3	—	6.5	>20
4000	~ 1.3	1.9	4.8	>20
5000	~ 1.3	2.6	—	>20

graph 6000. The rheological measurements on PC, PEN, HDPE, and their blends with LC5000 were carried out by using a capillary die 20 mm in length and 1 mm in diameter. A 10-mm-long die of 1 mm diameter was used for the PP related tests. In all cases, the die entry angle was 180°C. All the tests, except for two sets of tests on PEN, LC5000, and the PEN/LC5000 blends, were conducted at 280°C so that the LCP remained within its nematic temperature range. The viscosity data for PC, PEN, HDPE, and their blends with LC5000, along with the best-fit curves, are presented in Figures 3-5. The viscosity data for the PP and all its blends are tabulated in Table I. The equations of the best-fit curves obtained to help in the energy calculations are listed in Table II.

The tests on each of the five types of blend systems were carried out at different times. Because LC5000 from different batches was used for the different blend systems, the viscosity measurements were carried out separately on each of these batches of LCP. A small variation in the viscosity was observed for the different batches of LCP. For the energy calculations, to maintain the consistency, the test data for the respective batches of LCP were used as obtained without any averaging.

Morphological observations

The samples of PC/LCP and PP/LCP (with and without the silica filler) extrudates were selectively extracted for morphological studies. The PEN/LCP extrudates from the capillary die were quenched immediately in ice-chilled water to freeze their morphology. Otherwise the shear-enabled LCP fibers would relax because the melt temperature was higher than nematic temperature of the LCP.

Subsequently, a scanning electron microscope (SEM) was used to examine the sample morphology, especially of the LCP phase. The aspect ratio of LCP fibers for the PC/LCP and PEN/LCP blends obtained by analysis of the SEM images are listed in Tables III

and IV, respectively. The microstructure of the HDPE/LCP blend was studied at 180°C by using a Linkam hot stage microscope. The HDPE melted at 140°C while the LCP was still in the solid state. The hot stage micrographs of the HDPE/LCP blends are shown in Figure 6. The pictures were captured digitally and analyzed later to determine the quality of the LCP fibers. The aspect ratio data for LCP phase for the unfilled and silica-filled PP/LCP extrudates are presented in Table V.

Note that the shear rates that designate the various morphological observations refer to the shear rates used for the rheological tests on the blends. Thus, the notations $\dot{\gamma}$ and $\dot{\gamma}_b$ are interchangeable.

PREDICTIONS ON FIBER FORMATION

The application of the existing viscosity-ratio criterion and the proposed energy-ratio criterion for predicting LCP fibrillation in the various blend systems under investigation are discussed below.

Viscosity ratio ($\lambda = \eta_d/\eta_m$) criterion

To examine the reliability of the viscosity-ratio criterion, η_d/η_m ratios were calculated for all the blend systems by using the viscosity data for the individual blend components. The plots of λ versus $\dot{\gamma}$ for all the blends are shown in Figure 7.

It may be seen from Figure 7 that λ was less than unity for all the polymer blends at all the shear rates considered. Thus, good LCP fibrillation was expected at all shear rates for all the blends.

However, for some of the blend systems, the morphological observations were contradictory to the prediction. Table III shows that the average aspect ratio of LCP droplets in the PC/LCP (1 wt %) blend was less than 2, indicating that there was no fibrillation. In the case of the HDPE/LCP blend, no fibers were observed from the hot stage micrographs at low shear rates (see Fig. 6). Similarly, the values in Table V indicate that the percentage of high-aspect-ratio LCP fibers developed in the unfilled PP/LCP blend was insignificant. It was reported⁷ that most of the LCP particles existed as spheroids, which had an aspect ratio of 1.0.

The proposed energy ratio (\dot{E}_m/E_d) criterion

Employing the procedure outlined in Energy in a LCP/TP blend, the quantities, and their ratio, were

TABLE IV
Aspect Ratio Measurements on LCP Fibrillation for the PEN/LCP Blends

Temperature (°C)	$\dot{\gamma} = 50 s^{-1}$	$\dot{\gamma} = 1000 s^{-1}$	$\dot{\gamma} = 5000 s^{-1}$
290	5.75	6.4	10.25
300	2.41	2.78	4.49

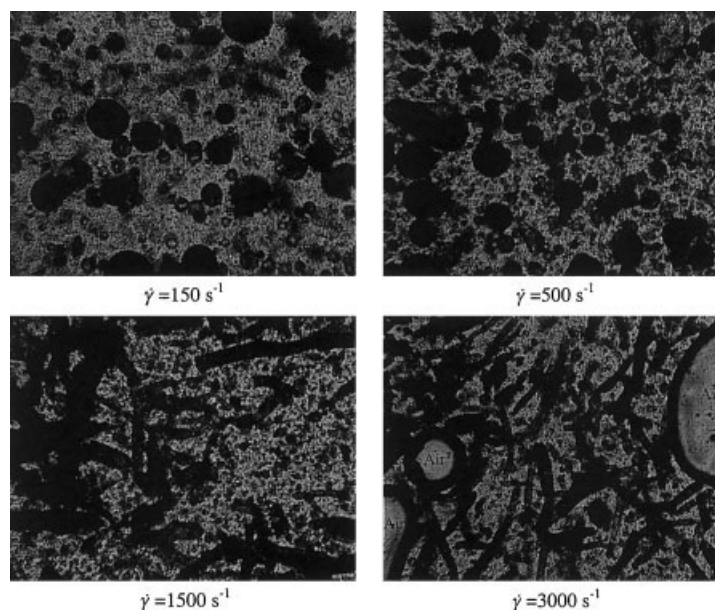


Figure 6 Hot stage micrographs of HDPE/LCP (30 wt %) extrudates sampled at various shear rates.

calculated for all the blends; the corresponding \dot{E}_m/\dot{E}_d plots are presented in Figure 8.

It may be seen from Figure 8(a) that for PC/LCP (1 wt %) blend, $\dot{E}_m/\dot{E}_d > 1$ at all shear rates. This indicated that the conditions were not favorable for LCP fibrillation. For the remaining PC/LCP blends with higher LCP concentration, \dot{E}_m/\dot{E}_d was much less than unity, suggesting that good LCP fibers would form in those blends. The measurements of aspect ratio of the LCP fibers presented in Table III substantiate these predictions.

Some of the results presented in Table III, however, showed inconsistency in the magnitude of fiber aspect

ratio at higher shear rates. This indicated that there was some fiber break up in the capillary at higher shear rates. Nevertheless, the magnitudes of the aspect ratio were significant enough to confirm that the LCP fibrillation did take place.

For the HDPE/LCP blend, the energy ratio was higher than unity at low shear rates [refer to Fig. 8(b)]. This suggested that the processing conditions did not favor the conversion of the LCP droplets into fibers at low shear rates. Accordingly, the fiberless HDPE matrix was seen during the hot stage microscopic examination of the extrudate extracted at $\dot{\gamma} = 150 \text{ s}^{-1}$ (Fig. 6). At $\dot{\gamma} = 500 \text{ s}^{-1}$, some of the LCP droplets were

TABLE V
Aspect Ratio Measurements for LCP Phase in the Unfilled and Silica-Filled PP/LCP Blends

Shear rate, $\dot{\gamma} \text{ (s}^{-1}\text{)}$	Range of aspect ratio for LCP fibers and percentage fibers in that range									
	No silica filler					SiO ₂ filler (5 wt %)				
	1-5	6-10	11-15	16-20	21-25	1-5	6-10	11-15	16-20	21-25
50	99.5	0.5	—	—	—	92.7	3.4	—	—	—
200	95	0.6	—	—	—	92.9	7.1	—	—	—
500	95	5	—	—	—	78.9	18.6	2.5	—	—
1000	90.1	9.2	0.7	—	—	62	31	5.3	0.6	—
3000	89.9	8.4	1.7	—	—	61.5	29.9	5.8	1.1	—

Shear rate, $\dot{\gamma} \text{ (s}^{-1}\text{)}$	Range of aspect ratio for LCP fibers and percentage fibers in that range									
	SiO ₂ filler (10 wt %)					SiO ₂ filler (15 wt %)				
	1-5	6-10	11-15	16-20	21-25	1-5	6-10	11-15	16-20	21-25
50	92.1	7.9	—	—	—	81.6	14.1	3.8	0.5	—
200	78.7	21.7	2.9	—	—	75.3	14.7	11.6	0.5	—
500	70.1	20.1	9.8	—	—	69.5	28	2.4	—	—
1000	37	20.1	27.8	15.7	0.9	34.3	40.2	14.7	6.9	3.9
3000	11.1	47.2	27.8	15.7	0.9	27.4	55.4	14.6	6.5	1.4

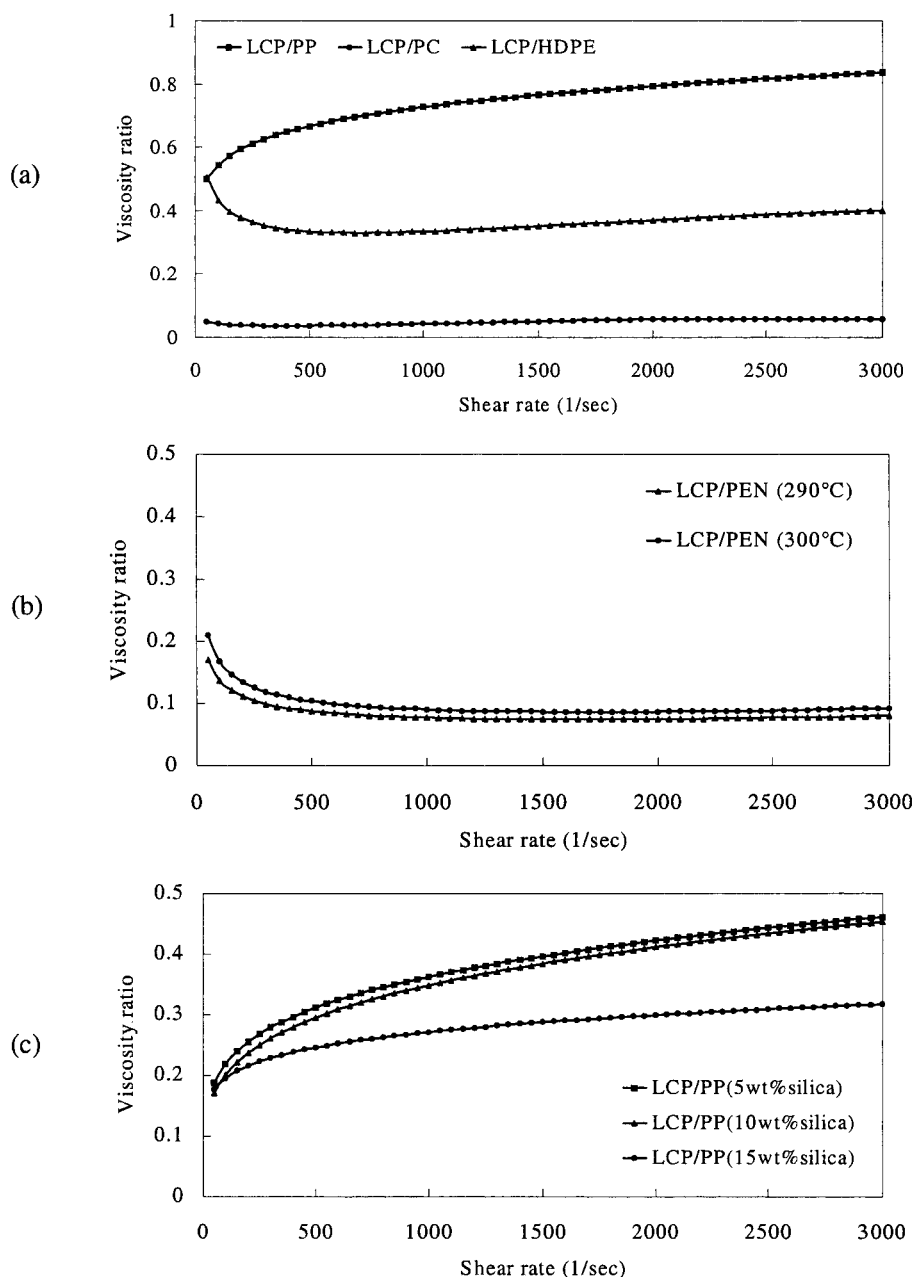


Figure 7 η_d/η_m plots for the PC, PEN, HDPE, and PP blends with LCP as dispersed phase.

ellipsoidal. Good LCP fibers were seen at $\dot{\gamma} = 1500 \text{ s}^{-1}$ and above. As expected, the energy ratio, which was greater than unity at lower shear rates, dropped gradually below 1.0 as the shear rate increased. At $\dot{\gamma} = 1500 \text{ s}^{-1}$, \dot{E}_m/\dot{E}_d was just below 0.8. Thus, the predictions of the proposed criterion were consistent with the morphological observations.

It may be seen from Figure 8(b) that \dot{E}_m/\dot{E}_d was always less than unity for the PEN/LCP blends. Thus, as shown in Table IV, good LCP fibers were obtained in these blends at all shear rates at both test temperatures.

Figure 8(c) shows that \dot{E}_m/\dot{E}_d that was in the range of 1.5–3.0 for the PP/LCP blend without the silica

filler, whereas it was less than unity for the silica-filled blends. Thus, good fiber formation was expected for all the PP/LCP blends, except for the unfilled blend. This can be ascertained from the aspect ratio measurements on LCP phase for the PP blends presented in Table V.

Comparison between η_d/η_m and \dot{E}_m/\dot{E}_d criteria

The comparison between the predictions based on these two criteria and the experimental observations is given in Table VI.

It was observed that the predictions based on the viscosity ratio were not accurate and conclusive for

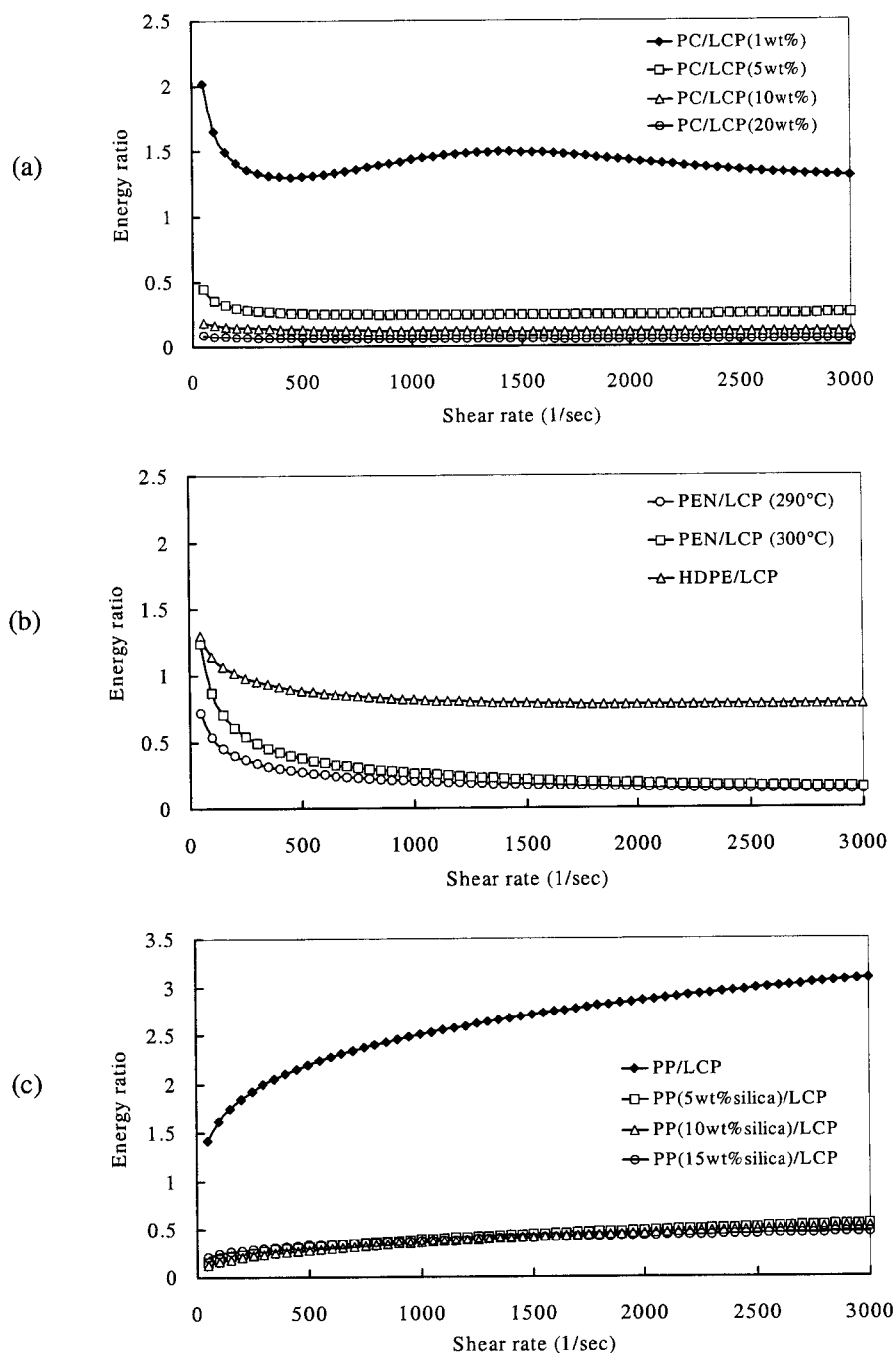


Figure 8 \dot{E}_m/\dot{E}_d plots for the blends of LCP with PC, PEN, HDPE, and PP with and without silica fillers.

some of the blend systems, whereas \dot{E}_m/\dot{E}_d ratio criterion provided consistent predictions for all cases.

As HDPE and PP are semicrystalline polymers of similar nature, it is generally expected that their blends with 30 wt % of LC5000 should show similar characteristics. At low shear rates, both blends showed no fibrillation. The HDPE/LCP blend showed significant fibrillation with high-aspect-ratio fibers at higher shear rates. However, no notable fiber formation was observed in the unfilled PP blends. This may be attributed to the length of the capillary die used for the

HDPE/LCP blend, which was twice as long as the die used for the PP/LCP blend. It was likely that the unfilled PP/LCP blend could not have a sustained fibrillation at higher shear rates because of the shorter die length. This effect was captured only by the \dot{E}_m/\dot{E}_d criterion.

CONCLUSIONS

The results of the present investigations showed that the proposed \dot{E}_m/\dot{E}_d criterion is a reliable indicator of

TABLE VI
Comparison Between the η_d/η_m and \dot{E}_m/\dot{E}_d Based Predictions and Morphological Observations on LCP Fiber Formation

TP/LCP blend	LCP fibrillation		
	η_d/η_m predictions	\dot{E}_m/\dot{E}_d predictions	Morphological observations
PC/LCP (1 wt %)	Yes (no accounting for LCP concentration)	No	No
PC/LCP (5 wt %)		Yes	Yes
PC/LCP (10 wt %)		Yes	Yes
PC/LCP (20 wt %)		Yes	Yes
PEN/LCP (30 wt %) at 290°C	Yes	Yes	Yes
PEN/LCP (30 wt %) at 300°C	Yes	Yes	Yes
HDPE/LCP (30 wt %)	Yes	No at low $\dot{\gamma}$ Yes at high $\dot{\gamma}$	No at low $\dot{\gamma}$ Yes at high $\dot{\gamma}$
PP/LCP (30 wt %)	Yes	No	No
PP (5 wt % silica)/LCP (30 wt %)	Yes	Yes	Yes
PP (10 wt % silica)/LCP (30 wt %)	Yes	Yes	Yes
PP (15 wt % silica)/LCP (30 wt %)	Yes	Yes	Yes

the *in situ* development of LCP fibers in LCP/TP blends under shear. This criterion worked well even for cases where the conventional criterion had failed to provide consistent predictions. The criterion proved to be more comprehensive and predictions could be made for a variety of LCP/TP blends under different processing conditions. Unlike the existing viscosity-ratio criterion, the proposed energy criterion could account for the effects of different LCP concentrations.

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