

The Effect of Blending Temperature, Composition, and Shear Rate on PET/Vectra A900 LCP Blend Viscosity and Morphology

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SYNOPSIS

The rheological and morphological properties of several melt-blended compositions of poly(ethylene terephthalate) (PET) and Vectra A900 liquid crystalline polyester were investigated, using blending temperature, composition, and shear rate as variables. Rheological behavior was determined at several shear rates on an Instron capillary rheometer at 300°C, and three-dimensional surface plots of the results were prepared, detailing the effect on melt viscosity of changes in the variables. Scanning electron microscopy was used to examine the internal morphology of selected samples. In the preparation of melt blends containing an isotropic and anisotropic polymer, blending temperature and composition both influence the resulting morphology. These effects are accentuated during extrusion of the blends at low shear rates and diminished at high shear rates.

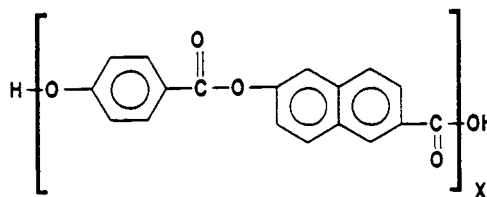
INTRODUCTION

Poly(ethylene terephthalate) (PET) enjoys wide success as an industrial fiber because of its high melting point and excellent mechanical properties. There is strong interest in increasing both strength and modulus of industrial fibers, but in the case of PET, this is difficult. Higher molecular weight polyester can lead to higher strength, but the resulting higher melt viscosity can overload processing machinery or lead to severe molecular weight loss through mechanical shearing. To overcome this difficulty, yet retain or enhance fiber properties, various amounts of liquid crystal polyester (LCP) were melt blended with high molecular weight PET.

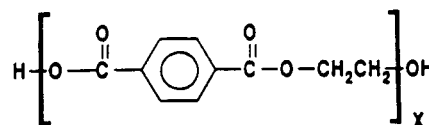
BACKGROUND AND THEORY

For several years, polymer processors have been blending two or more generally incompatible ma-

terials in order to improve physical or mechanical properties. Depending on the degree of compatibility and dispersion, various goals may be attained: improved modulus, impact strength, thermal or chemical stability, etc. Another possible consequence of polymer blending is improved processing through decreased melt viscosity and greater shear-thinning



VECTRA A900



PET

Figure 1 Polymer structures.

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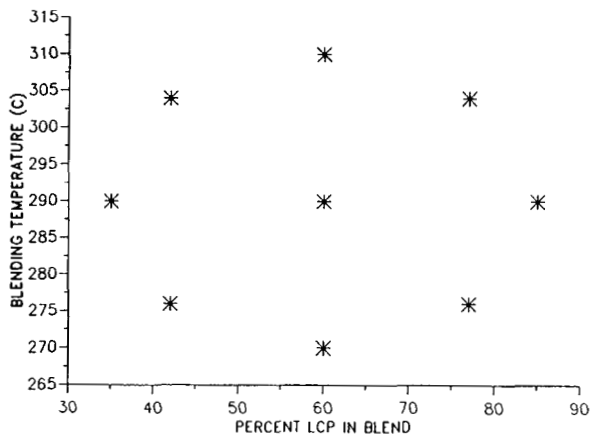


Figure 2 Experimental design.

behavior. This usually translates into faster production cycles and/or lower melt temperatures, which are always desirable.

Because of the incompatible nature of most polymer mixtures, a two-phase morphology is typically formed in a binary blend. Rheological properties of such two-phase systems depend on the viscosities and elasticities of each component, composition ratio, and melt temperature.¹ The nature of the pro-

cessing equipment and its design details are also important insofar as shear/elongational stresses and strains are directly related to melt morphology²⁻⁴ and, thus, to extrudate properties.

The formation of a fibrous phase during melt-blend extrusion involving nylon 6 with either HDPE or PET has been observed by several workers.⁵⁻⁷ Altered crystallization behavior^{5,7} and elongational stresses at the die entry⁶ were cited as important contributing factors to the observed morphology. With amorphous polymers, viscosity ratios and blend composition were found to control the development of a fibrillar morphology.⁸ Two good general reviews of blend fiber formation have been published.^{9,10}

Because thermotropic liquid crystal polymers are known to orient in a converging flow field,¹¹ they can improve fiber mechanical properties over those of isotropic polymers.¹² Fibers and moldings from blends of LCPs and isotropic polymers have also shown improved mechanical properties over those of the unblended isotropic component.^{13,14} This same tendency to orient in a converging flow field is responsible for the marked shear-thinning behavior observed with liquid crystalline polymers¹⁵ and their blends with isotropic polymers.¹⁶

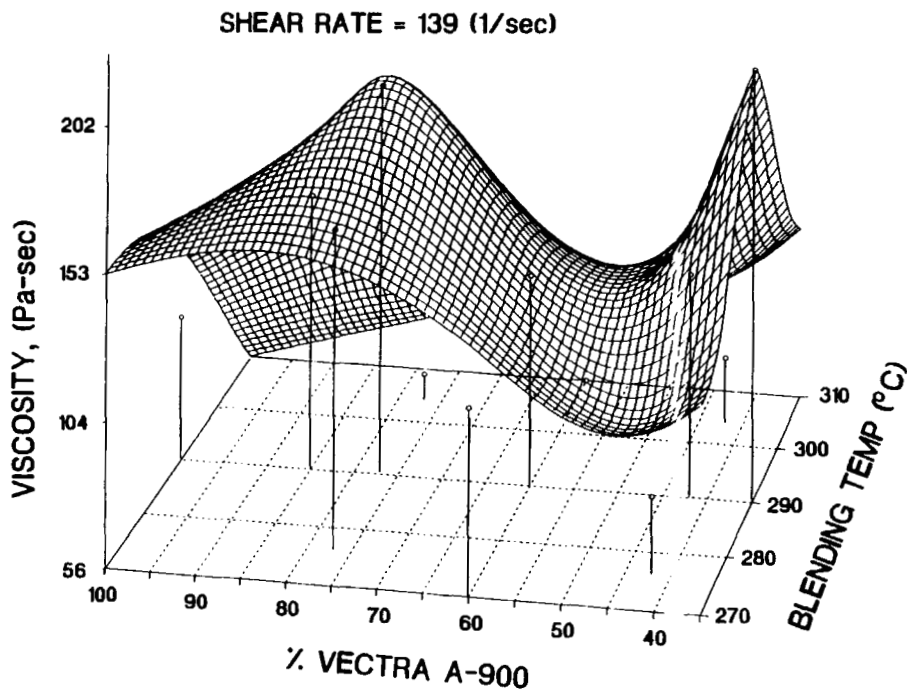


Figure 3 Melt viscosity vs. percent Vectra A900 (seven shear rates).

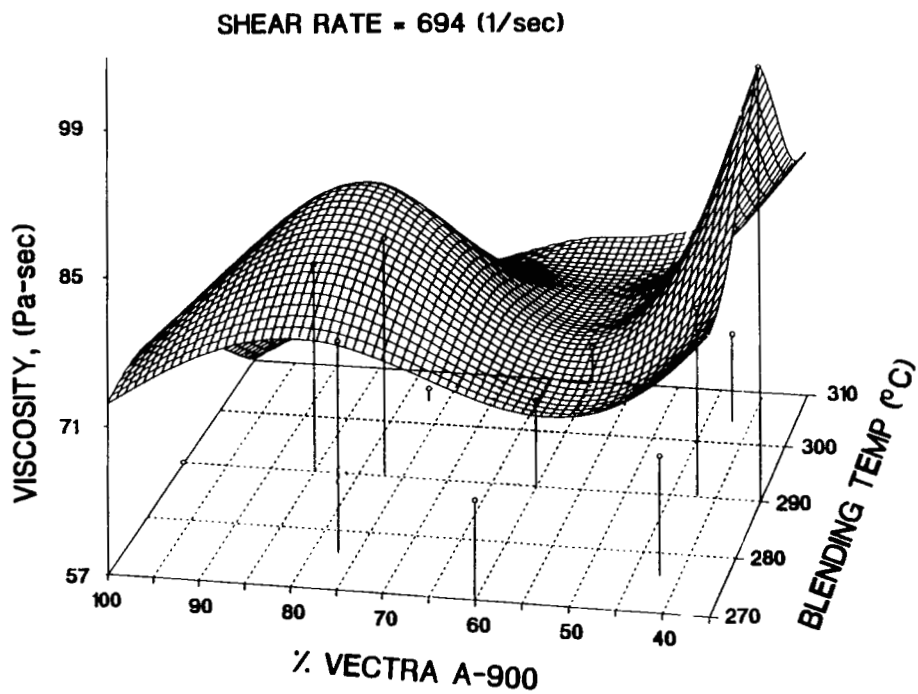
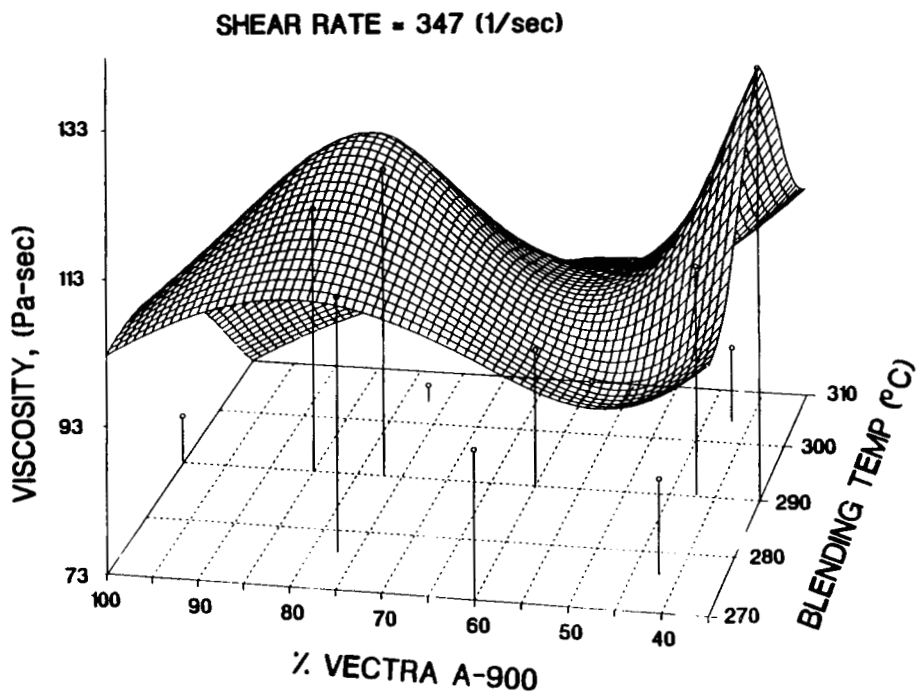


Figure 3 (Continued from the previous page)

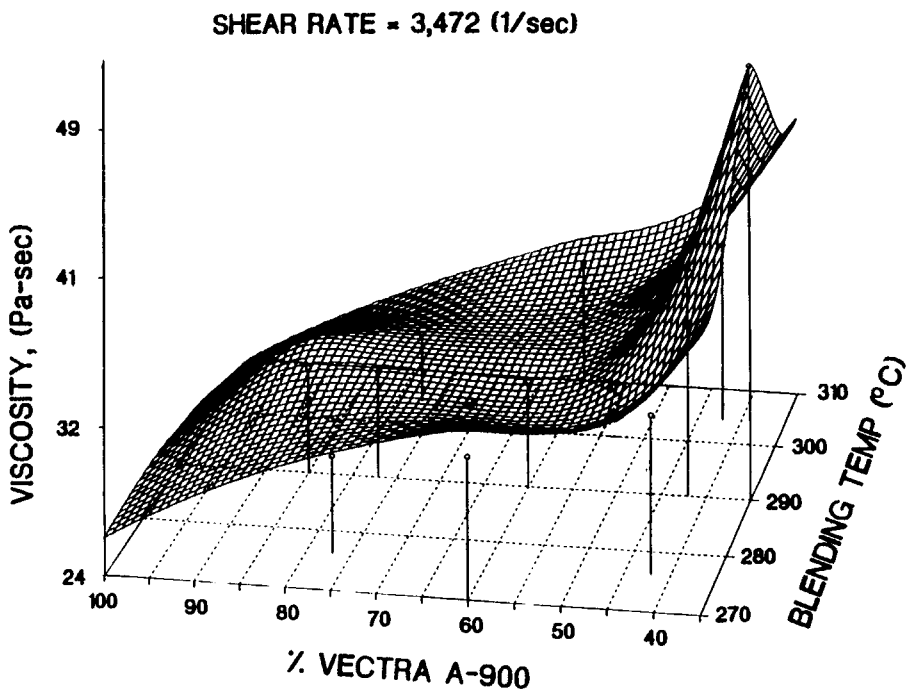
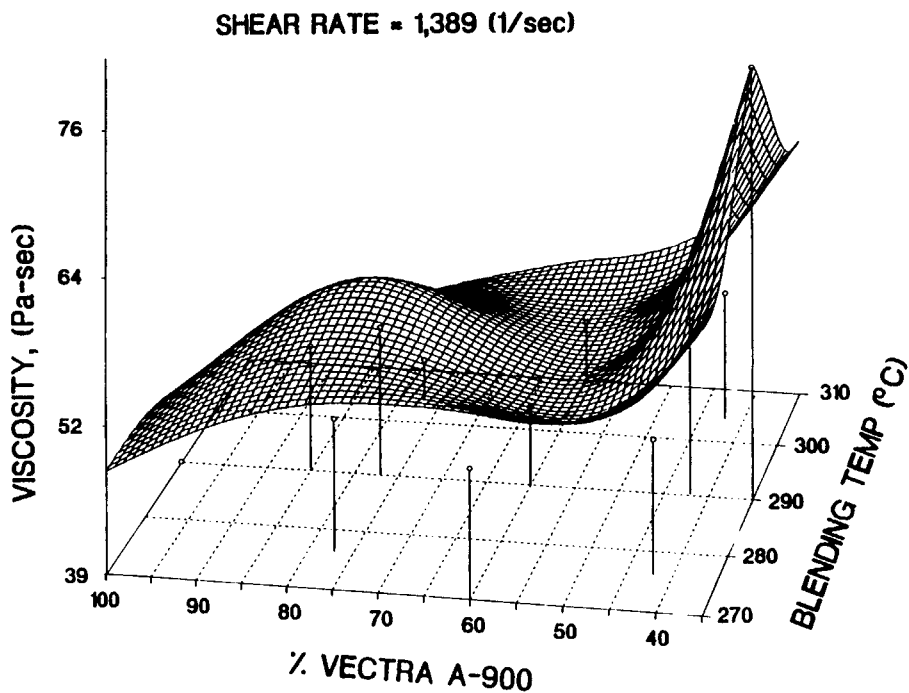


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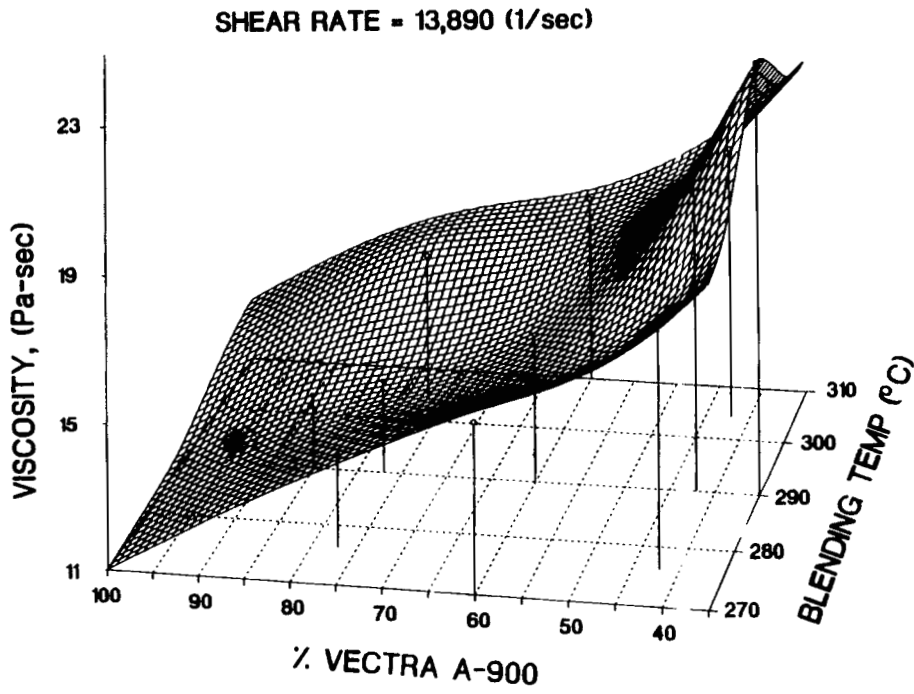
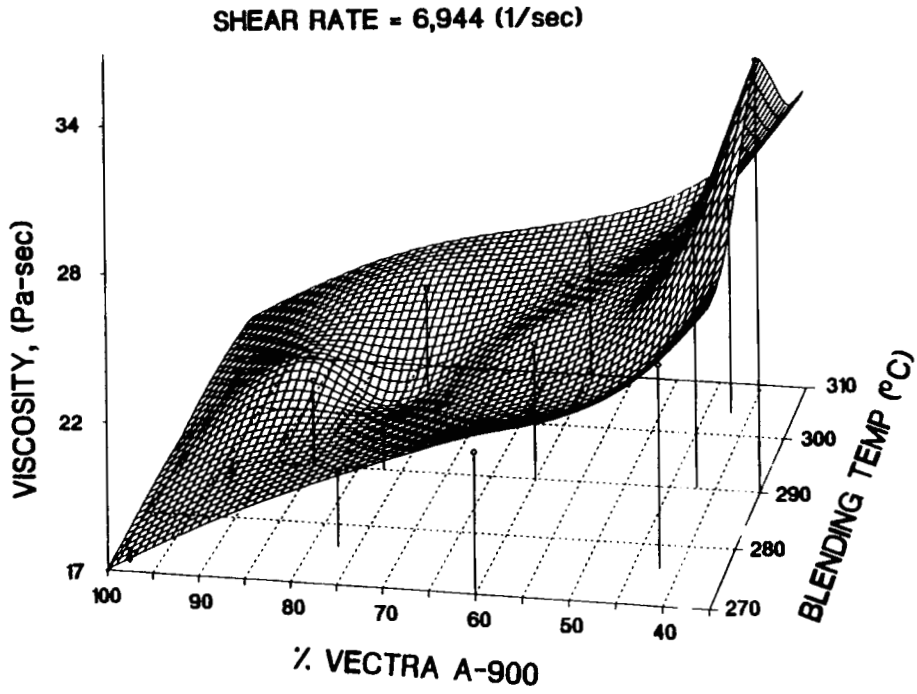


Figure 3 (Continued from the previous page)

The present work extends the study of LCP/isotropic blend rheology by considering blending temperature as a variable, as well as shear rate and composition.

EXPERIMENTAL

The polymers blended in this study were poly(ethylene terephthalate) produced by the Goodyear Tire & Rubber Company with a number-average molecular weight of approximately 42,000, based on intrinsic viscosity in a 60/40 phenol-tetrachloroethane solution at 25°C, and Vectra A900 liquid crystalline polyester from the Hoechst-Celanese Corporation. The structures of each material are shown in Figure 1. The PET and A900 were dry blended and dried overnight under vacuum at 130°C. They were then melt blended in a 1 in. (24 : 1 L/D) Killion extruder at 270, 276, 290, 304, and 310°C, with LCP contents of 35, 42, 60, 77, and 85 weight percent, based on a central composite statistical de-

sign using a centerpoint of 60% A900 and 290°C (Fig. 2). Unblended PET and A900 were also examined, the PET being first run through the blending extruder to give it a thermal history similar to the blends. This unblended PET number-average molecular weight was calculated to be 30,600 after extrusion. The rheological evaluations were done on an Instron tensile testing machine model TTC equipped with a capillary extrusion rheometer.

The above blends and control resins were dried overnight in a vacuum oven at 130°C prior to rheological evaluation. For each run, approximately 15 g of polymer were packed into the rheometer barrel under a nitrogen purge, preheated for 5 min, and extruded through a 2.54 cm-length by 0.0762 cm-diameter tungsten carbide Instron die ($L/D = 33$) at 290°C. Shear rates were varied from 140 to 14,000 1/s by varying crosshead speeds from 0.508 to 50.8 cm/min. The experimental design, shown in Figure 2, includes nine data points, each of which was run through seven shear rates. For completeness, four additional points were included in the experiment,

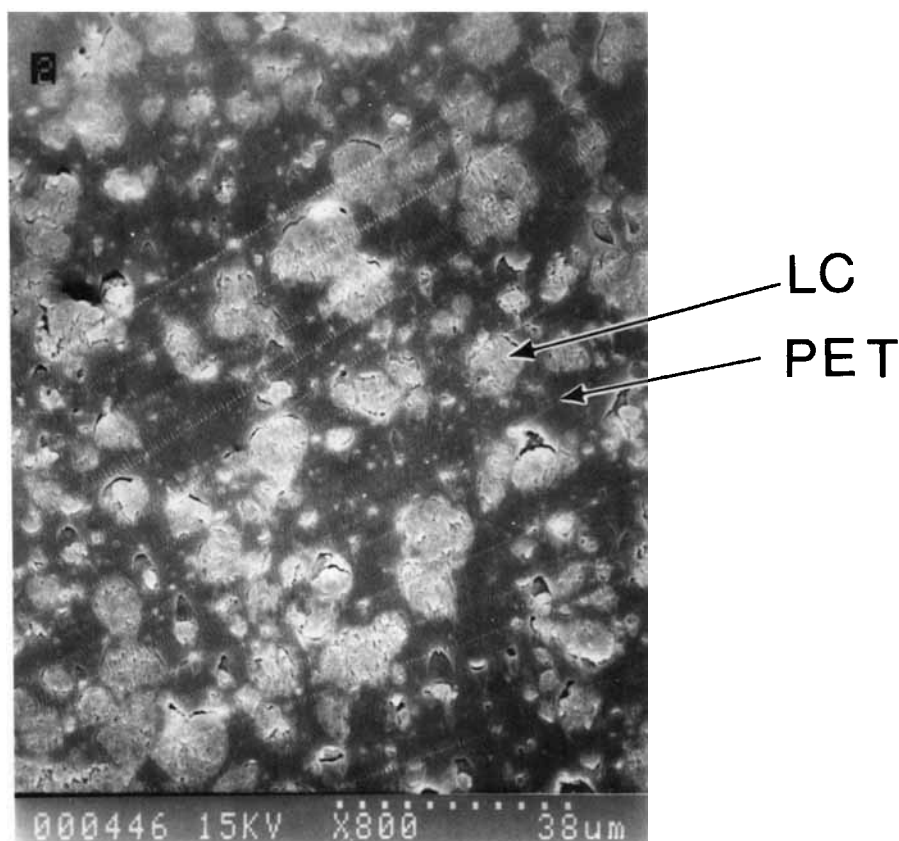


Figure 4 SEM photograph of 58% PET/42% LCP composition. Etched surface. Magnification: 800 \times .

all at the 290°C blend temperature: 42% and 77% LCP, and the unblended controls, 0% and 100% LCP.

Scanning electron microscopy was used to ascertain the morphology of several fibers. Selected samples were etched with 40% methylamine in water for times varying from 2½ to 5½ h. Because the etching rate of methylamine is different for Vectra A900 and PET (unpublished results), textural and topographical differences can be discerned in an etched sample containing the two polymers. To examine cross-sectional areas of the fibers, a razor blade was used to cut the fibers perpendicular to the fiber axis.

RESULTS AND DISCUSSION—RHEOLOGY

Figure 3(a–g) shows the experimental results as computer-generated surface plots of viscosity vs.

composition and blending temperature, for each of the seven shear rates. Included for reference are the actual data points. Although the surface is not completely defined by these data points, it gives a general idea of what is happening rheologically, as blending temperature and composition are varied. For greater accuracy, all compositions but the 0% LCP are included. This latter point had an extremely high melt viscosity and distorted the surface plots inordinately.

Several aspects of the plots are apparent. At any shear rate, the highest melt viscosity occurs at the lowest LCP content and at an intermediate (290°C) blending temperature. This blending temperature effect is pronounced at low shear rates, whereas at the higher shear rates, it is diminished [Fig. 3(a–g)]. It is possible that thermal/hydrolytic degradation is enhanced at blending temperatures greater than 290°C, whereas at lower temperatures, molecular weight degradation due to excessive shear might be responsible for the observed viscosity drop.

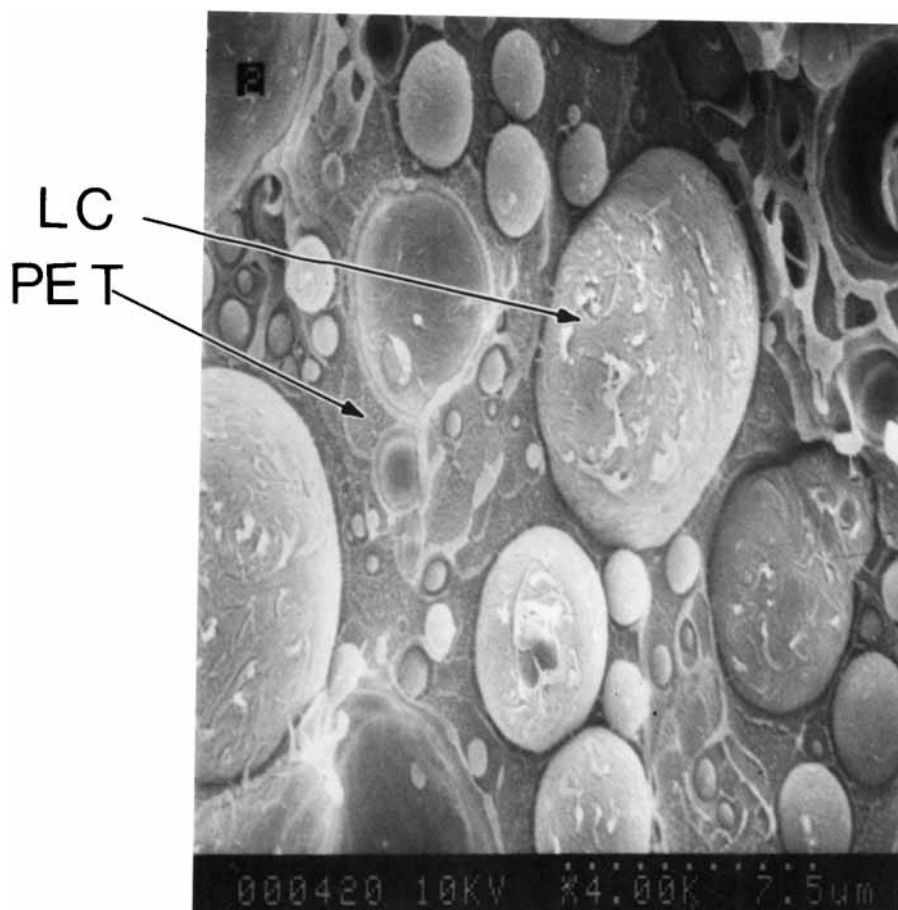


Figure 5 SEM photograph of 58% PET/42% LCP composition. Fractured surface. Magnification: 4000×.

Dilute solution viscosity is the usual method used to determine polyester molecular weight (actually molecular size), but with a blend of two polymers, the molecular size/molecular weight relationship is unclear, so as yet the above suppositions are unsubstantiated by experimental results.

It is not surprising that the blending temperature effect decreases with increasing flow deformation, as it has been generally observed in the literature that molecular weight effects are diminished at high rates of shear.¹⁷ This may result from the greater anisotropy of longer molecules allowing more flow efficiency or, especially at the highest shear rates, from fracture of the longest molecules¹⁷ and subsequent narrowing of the molecular weight distribution. Of course, as expected for pseudoplastic materials, the absolute melt viscosity for any experimental point decreases with increasing shear, as apparent from the ordinate axes of Figure 3.

Blend composition effects are also obvious from

Figure 3 (a-g). At a given blend temperature, as the Vectra A900 LCP content increases up to about the 50% level (moving toward the left in the figures), melt viscosity at first decreases. This decrease, dramatic at low shear rates, is expected as the LCP begins to dominate the blend morphology. SEM results (Figs. 4 and 5) have confirmed a two-phase morphology at the 58% PET/42% LCP composition, wherein the LCP is dispersed as droplets in the PET matrix.

At the lower shear rates [Fig. 3 (a-d)], this trend toward lower melt viscosity reverses, between 42 and 60% LCP content, and the viscosity actually begins increasing with higher LCP content. SEM results confirm a co-continuous morphology at the 60% LCP composition (Figs. 6 and 7), which is apparently not the morphology desired for melt viscosity reduction. On the other hand, high shear rate results [Fig. 3 (e-g)] show no tendency toward higher melt viscosity as LCP content is increased and the vis-

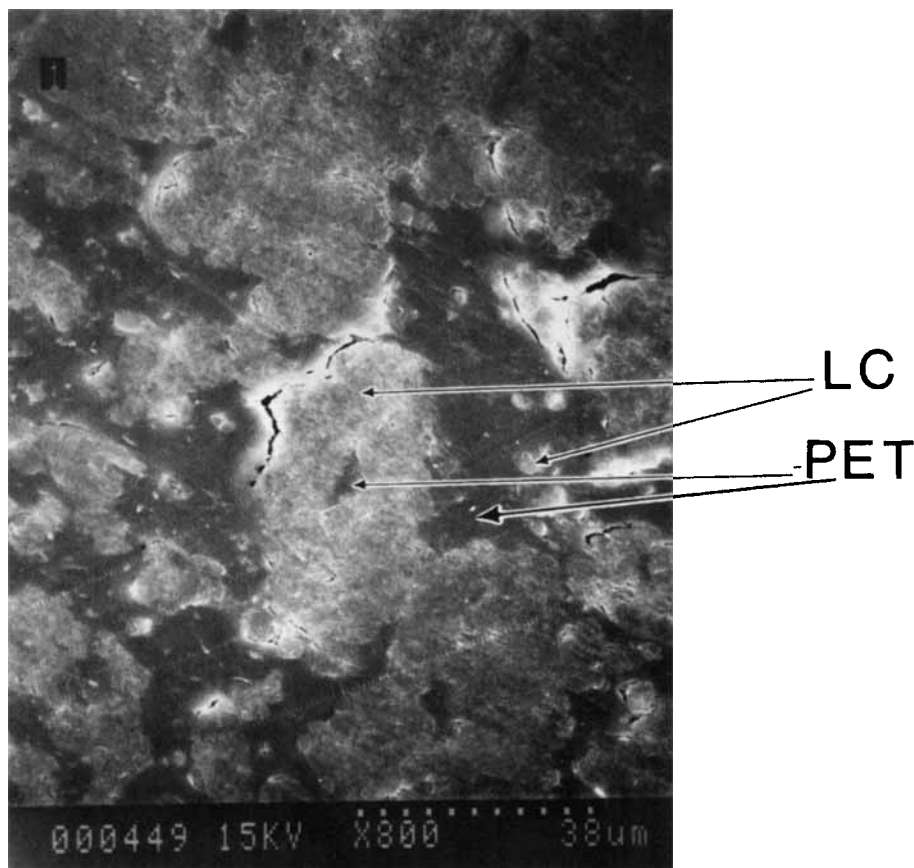


Figure 6 SEM photograph of 40% PET/60% LCP composition. Etched surface. Magnification: 800X.

cosity drops monotonically with increasing amount of Vectra A900. Under these (high shear) conditions, LCP content alone seems to be responsible for the rheological behavior, irrespective of the blend morphology.

As LCP content is then increased to 77%, the viscosity again drops, and here the SEM photomicrographs (Figs. 8 and 9) show a two-phase morphology wherein PET is dispersed in the A900 as

both globular and elongated domains, oriented in the extrusion direction.

This rheological behavior was shown in a seminal paper by Jackson and Kuhfuss¹⁸ for copolyesters prepared by reacting *p*-acetoxybenzoic acid with PET. Although their molecular arrangements were obviously different from those in the present case (copolymer vs. blend), the rheological similarities are interesting.

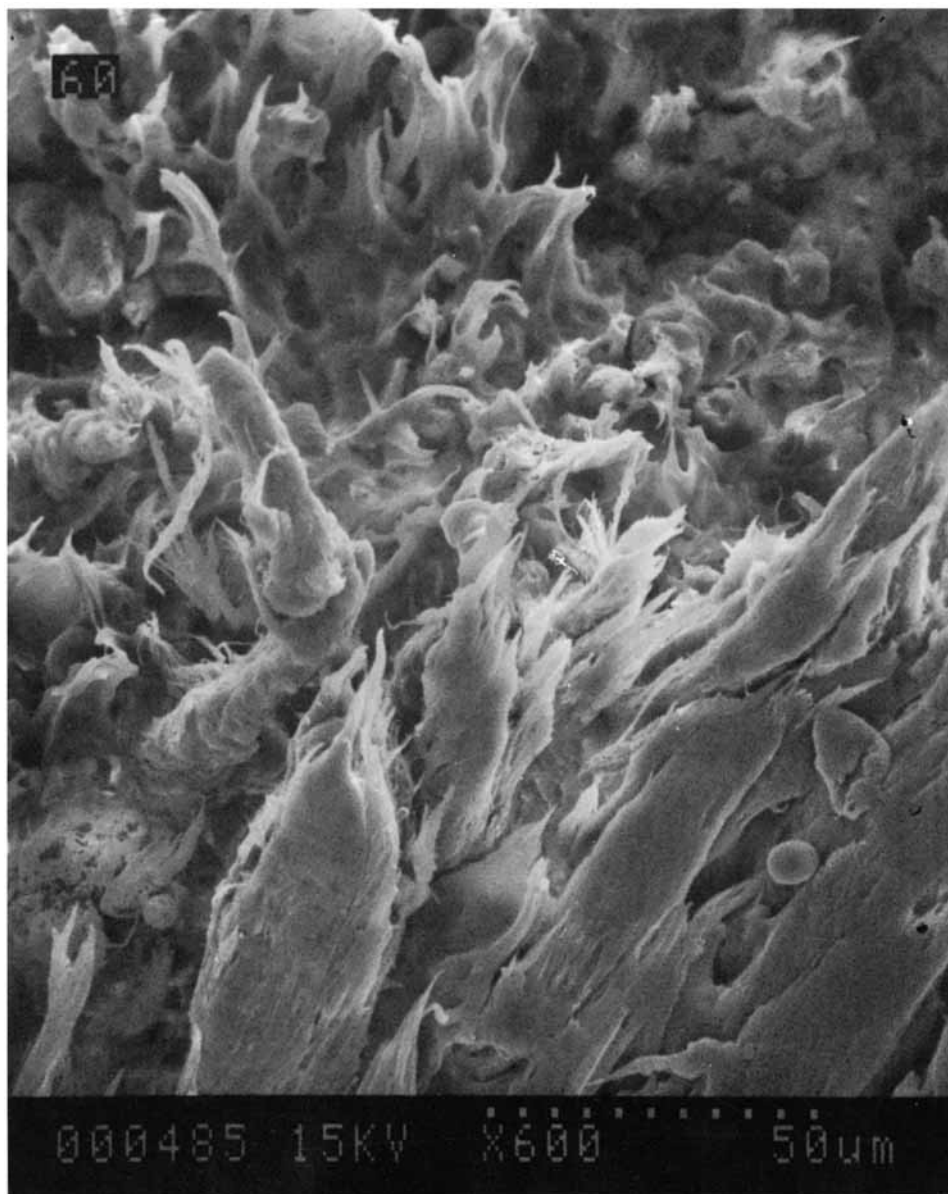


Figure 7 SEM photograph of 40% PET/60% LCP composition. Fractured surface. Magnification: 600 \times .

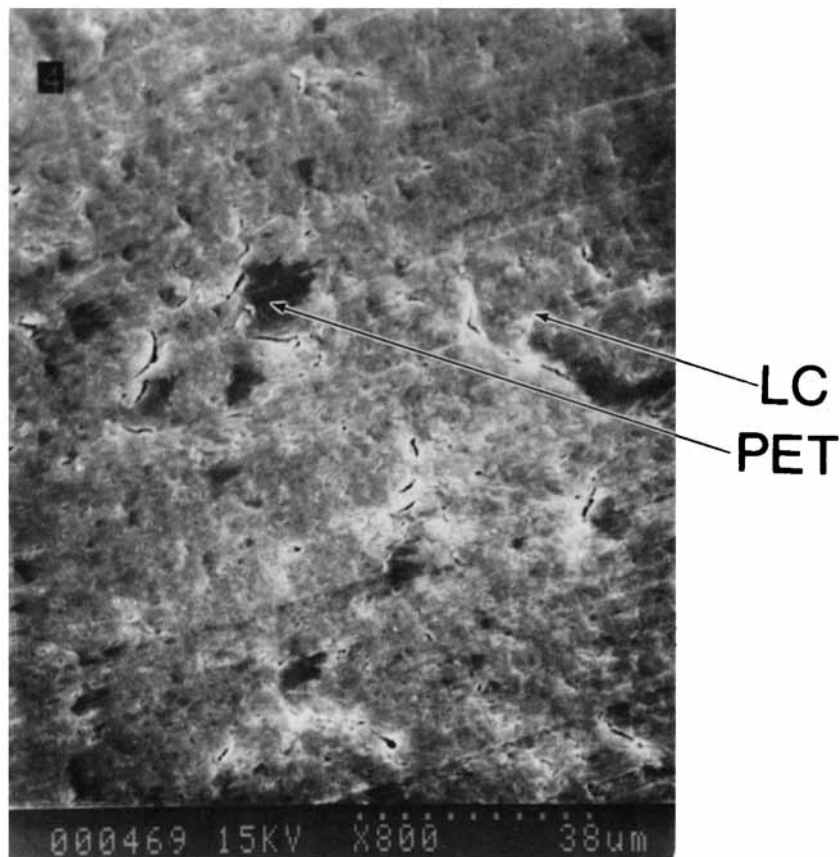


Figure 8 SEM photograph of 23% PET/77% LCP composition. Etched surface. Magnification: 800X.

RESULTS AND DISCUSSION— MICROSCOPY

Selected fiber samples were examined by scanning electron microscopy (SEM). The inversion of phases with changing composition can be seen, in the case of the lowest shear rate studied (139 1/s) in Figures 4–9. Figure 4 is an SEM photograph of the etched 58% PET/42% LCP composition. The Vectra A900 LCP can clearly be seen as the light areas dispersed in the darker PET matrix. Figure 5 is a cross section of the same composition after fracturing. Here, the LCP is seen as dispersed globules in the PET matrix, with apparently poor adhesion between the two phases, as craters are visible where globules have pulled out of the matrix.

If the composition is essentially reversed, with 40% PET/60% LCP, the two polymers exist together as co-continuous phases, shown in Figures 6 and 7. The etched surface (Fig. 6) clearly shows this, again with the LCP being the light and the PET the

dark areas. The fractured surface shown in Figure 7 shows the co-continuity in three dimensions.

Finally, with high loadings of LCP, 23% PET/77% LCP, the LCP becomes the matrix, and PET, the dispersed phase. This is shown in Figures 8 and 9 for the etched and fractured samples, respectively.

CONCLUSIONS

In the preparation of melt blends containing an isotropic and anisotropic polymer, the temperature of the mixing apparatus can have a dramatic effect on the rheological properties of the resulting blend. As LCP content in the blend is varied, different morphologies are created that have a significant influence on the resulting rheological behavior. All effects of blending temperature and blend morphology are accentuated at low shear rates and diminished at high rates of shear. The rheological behavior of the present blends is similar to that seen for copolyesters containing *p*-hydroxy benzoic acid and PET.

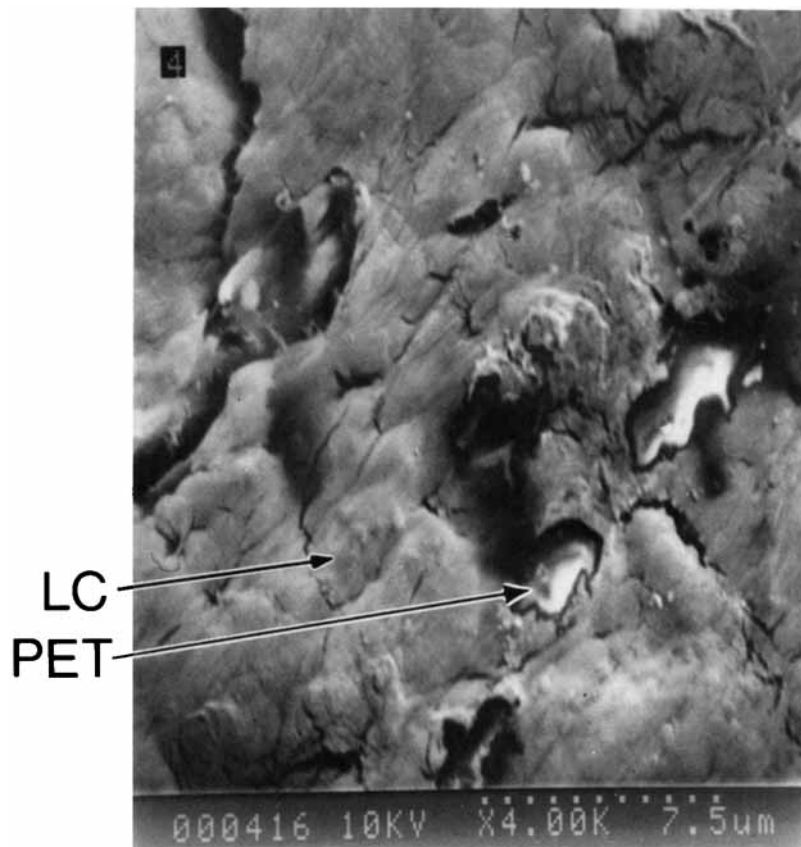


Figure 9 SEM photograph of 23% PET/77% LCP composition. Fractured surface. Magnification: 4000X.

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