

# IN-LINE INVESTIGATION OF SHEAR-INDUCED MORPHOLOGY TRANSITION IN LIQUID CRYSTALLINE POLYMER/PET BLENDS

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## ABSTRACT

The morphology of a compatibilized polyethylene terephthalate and thermotropic liquid crystalline copolyester blend is investigated via in-line optical microscopy and light scattering. It was found that the droplet-fiber transition in the liquid crystalline polymer is dependent upon the reactivity, the viscosity ratio and the shear field. The fibers are strongly oriented along the flow direction. The formation, deformation and stability of fiber microstructure under different flow conditions are discussed.

## INTRODUCTION

A promising class of composite materials is composed from a blend of a liquid crystalline polymer (LCP) and an amorphous polymer. Under shear and elongational flow, the LCP can elongate into long fibers with diameters on the order of a few microns. These materials display *in situ* self-reinforcing properties and are termed molecular or micro-fibrillated composites (1, 2). The morphology of the LCP domains dominates many of the final physical properties of the blend. The rheological behavior of blend components, interfacial tension and processing conditions are the key factors governing the morphology.

The issues controlling the morphology and ultimate physical properties of a LCP in an amorphous melt are quite complex. Poor interfacial adhesion between the two phases generally results in poor mechanical properties. Compatibilization of the two phases (either reactive or non-reactive) often improves interfacial adhesion but prevents in-situ fiber formation. Recently, there have been reports that compatibilized LCP / polymer blends can actually enhance the formation of LCP fibers and result in substantial property improvement (3). This technology uses an epoxy as a reactive coupling agent, causing crosslinking between the LCP and the melt, as well as some crosslinking within the melt itself.

However, the relationship between compatibilization and fiber formation is not understood, and effective tools

are lacking in carrying out in-line investigations of morphology during reactive processing of LCP / Polymer blend. To better understand the effect of interfacial bonding on morphological transitions in these systems, we carried out in-situ investigations of blends of PET with liquid crystalline copolyester under different interfacial modification and processing conditions. The observed morphology is correlated with the processing conditions and interfacial activities.

## EXPERIMENTAL

Blends of polyethylene terephthalate (PET) and a liquid crystal polymer (LCP) as the minor phase are prepared. The LCP is Vectra B950 from Hoechst-Celanese Company\*, a wholly aromatic copolyester, which is an industrial liquid crystal poly (ester-co-amide) with reported chemical composition of mol fraction, 58 % *hydroxyphthoic acid*, 21 % *terephthalic acid* and 21 % *para-aminophenol*. DSC measurement shows the LCP has a crystalline to nematic transition at 271 °C. The matrix phase is PET Merge 3934 from Dupont Company. It is a homo-copolyester with a quoted intrinsic viscosity of 0.662. The mass fraction of LCP in PET is 0.2 % in all three cases. The interface is modified by introducing a small amount (0.5 % mass fraction) of tetra-functional epoxy resin, *N, N, N', N'-Tetraglycidl-4, 4'-methylene bisbenzenamine*, and a catalyst (0.025 % mass fraction in one case), *ethyl triphenyl phosphonium bromide* purchased from Lancaster Synthesis Inc. Three systems of PET and LCP are investigated: uncompatibilized, compatibilized with epoxy, and compatibilized with both epoxy and catalyst.

The blend is extruded into the narrow channel of a slit die equipped with sapphire windows, located at the end of a corotating conical twin-screw extruder (4). Both optical microscopy and light scattering are employed for morphological measurement. The optical microscopy can measure individual particles down to about 1  $\mu\text{m}$  in size, while the light scattering can extract averaged information from particles as small as about 100 nm. Thus, the length scale of a typical polymer blend is well matched with the instrument. A typical temperature profile along the axis of the extruder from the feeding zone to the slit die is

260 °C , 270 °C, 275 °C, and 280 °C.

## RESULTS

Figure 1 shows microscopic images and the corresponding light scattering patterns for the three LCP / PET systems, as a function of extruder screw RPM (revolutions per minute). Figure 1(a) shows the uncompatibilized blend of PET / LCP, in which the LCP nematic domains are mostly polydisperse spherical droplets with average droplet diameter 6  $\mu\text{m}$  to 12  $\mu\text{m}$ . With increased shear rate, modest changes in the LCP particle size are found, and the aspect ratio is near 1. The aspect ratio distribution is shown in Figure 2(a) and the average size and aspect ratio is shown in Table 1, where the bold fonts represent the mean values and the value underneath is the standard deviation, a measure of the polydispersity.

The addition of the epoxy dramatically alters the size and shape of the dispersed LCP (Fig. 1b). Additionally the effect of increasing the RPM also strongly alters the morphology. At the lowest RPM, a coexistence of polydisperse spherical droplets with thick fibers is observed, whereas at higher RPM, the fiber structure predominates. This trend is demonstrated in the plot of the aspect ratio distribution Fig. 2b. At 10 RPM, there is a significant fraction at  $L / d = 1$ , falling off quickly to zero for  $L / D > 15$ . However, at RPM = 40, the peak occurs at  $L / d = 4$  there is still a significant fraction at  $L / d = 50$ .

When a stronger interfacial reaction is employed by addition of both the epoxy and the catalyst, the morphology is given in Figure 1(c) with average sizes given in Table 1 and corresponding distributions in Figure 2(c). Here again we observe fiber formation, but the microfibrillation has shifted to the range of relatively lower critical shear rates, with thick fibers formed at lower shear rates and thinner fibers at relatively higher shear rate. We do observe some elongated strings and ellipsoidal droplets. Some of the strings are clearly part of a longer extended fiber that broke up due to an instability under high shear. Examination of Fig. 2 (c) demonstrates that at low RPM, there is a long tail in the aspect ratio distribution whereas at high RPM, there are relatively few fibers with  $L / d > 15$ . This indicates that under strong enough shear, there is an instability in the fibers that breaks them up into shorter segments.

Comparing the optical micrographs between compatibilized and uncompatibilized PET / LCP blends, the difference in LCP domain orientation and size is primarily a result of viscosity ratio and interfacial adhesion at comparable processing conditions. This

morphological transition provides clear evidence that fiber formation is strongly dependent on interfacial reactions under specific shear flow field. Microfibrillation can be obtained even under very low LCP concentration, where the fibrillation process is controlled by the interfacial tension and viscosity ratio.

Morphological information is also available from the light scattering data. While we defer a detailed discussion to a later publication, we show in Figure 3 a comparison of aspect ratios as determined from optical microscopy  $a_{r,o}$  and light scattering data  $a_{r,s}$ . While optical microscopy gives the morphological distribution on an order of many microns, light scattering data gives the information of dispersed phase shape on a smaller scale. Comparing the aspect ratio obtained from the data from optical microscopy with that from light scattering, we can see qualitative agreement. In the uncompatibilized blend, both aspect ratios are near unity, independent of RPM. In the epoxy-compatible blend, both methods show a peak at a RPM of 40, whereas for the epoxy plus catalyst, the peak occurs at a RPM of 20.

## DISCUSSION

In the theory developed by Taylor and Tomatika (5, 6), there are two dimensionless parameters governing the process of deformation and break-up of an isolated droplet in viscous media, the viscosity ratio between the dispersed phase and continuous phase,  $\kappa = \eta_d / \eta_m$ , and the capillary number which is defined as  $Ca = \tau R / \sigma$ .  $Ca$  is the ratio of stress  $\tau$  imposed by the flow field to the stabilizing interfacial stress  $\sigma / R$  (where  $\sigma$  is interfacial tension and  $R$  is the droplet radius). When  $Ca$  slightly exceeds a critical capillary number  $Ca_c$  the shear stress causes the droplet to elongate. As the droplet deforms, its radius in the direction perpendicular to the flow decreases and ultimately the elongated droplet (or fiber) breaks up. The breakup is caused by the interfacial tension that seeks to minimize surface area. For shear flow, droplet breakup does not occur for  $\kappa > 4$ .

For the PET / LCP system, the effect of the compatibilizers is to change the viscosity ratio and to decrease the interfacial tension. When the epoxide group reacts with the polyester, it causes crosslinking of the PET which greatly increases its viscosity. This reduces  $\kappa$  to a level below four, thus permitting fiber formation. When the epoxide reacts between the LCP and the PET, it causes a reduction in the interfacial tension  $\sigma$ , which further decreases  $Ca_c$ . Thus we obtain a material with lower  $Ca_c$  and  $\kappa$ , and the critical condition  $Ca > Ca_c$  can be easily satisfied when shear stress is applied.

When the catalyst is added to the interface between the PET and LCP the crosslinking reaction between the two phases is further enhanced. This lowers the critical shear rate for fiber formation and also causes the subsequent breakup.

## CONCLUSIONS

In conclusion, the morphological observation by the in-line light scattering/optical microscope provides clear evidence that a droplet-fiber transition occurs for a reactive LCP / PET blend. By comparing the micrographs between compatibilized and uncompatibilized PET / LCP blends, it is clear that the difference in LCP domain alignment and size change is primarily caused by the interfacial modification and viscosity ratio change at otherwise comparable processing conditions. It is clear that the micro-fibrillation can be obtained even under very low LCP concentration, where fibrillation process is controlled by shear when suitable interfacial conditions are satisfied.

This study also demonstrates the effectiveness of using multi-functional epoxy resins as a reactive compatibilizer which subsequently affects morphology development and viscosity. A small amount of tetra-functional epoxy can significantly promote micro-fibrillation.

## KEY WORDS

*in situ* composite, in line optical and light scattering microscopy characterization, reactive compatibilization, and shear-induced micro-fibrillation

## ACKNOWLEDGEMENTS

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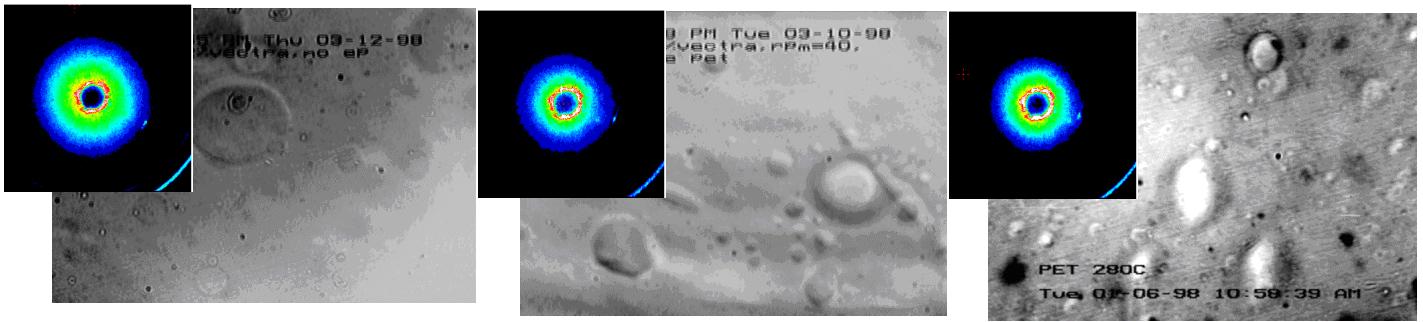
## REFERENCES

\* 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

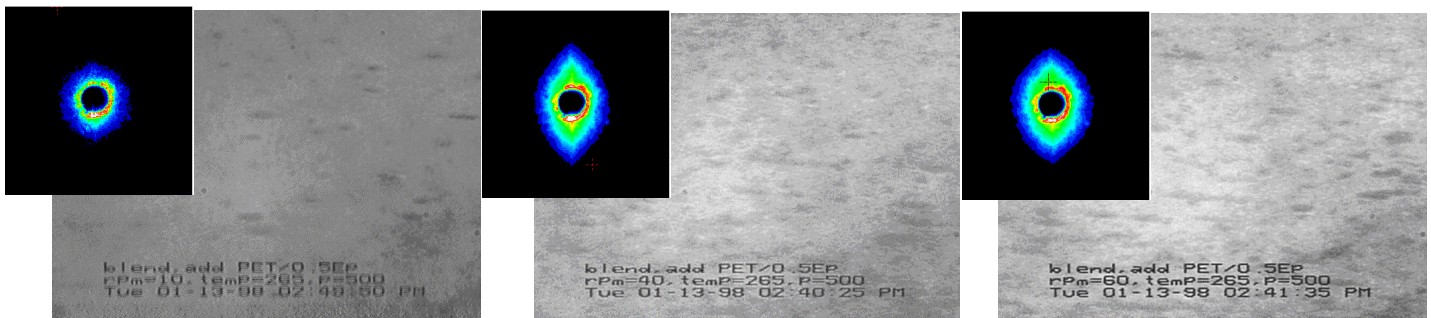
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Table 1. Aspect ratio  $a_{r,o}$  and particle diameter  $d_{r,\mu m}$  for PET/LCP and its compatibilized systems as a function of shear rate. The bold fonts represent the mean values and the value underneath is the standard deviation.

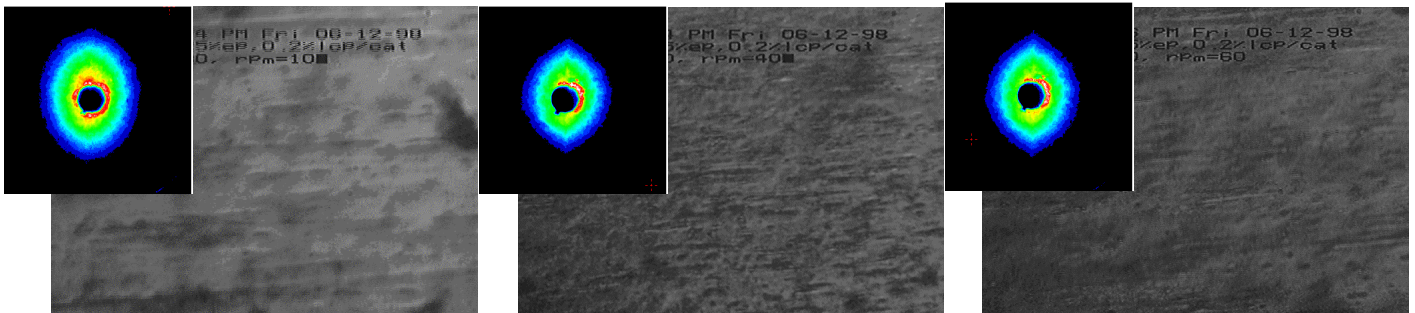
Screw Rate (RPM) Materials	10		20		40		60		Morphology
	$d_{r,\mu m}$	$a_{r,o}$	$d_{r,\mu m}$	$a_{r,o}$	$d_{r,\mu m}$	$a_{r,o}$	$d_{r,\mu m}$	$a_{r,o}$	
PET / LCP	<b>10.1</b> 9.4	<b>1.2</b> 0.3	<b>12.2</b> 6.4	<b>1.1</b> 0.29	<b>9.6</b> 6.7	<b>2.8</b> 4.6	<b>8.9</b> 5.9	<b>0.99</b> 0.2	Polydisperse sphericle droplets or deformed droplets, smaller droplets at high shear rate
PET / LCP / EPOXY	<b>3.6</b> 1.9	<b>3.4</b> 2.9	<b>3.1</b> 1.1	<b>4.1</b> 2.0	<b>2.1</b> 1.6	<b>7.1</b> 5.3	<b>3.6</b> 1.2	<b>5.2</b> 2.5	Elongated droplets at lower shear rate, smaller diameter fibers at higher shear rate
PET /LCP / EPOXY / CAT.	<b>4.6</b> 1.9	<b>10.7</b> 12.3	<b>2.6</b> 0.9	<b>13.9</b> 11.4	<b>2.1</b> 0.7	<b>6.0</b> 3.1	<b>2.5</b> 0.7	<b>7.0</b> 4.6	Thick fibers at low shear rates, short smaller diameter fibers at high shear rate



a

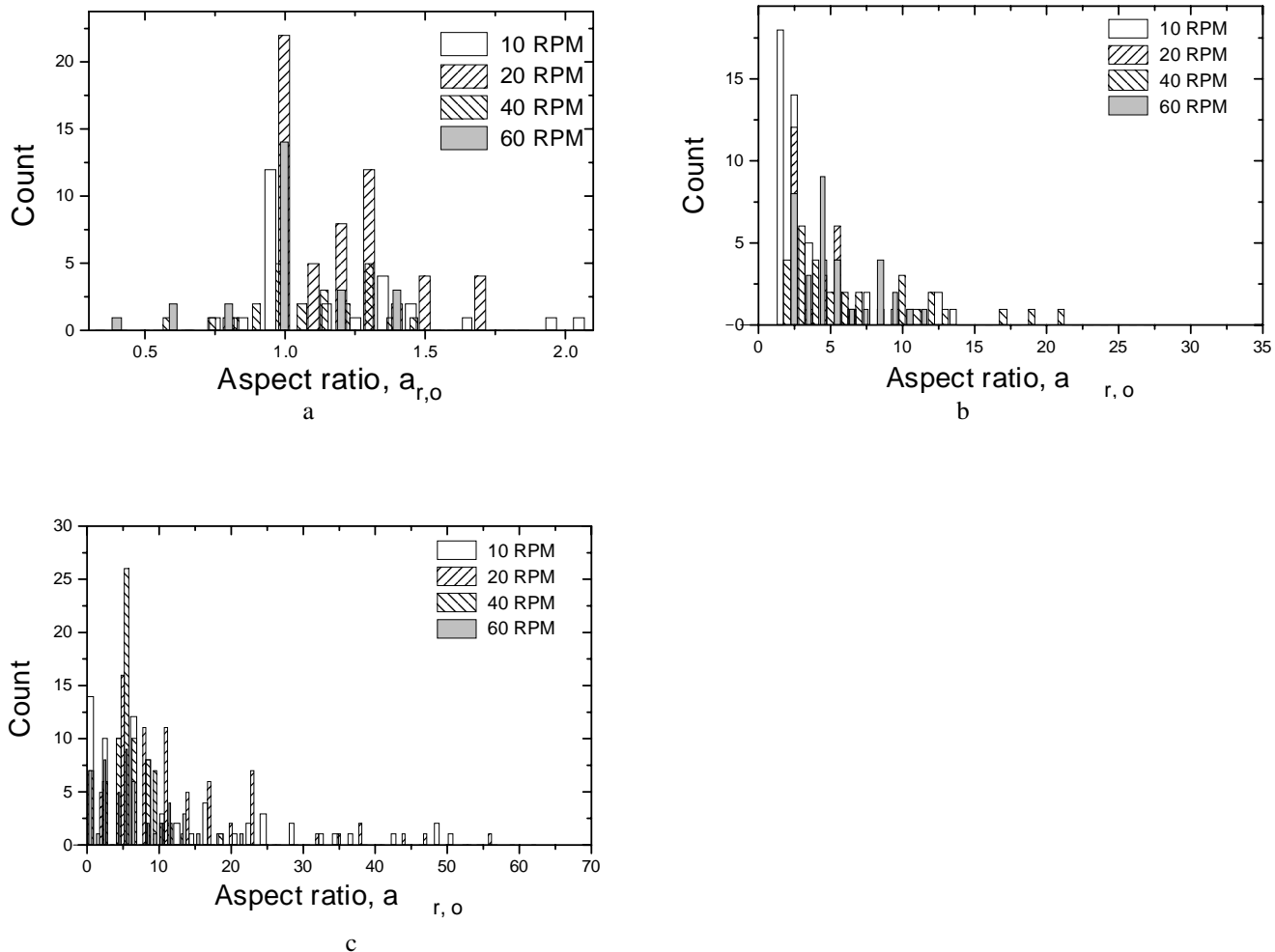


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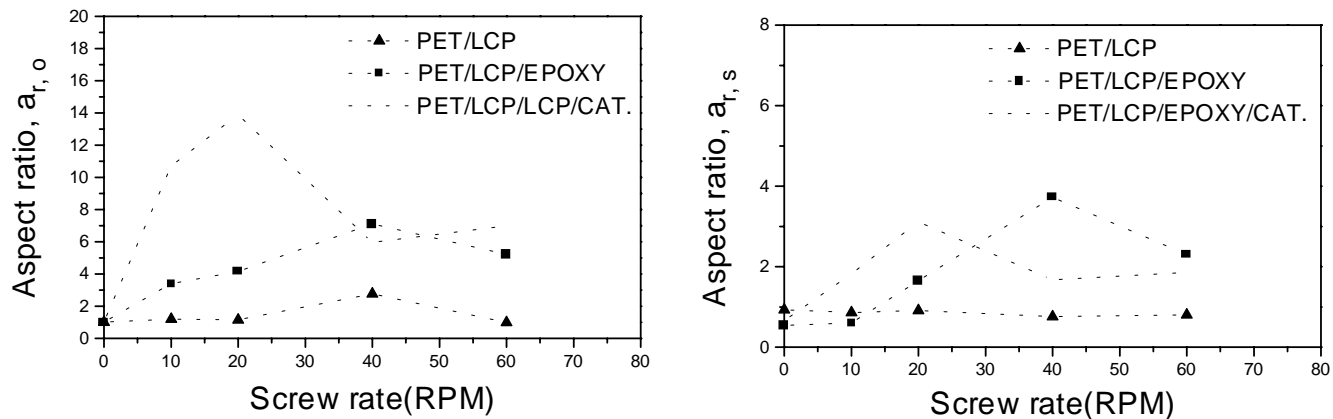


c

**Figure 1.** Optical digital-video-micrograph/Light-scattering image pairs for an extrusion of mass fraction of 0.2 % Vectra B950 liquid crystal polymer dispersed in Polyethylene Terephthalate at 280 °C under various flow rates. The width of the micrograph from left to right is 200  $\mu\text{m}$ , and the width of the light-scattering image corresponds to a scattering angle of about  $\pm 40^\circ$ . The blend is pass through a slit die, with the x direction (flow direction) from right to left, the z direction (vorticity direction) from top to bottom, and the y direction (gradient direction) into the page. The flow rate from left to right: 10 RPM, 40 RPM, and 60 RPM. (a). PET / LCP; (b). PET/LCP/Epoxy; (c).PET / LCP / Epoxy / Catalyst



**Figure 2.** Distribution of LCP dispersed phase aspect ratio extracted from optical micrographs at different shear rate. The relative uncertainty for the count is less than 15 %. (a). PET / LCP (b). PET / LCP/Epoxy (c). PET / LCP / Epoxy / Catalyst.



**Figure 3.** Plots of aspect ratio  $a_{r,s}$  extracted from light-scattering data and aspect ratio  $a_{r,o}$  from statistics analysis on the optical microscopy as a function of applied screw rate. The relative expanded uncertainty for the light scattering data is 5 %.