STABILITY OF BLENDS OF POLYETHERSULFONE WITH THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

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ABSTRACT

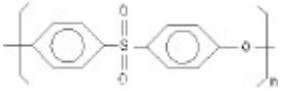
The formation and stability of various liquid crystalline polymers in an amorphous polymer matrix, Polyether sulfone (PES) over the melting temperature has been studied by *in-line* optical video microscopy and light scattering. The fiber breakup morphology profiles after shear cessation was examined to study the stability of the thermotropic liquid crystalline polymers (TLCP) fibers in the PES matrix. The TLCP are aromatic copolyesters with different chain structures, Ln 001 and LC-5000. Shear induces a droplet-fiber transition along the flow direction, but the TLCP fibers are highly unstable and can break up in a few seconds upon cessation of shear. The TLCP fibers break up into droplets by the combination of Rayleigh distortions, end pinching and retraction. The apparent values for the interfacial tension was calculated with Tomotika's theory and compared with the individual fiber experiment in literatures. The results suggest that the viscosity ratio and the interfacial tension between the materials components control both the shear-induced fiber formation and fiber stability.

INTRODUCTION

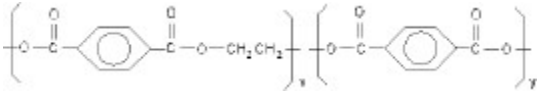
The blending of thermotropic liquid crystalline polymers (TLCPs) with thermoplastic polymers usually results in improvement of both the mechanical and processing properties, because of the molecular orientation inside the thermoplastics matrix and the low viscosity of micro-fibrous domains (1-2). When TLCPs blend with various engineering plastics such as PES, PEEK, PPS, and PEI etc, high-performance engineering materials can be created with enhanced physical property as well as processability (3-5). Most studies of *in-situ* composites have focused on the formation of fibrous structure and the dependence of fiber-like morphology on the rheology and processing conditions. However, the stability of a fibrous phase in melt state may be as important as its formation, because TLCP fibrous phase embedded in thermoplastic mediums during processing represents a non-equilibrium morphology that it may rapidly breakup into droplets by a combination of Rayleigh distortions, end-pinching and retraction. Such a fast fiber breakup would kill the self-reinforcing properties by a fiber / matrix morphology. Even through it is well known that interfacial tension plays a critical role in determining the formation and stability of the fiber microstructure in the melt state, little attention has been paid to the stability of fiber and the interfacial tension between the TLCP and matrix. This is probably because of the experimental difficulties in accurate measurement of the interfacial tension, especially during melt processing. Machiels et al conducted a single capillary instability experiment to obtain the apparent values of the interfacial tension (s_a) of the blends of PES / Vectra TLCP, which was calculated with Tomotika's theory (6, 7). In order to better understand the formation and stability of fiber presented in the real processes of extrusion or injection molding, we present in this study an alternative approach to "*in-situ*" measure the interfacial tension by using an in line strobostic video microscopy and light scattering microscopy.

EXPERIMENTAL*

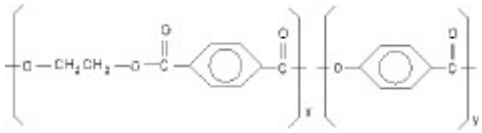
The amorphous polymer matrix is RADEL® A Polyethersulfone from Amoco Campany, the PES has a glass transition tempreture of 224°C as determined by DSC. The TLCPs used in this study are LC-5000 from Unitika Company and Ln 001 from Eastman Chemical Company. DSC measurement shows LC-5000 has a crystalline to nematic transition melt point temperature of 291.4°C and Ln 001 has a melt point of 326.7 °C :



PES



Ln 001



LC-5000

The blend was extruded into a narrow channel of a slit die equipped with optical sapphire windows, located at the end of a corotating conical twin-screw extruder, a detailed description of this device is described by Li et al (8). A typical temperature profile along the axis of the extruder from the feeding zone to the slit die is 310 ^{o}C, 320 ^{o}C, 320 ^{o}C, and 330 ^{o}C. The experiment was conducted on such a pattern that we increased the shear rate to a critical shear rate for various PES / TLCP pairs, at which a fibrous morphology was obtained and observed by in-line optical microscopy and light scattering, then the stop the shear and recorded growth distortion of fibers with a stroboscopic video camera and a light scattering microscopy in time scale of seconds. The apparent shear rates $\dot{g}_a$ and apparent viscosity h_a of PES and its blends with TLCP was measured and calculated by the classical working equations for slit rheometer (9) with a relative uncertainty of 10 %.

RESULTS AND DISCUSSION

Figure 1 displays the optical images of PES / TLCPs under a shear flow field and corresponding light scattering profiles. Here we observe a variety of deformations of TLCP droplets in the PES matrix as a function of apparent shear rate ($\dot{g}_a$). For the blend of PES / Ln 001 as shown in Figure 1A, at a low shear rate ($\dot{g}_a$ < 2.3 s^{-1}) TLCP droplets are polydisperse spherical domains that do not show fiber formation. In the case of moderate shear flow, TLCP droplets are well elongated when the shear rate is over a critical value ($\dot{g}_a$ > 3.93 s^{-1}) and shear-induced fiber formation along $\hat{x}$ is observed. The TLCP fibers were highly oriented as a result of shear flow as observed from both optical microscopy and light scatting patterns. In the second polymer pair of PES / LC-5000 in Figure 1C, mildly extended droplets are observed at low $\dot{g}_a$, whereas spherical droplet elongates into elliptical domains at high $\dot{g}_a$ ($\dot{g}_a$ > 8.11 s^{-1}) as shown in Figure 1D. Comparing the two polymer pairs in this study, we see variation in the critical shear rate $\dot{g}_{a,c}$ over which an *in-situ* fiber formation can be achieved. These results suggest that the viscosity ratios and the interfacial tensions (σ) between the material components control the shear induced morphological transitions.

Experimental evidence on immisible polymer blends indicates that the fibers formed during shear flow may develop instabilities at the interface, at large deformation the interfacial tension will breakup fibers either during flow or upon flow cessation (10, 11). Theoretical treatments predicating thread break-up by Tomotika (12) consider the capillary wave instabilities in an elongated domain of a Newtonian fluid in shear flow. As shown in Figure 2 for PES / LC-5000, the fiber / matrix morphology are highly unstable in the quiescent melt state. The corresponding light scattering images with reduced scattering along $\hat{z}$ as a function of time present complementary evidence of fiber instability. The TLCP fibers in all cases breakup within several seconds, and we indeed observed capillary wave instability with sinusoidal distortion during the fiber breakup process. As a first approach we apply the Tomotika's theory to our system to estimate the apparent value of interfacial tension, which dominate the stability of fibers during melt processing.

In the Tomotika's theory a sinusoidal distortion α imposed upon a thread grows exponentially with time:

$$a = a_0 e^{qt} \qquad (1)$$

where a_0 is the distortion at t = 0 and q is the growth rate:

$$q = \frac{s}{2h_m R_0}\Omega(x, p) \qquad (2)$$

where σ is the interfacial tension, η_m is the viscosity of the matrix, R_0 is the initial thread radius, p is the viscosity ratio, $p = h_d / h_m$, x the dimensionless wave number. The dimensionless growth rate Ω is a function of p and x.

Tomotika's theory enables calculation of the interfacial tension from equation (2), using the experimentally determined growth rate (q_{exp}) and wave number x_{exp} of a distortion, and the viscosity of the TLCPs and matrix phase. The wavelength is measured from the optical images and the distortion amplitude determined as a function of time:

$$a = \frac{D_{max} - D_{min}}{4} \qquad (3)$$

The apparent viscosity of the individual TLCP phase embedded in PES matrix can be approximately evaluated with a fluidity-additive rule, which relates the fluidity of an immisible biphasic system as the sum of individual contributions of the fluidity of the components under the condition of low dispersed phase contents and low steady

shear rate (13). After flow cessation the shear rate ($\dot{g}$) of the fibers during fiber distortion growth can be estimated by the similar approaches by Machiels from the deformation $g = \alpha / R_0$. According to equation (1), the shear rate is given by $\dot{g} = dg/dt = q(a/R_o)$. The deformation increases from $a_o / R_o \approx 0.1$ to 0.8. As a first-order approximation for the shear rate, we have $\dot{g} \approx q / 2$. Table 1 lists the results of our calculations of the apparent interfacial tension for the PES / Ln 001 and PES / LC-5000 polymer pairs together with the results obtained from other researchers who use other methods to determine the interfacial tension.

From Table 1, the apparent values of interfacial tension calculated from the Tomokita's theory are in the correct order of magnitude while compared with other researchers, suggesting that Tomokito's theory is applicable for describing the growth of distortion of TLCP in a polymer matrix in melt processing. We also show that the interfacial tension presented in the PES / LC-5000 is relatively higher than that of PES / Ln 001 which may be used to explain the differences of fibrillation dependence on the critical $\dot{g}_a$. For a polymer / TLCP pair with higher interfacial tension, a higher deformation force is needed to overcome the interracial tension, leading to a higher critical $\dot{g}_a$.

CONCLUSIONS

We have observed shear-induced droplet - fiber transition along the flow direction for blends of PES / TLCPs when a critical shear rate have been reached, but the fiber / matrix morphology is highly unstable and fibers can break up within a few seconds after shear cessation. The calculated apparent values of interfacial tension based on the Tomokito's theory is in the correct order of magnitude, suggesting that Tomokito's theory is applicable for describing the growth of distortion of TLCP in a polymer matrix in melt state. In-line measurement by optical and light scattering techniques provides a powerful approach to the "*in-situ*" characterization of the interfacial parameters under the real processing conditions.

KEY WORDS

PES / TLCPs, in line optical and light scattering microscopy, fiber stability, interfacial tension

* Certain equipment or materials are identified in this paper in order to adequately specify the experimental conditions. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that the materials are necessarily the best available for the purpose.

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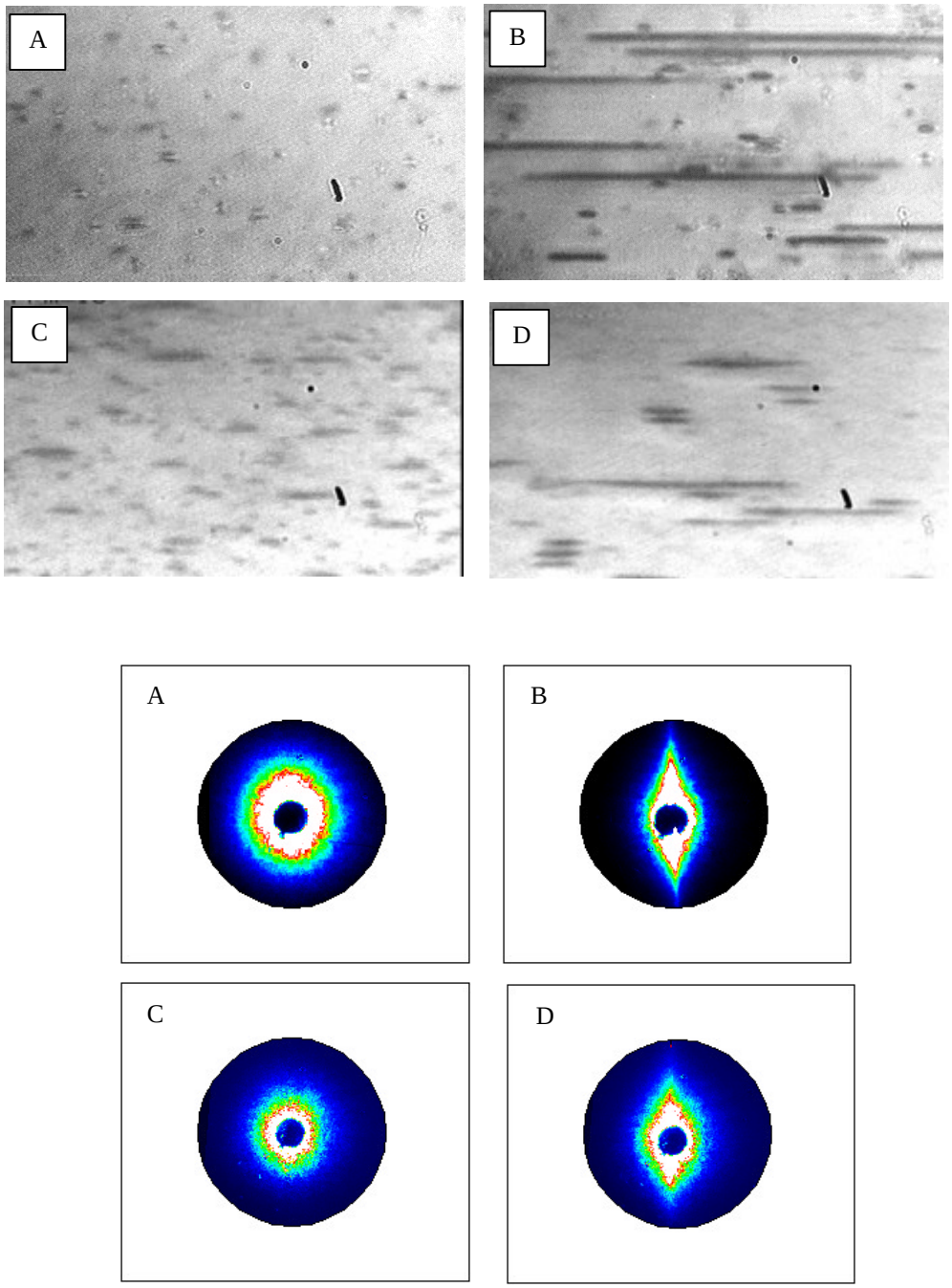

Figure 1. Optical digital-video-micrograph / Light-scattering image pairs for an extrusion of blends of PES / TLCP at 330 ^{0}C. The width of the micrograph from left to right is 170 µm, and the width of the light scattering image corresponds to a scattering angle of about ± 40 ^{0}. The blend is pass through a slit die, with the x direction (flow direction) from left to right, the z direction (vorticity direction) from top to bottom, and the y direction (gradient direction) into the page. A. PES / Ln 001, $\dot{g}_a$ = 0 s^{-1}; B. PES / Ln 001, $\dot{g}_a$ = 3.93 s^{-1}; C.PES / LC-5000, $\dot{g}_a$ =0 s^{-1}; D. PES / LC-5000, $\dot{g}_a$ = 8.11 s^{-1}

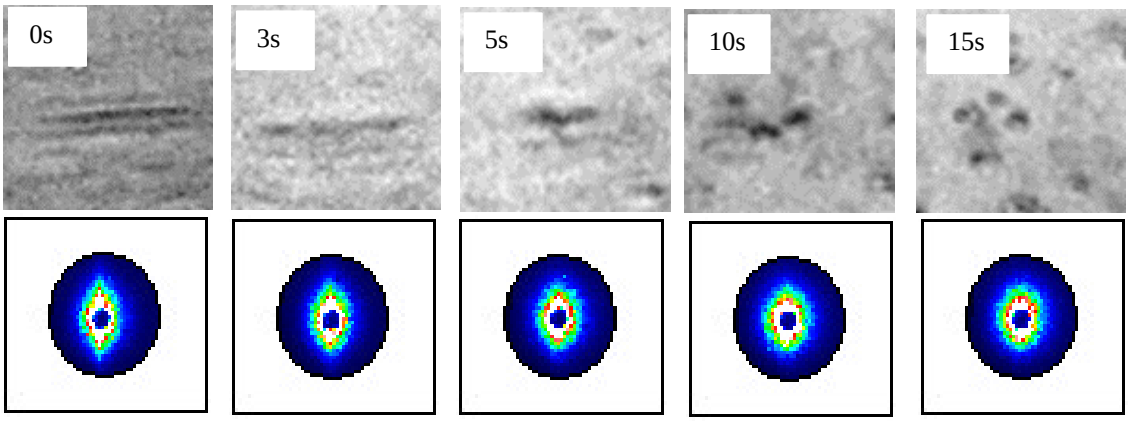

Figure 2. The breakup process of LC-5000 fiber (initial D_0: 2.43μm) embedded in PES at 330 ^{0}C after shear cessation.

Table 1. Apparent interfacial tension s_a between PES and TLCPs at 330°C. The relative uncertainty for morphology measurement is less than 15 %. The relative uncertainty for viscosity measurement is 10 %.

$D_0 \times 10^6$ (m)	q_{exp} (s^{-1})	$\dot{g}$ (s^{-1})	h_{PES} (Pa.s)	h_{TLCP} (Pa.s)	p	$\Omega(x, p)$	s_a (mN/m)	s_a (mN/m, ref. 6)	s_a (mN/m, ref. 14)
PES / LC-5000 2.43 ($\dot{g}_a$ = 7.98 s^{-1})	0.233 0.181 0.110 0.109	0.117 0.090 0.055 0.045	11436 11436 11436 11436	1072.3 1072.3 1072.3 1072.3	0.0936 0.0936 0.0936 0.0936	0.24 0.24 0.24 0.24	37.0 28.0 17.5 17.5	PES / Vectra[a] 7±1.2	PES /TLCP[b] 39±10
PES / Ln 001 1.64 ($\dot{g}_a$ = 4.02 s^{-1})	0.241 0.161 0.179 0.136	0.120 0.081 0.089 0.068	11063 11063 11063 11063	3036.9 3036.9 3036.9 3036.9	0.273 0.273 0.273 0.273	0.15 0.15 0.15 0.15	28.9 19.3 21.5 16.3	Individual thread experiment	Contact angle test

[a, b] 73 % 4-hydroxybenzoic acid (HBA) and 27 % 2-hydroxy-6-naphthoic acid (HNA)