

DTIC FILE COPY

4

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-86-K-0772

TECHNICAL REPORT NO. 30

The Effect of Deformation History on the Morphology of Blends of Polycarbonate and a Thermotropic Liquid Crystalline Polymer

by

A. Kohli, N. Chung and R. A. Weiss

Liquid Crystalline Polymer Research Center
University of Connecticut
Storrs, CT 06269-3136

Prepared for Publication

in

The Proceedings of SPE ANTEC
New York, April 1989

December 29, 1988

DTIC
SELECTED
S 10 JAN 1989 D
E

REPRODUCTION IN WHOLE OR IN PART IS PERMITTED FOR ANY
PURPOSE OF THE UNITED STATES GOVERNMENT.

THIS DOCUMENT HAS BEEN APPROVED FOR PUBLIC RELEASE
AND SALE; ITS DISTRIBUTION IS UNLIMITED.

AD-A203 061

89 1 09 254

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified		1b RESTRICTIVE MARKINGS None	
2a SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release, Distribution Unlimited	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE		5 MONITORING ORGANIZATION REPORT NUMBER(S)	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 30		7a NAME OF MONITORING ORGANIZATION Office of Naval Research	
6a. NAME OF PERFORMING ORGANIZATION University of Connecticut	6b. OFFICE SYMBOL (if applicable)	7b ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217	
6c. ADDRESS (City, State, and ZIP Code) Storrs, CT 06268		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0772	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable) ONR	10 SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11 TITLE (Include Security Classification) The Effect of Deformation History on the Morphology of Blends of Polycarbonate and a Thermotropic Liquid Crystalline Polymer (Unclassified)			
12 PERSONAL AUTHOR(S) A. Kohli, N. Chung and R. A. Weiss			
13a TYPE OF REPORT Interim technical	13b TIME COVERED FROM TO 12/29/88	14 DATE OF REPORT (Year, Month, Day) 1988-12-29	15 PAGE COUNT 13
16 SUPPLEMENTARY NOTATION Prepared for presentation at SPE ANTEC New York, April, 1989 (LCPRC Publication No. LCPRC88-21)			
17 COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	LCP Polymer blends. (mgm) ←	
19 ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>The addition of an immiscible liquid crystalline polymer (LCP) to polycarbonate improved its melt processibility. In addition, when a suitable deformation history was employed, the LCP phase was elongated and oriented such that a microfibrillar morphology was retained in the solid state mixture. This has important ramifications for the development of self-reinforcing polymer blends to compete with conventional fiber-reinforced plastics.</p> <p>Shear flows are generally ineffective at developing these morphologies, but flows that incorporate extensional stresses, such as the converging flow at the entrance to a capillary or die can produce an elongated phase. Single extensional flows, such as in melt drawing operations, are most effective at producing LCP microfibrils, and their efficiency increases with increasing draw ratio. The moduli of highly drawn blends were well approximated by a composite analogy of long uniaxially aligned LCP fibers in a polycarbonate matrix.</p>			
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth J. Wynne		22b TELEPHONE (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL ONR

INTRODUCTION

Blending LCP's with other, less expensive thermoplastics offers the possibility for exploiting many of their desirable characteristics, but at a reduced material cost. It is not surprising, therefore, that a growing interest in LCP/polymer blends has developed in recent years (1). The work of a number of laboratories has been directed at developing compositions in which a discrete LCP phase functions both as a processing aid and as a solid-state reinforcement. At elevated temperature, the melt viscosity is lowered by the presence of the LCP domains (2-6). During processing of the blend, it is possible to deform and orient the LCP phase such that the solidified compound contains a microfibrillar LCP phase (2). The morphology and properties of such blends are similar in many respects to more conventional short-fiber reinforced plastics.

The objective of the research described herein was to assess the effect of the deformation history on the morphology of LCP/polymer blends. Specifically, the relative importance of extensional and simple shear flows on the development of a microfibrillar LCP domain structure was investigated.

EXPERIMENTAL

The thermotropic liquid crystalline polymer, Vectra RD500, used in this study was kindly provided by Dr. Larry F. Charbonneau of Hoechst-Celanese Corporation. It was a terpolymer comprised of 52 mole% 4-hydroxybenzoic acid (HBA), 28 mole% 6-hydroxy-2-naphthoic acid (HNA), 10 mole% terephthalic acid, and 10 mole% hydroquinone. The inherent viscosity at 25°C for 0.1 wt% concentration in a 1:1 mixture of pentafluorophenol:hexafluoropropanol was 3.08 (7). The polycarbonate (PC) used had a number average molecular weight of 16,000 and weight average molecular weight of 34,000 as determined by gel permeation chromatography.

Blends of LCP and PC ranging in composition from 5-80 wt% LCP were prepared by melt blending at 270°C with a Custom Scientific Instruments (CSI) Max-mixing extruder. Before blending, the neat polymers were dried in a vacuum oven at 115°C for not less than 24 hours. The CSI extruder was also used with a take up device to prepare melt drawn fibers.

Transition temperatures of the blends as well as the neat polymers were measured with a Perkin-Elmer DSC 7 differential scanning calorimeter. In order to remove any previous thermal histories, the samples were initially scanned from 30°C to 290°C at a heating rate of 20°C/minute and then quenched as rapidly as possible in the instrument. Thermal transitions were determined from the second heating at a scan rate of 20°C/minute. Samples of 9-13 mg were encapsulated in aluminum pans and the measurements were made under a nitrogen atmosphere.

Shear viscosity measurements were made with a Rheometrics System 4 mechanical spectrometer using a cone and plate geometry. The cone had a angle of 0.1 radians and a diameter of 25 mm. The shear rate range covered was from 0.01 to 10.0 s⁻¹. The experiments were conducted in a gas convection environmental chamber at 270°C. For higher shear rates, viscosity measurements were made with an Instron capillary viscometer. All experiments were done at 270°C and at least three experiments on fresh samples were made for each composition. A capillary with L/D = 40 and D = 0.05 inches was used. Entrance pressure corrections were ignored, but the Rabinowitsch correction for non-Newtonian behavior was applied. For the morphology studies, capillaries with L/D = 20 and 10 were also used.

Scanning electron micrographs of fracture surfaces of the blends were obtained with an AMR model 1200 scanning electron microscope (SEM). The samples were fractured under tension in liquid nitrogen and sputter coated with a 10 nm thick layer of gold in order to provide a conductive path. In order to preserve the structure of the melt formed during the rheological measurements, the samples were quenched in ice water. In the case of the capillary experiments, this simply required extrusion into ice water. For the cone and plate experiments, it required quickly removing the fixtures after stopping the flow and placing the cone/sample/plate sandwich into ice water.

RESULTS AND DISCUSSION

The DSC thermograms of the blends as well as the neat polymers are shown in Fig. 1. The glass transition temperatures of the LCP and the PC were 101°C and 147°C, respectively, and the crystalline to nematic transition (K→N) for the LCP was about 236°C. The nematic nature of the LCP mesophase was

confirmed by a threaded-Schilieren texture observed by polarized optical microscopy. The nematic to isotropic transition was not observed before decomposition of the LCP occurred.

The K->N transition of the LCP remained constant in the blends at the same temperature as for the pure LCP. Although the enthalpy change was dependent on the sample's thermal history, the position of the endotherm was not. Similarly, the $T_g(\text{PC})$ was relatively unaffected by thermal history of the blend. $T_g(\text{LCP})$, however, increased when the cooling rate was lowered. Both T_g s were slightly composition dependent, though it was not clear whether this was due to some miscibility or to phase size. Annealing the LCP and the blends gave rise to a lower temperature peak near 200°C and a shoulder on the low temperature side of the upper endothermic peak. This was consistent with reports of a fast and a slow crystallization process in HBA/HNA copolymers (8).

The viscosity vs. shear rate data at 270°C for the starting materials and the blends are given in Fig. 2. In all cases, over the entire shear rate range studied, the melt viscosity was lowered by the addition of the LCP. The overlap of the viscosity data obtained from the cone and plate rheometer and the capillary viscometer was poor, which is not too surprising since the shape and size of the dispersed phase was dependent not only on the rate of deformation, but also on the instrument used to measure the viscosity. Although both instruments yield a simple shear flow field, the simple shear flow in the capillary is preceded by a region of extensional flow at the capillary entrance. This has a significant effect on the dispersed phase morphology.

The capillary viscometer data in Fig. 2 are consistent with other LCP-blend studies that used a capillary viscometer and showed that relatively low concentrations of LCP can dramatically lower the melt viscosity. For example, at a shear rate of 150 s⁻¹ the addition of 5% and 10% LCP to PC lowered the melt viscosity by 54% and 75%, respectively.

The data for the cone and plate geometry also showed a lowering of the viscosity by the LCP phase. This agrees with the results of Blizzard and Baird (4), but are inconsistent with those of Weiss et al. (2). In the latter study, the authors found that for steady shear flows without pre-extension, the

addition of an LCP liquid phase in a polystyrene melt increased the melt viscosity. Fluid dynamic theories also predict a viscosity increase for flows in which the dispersed phase is not deformed (9). The reason for the different results is the subject of current studies in our laboratory.

The viscosity curves for the blends containing up to 20% LCP reflected the viscosity-shear rate characteristics of the PC. At low shear rates, the curves were Newtonian, though shear thinning was observed at the higher shear rates. The magnitude of the shear thinning increased and the shear rate for the onset of shear thinning decreased with increasing LCP concentration. The flow curves for the higher LCP compositions were more typical of that of the pure LCP in that no clear Newtonian region was observed. Based on the SEM micrographs of fracture surfaces, it appeared that phase inversion occurred in these blends at about 40% LCP.

The morphology of a 20% LCP/80% PC blend resulting from simple shear melt flow is shown in Fig. 3 as a function of rate of deformation. In agreement with theories for two-phase suspensions, simple shear flow was not effective at deforming or orienting the LCP domains. The morphology following simple shear was characterized by micrometer-sized spherical domains of the LCP. Increasing the shear rate reduced the sphere size, but did not greatly deform the phase.

Fig. 4 shows the effect of deformation rate and the capillary aspect ratio (L/D) on the morphology of the same 20% LCP/80% PC blend. Fluid dynamic theories as well as flow visualization experiments on model systems in our laboratory (10) predicted that the LCP phase should elongate into a rod or fibrillar phase at the entrance of the capillary. In the shear region of the capillary, however, the elongated phase either relaxes back to a spherical shape or breaks up into smaller spherical droplets as a consequence of interfacial forces. The microphotographs in Fig. 4 are consistent with these predictions. For high L/D and low deformation rate, the LCP domains were spherical with no visible orientation. As the capillary aspect ratio decreased and the deformation rate increased, the LCP domains became more elongated with a preferential orientation parallel to the machine direction. The effect of increasing deformation rate was to more effectively elongate the LCP phase in the entrance region. In the capillary, the elongated LCP phase

either relaxed or broke-up into spherical or ellipsoidal droplets, and the efficiency of this increased with increasing capillary length. In order to develop and maintain dispersed LCP microfibrils in these blends, high extrusion rates and very short dies were required.

The effect of simple extension of the melt on the blend morphology is also shown in Fig. 4 for comparison. This morphology was obtained by manually pulling and then freezing the extrudate from the capillary viscometer. In this case, well developed LCP microfibrils with relatively high aspect ratios were formed. The orientation in the drawing direction was quite high.

The influence of the draw ratio (DR) on the effectiveness of microfibril formation is shown for the 10% LCP/90% PC blend in Fig. 5. DR was calculated from the ratio of the diameter of the drawn blend fiber to that of the extruder die. At a relatively low draw ratio, DR = 50, the LCP phase was elongated, but the microfibers formed were not well developed and had fairly low aspect ratios. An order of magnitude increase in DR (DR = 500) yielded well developed microfibrils oriented parallel to the draw direction.

CONCLUSION

The addition of an immiscible LCP phase can improve the melt processability of a host thermoplastic polymer. In addition, by employing a suitable deformation history, the LCP phase may be elongated and oriented such that a microfibrillar morphology can be retained in the solid state. This has important ramifications for the development of self-reinforcing polymer blends to compete with conventional inorganic fiber-reinforced polymers. Shear flows are generally ineffective at developing these morphologies, but flows that incorporate an extensional region, such as the entrance to a capillary or die, can produce an elongated LCP phase. Simple extensional flows, such as melt drawing, are most effective at producing LCP microfibrils, and their efficiency increases with increasing draw ratio.

ACKNOWLEDGEMENT

This work was supported by DARPA (Grant #ONR N00014-86-K-0772), by the Connecticut Dept. of Higher Education, and by Eastman Kodak Corporation.

We are especially indebted to Dr. Larry Charbonneau and the Hoechst Celanese Corporation for the donation of the liquid crystalline polymer.

REFERENCES

1. R.A. Weiss and A. Kohli, review article in preparation.
2. R.A. Weiss, W. Huh, and L. Nicolais, *Polym. Eng. Sci.*, 27, 684 (1987).
3. A.I. Isayer and M.J. Modic, *Polym. Composites*, 8, 158 (1987).
4. K.G. Blizzard and D.G. Baird, *Polym. Eng. Sci.*, 27, 653 (1987).
5. G. Kiss, *Polym. Eng. Sci.*, 27, 410 (1987).
6. A. Siegmann, A. Dagan, and S. Kenig, *Polymer*, 26, 1325 (1985).
7. L.F. Charbonneau, private communication (1987).
8. S.Z.D. Cheng and J.J. Janimak, *Proc. 17th NATAS Conf.*, Lake Buena Vista, FL, 1988, p. 358.
9. H.L. Goldsmith and S.G. Mason in *Rheology*, v.4, F.R. Eirich, Ed., Academic Press, 1967, p. 85.
10. P. Yanisko, M.S. Thesis, Univ. of Connecticut, 1988; P. Yanisko and R.A. Weiss, Tech Paper, SPE ANTEC, 1989.

FIGURE CAPTIONS

- Fig. 1. DSC Thermograms of LCP/PC Blends.
Fig. 2. Viscosity vs. Shear Rate for LCP/PC Blends.
Fig. 3. Effect of Shear Rate on the Morphology of 20% LCP/80% PC Blend.
Fig. 4. Effect of Deformation History on the Morphology of 20% LCP/80% PC Blend.
Fig. 5. Effect of Draw Ratio on the Morphology of 10% LCP/90% PC Blend.

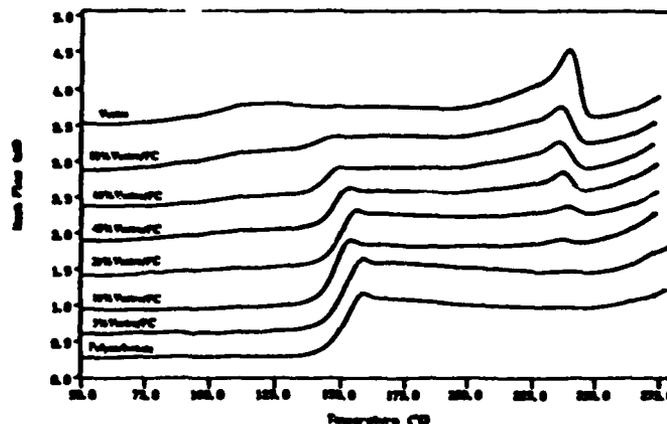


Fig. 1

We are especially indebted to Dr. Larry Charbonneau and the Hoechst Celanese Corporation for the donation of the liquid crystalline polymer.

REFERENCES

1. R.A. Weiss and A. Kohli, review article in preparation.
2. R.A. Weiss, W. Huh, and L. Nicolais, *Polym. Eng. Sci.*, **27**, 684 (1987).
3. A.I. Isayer and M.J. Modic, *Polym. Composites*, **8**, 158 (1987).
4. K.G. Blizard and D.G. Baird, *Polym. Eng. Sci.*, **27**, 653 (1987).
5. G. Kiss, *Polym. Eng. Sci.*, **27**, 410 (1987).
6. A. Siegmann, A. Dagan, and S. Kenig, *Polymer*, **26**, 1325 (1985).
7. L.F. Charbonneau, private communication (1987).
8. S.Z.D. Cheng and J.J. Janimak, *Proc. 17th NATAS Conf.*, Lake Buena Vista, FL, 1988, p. 358.
9. H.L. Goldsmith and S.G. Mason in *Rheology*, v.4, F.R. Eirich, Ed., Academic Press, 1967, p. 85.
10. P. Yanisko, M.S. Thesis, Univ. of Connecticut, 1988; P. Yanisko and R.A. Weiss, Tech Paper, SPE ANTEC, 1989.

FIGURE CAPTIONS

- Fig. 1. DSC Thermograms of LCP/PC Blends.
Fig. 2. Viscosity vs. Shear Rate for LCP/PC Blends.
Fig. 3. Effect of Shear Rate on the Morphology of 20% LCP/80% PC Blend.
Fig. 4. Effect of Deformation History on the Morphology of 20% LCP/80% PC Blend.
Fig. 5. Effect of Draw Ratio on the Morphology of 10% LCP/90% PC Blend.

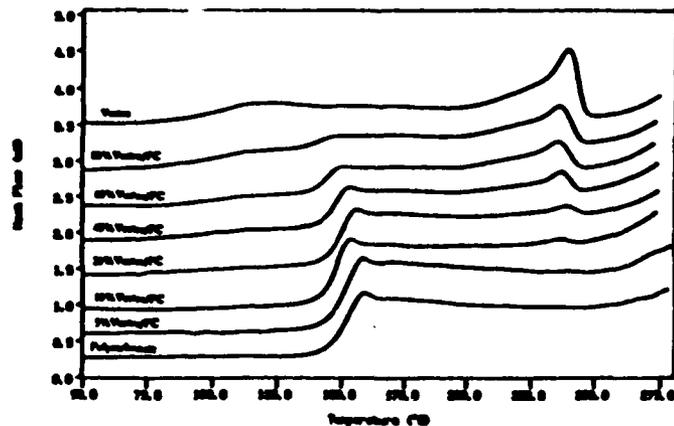


Fig. 1

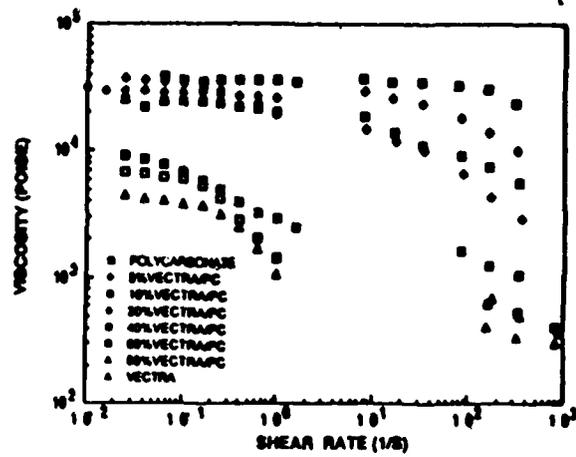


Fig. 2

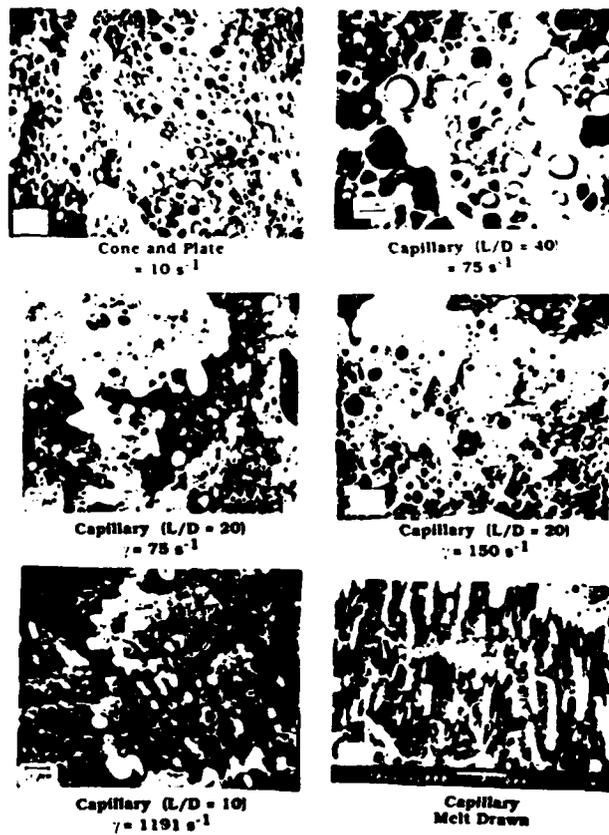


Fig. 3

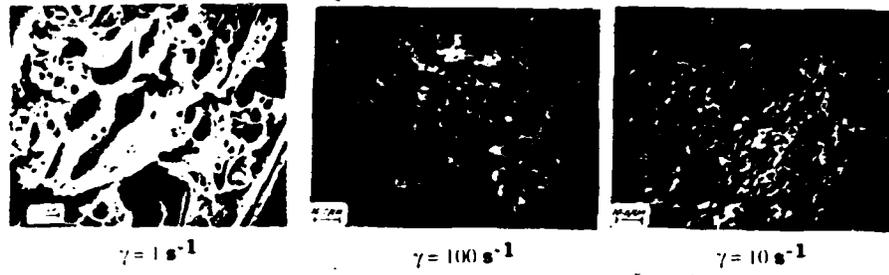
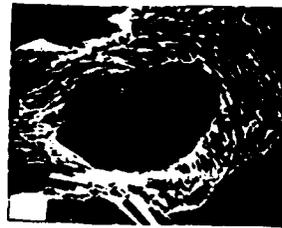


Fig. 4



Draw Ratio - 50 (1K X)



Draw Ratio - 500 (1K X)



Draw Ratio - 50 (2K X)



Draw Ratio - 500 (2K X)

Fig. 5

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1