

Rheology of Phase Separated Blends of Two Thermotropic Liquid Crystalline Copolyesters*

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The melt rheology of phase separated blends of two thermotropic liquid crystalline polymers (LCPs) have been studied. The two components are a random copolyester consisting of 73 mol% 4-hydrobenzoic acid (HBA) and 27 mol% 6-hydroxy-2-napthoic acid (Vectra A900 of Hoechst Celanese Corp.) and a poly(ethylene terephthalate-co-4-oxybenzoate) containing 60 mol% HBA units (PET/60HBA of Eastman Kodak Corp.). Most striking is the effect of adding 10% PET/60HBA to Vectra A900: The viscosity at 290°C drops by a factor of 4 and the terminal zone of the relaxation time spectrum is shifted to much shorter times. This is an interesting effect that could be used for LCP processing even if its origin is not yet understood. Differential scanning calorimetry measurements support the hypothesis that the blend is phase separated and that no transesterification reaction occurs during the experiments.

INTRODUCTION

The processing behavior of LCPs may be improved by blending two or more LCPs (1-3). LCP blends may have lower crystallization temperature (1) and melting temperature (1-3), and hence they might be processed at a lower and more convenient temperature range. Unlike small molecule liquid crystals for which components having similar mesophase may be miscible in all proportions (4), LCP blends can be either single phase or strongly phase separated, depending on temperature, chemical structure, and weight ratio of each component (1-3, 5). The viscosity of LCP blends has not been extensively studied. DeMeuse and Jaffe (1) reported that the viscosities of compatible LCP blends are between those of the two components, and a linear interpolation gives a good fit for the composition dependent viscosity. In the present work we extend these investigations to phase separated LCP blends. Both components are commercial materials that are well known for their good mechanical performance.

EXPERIMENTAL

Materials and Sample Preparation

Vectra A900 (Hoechst Celanese Corp.) is a random copolyester consisting of 73 mol% 4-hydroxyben-

zoic acid and 27 mol% 6-hydroxy-2-napthoic acid (HBA). The rate of melting is highest at the nominal melting temperature of about 285°C, above which the polymer is in the nematic state. Poly(ethylene terephthalate-co-4-oxybenzoate) containing 60 mol% HBA units (PET/60HBA of Eastman Kodak Corp.) has phase separated domain morphologies and exhibits a broad melting transition from 180°C to 265°C (6). At the melting transition, HBA-rich and PET-rich regions form nematic and amorphous phases, respectively. For blending, the powders of these two LCPs were first mixed in the solid state, and then melt blended in a micromixer (Custom Scientific Instruments Inc. CS-183MM-016) at 310°C for 3 min. Based on earlier rheological experience, each sample was first preheated to 320°C for a few seconds, molded, then cooled to 290°C and held there for the property measurement, which started 10 min later to allow relaxation of molding effects. The purpose of preheating to 320°C is to eliminate residual crystallites, which otherwise at 290°C would act as nuclei for recrystallization (7-9). For the following experiments, we wanted to avoid recrystallization.

Apparatus

Differential scanning calorimetry was carried out on a Perkin-Elmer differential scanning calorimeter (DSC-4). Rheological measurements were performed on a Rheometrics Mechanical Spectrometer (RMS-800), using cone/plate geometry.

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RESULTS

Differential Scanning Calorimetry

Phase separation of the LCP blends is evidenced by two independent crystallization peaks in the DSC measurements. To show this, samples were first heated to 320°C, and then cooled at a rate of 20 K/min (Fig. 1). Pure Vectra A900 shows a crystallization exothermic peak at 238°C, and pure PET/60HBA shows one at 144°C. These two crystallization peaks appear at the same temperatures for the blends of various compositions. With increasing weight ratio of Vectra A900, the enthalpic change (peak area in DSC scan) of the crystallization at 238°C increases linearly, and that of the crystallization at 144°C decreases linearly (Fig. 2).

Shear Flow Measurements

The stress evolution during the startup of shear flow was monitored at a constant rate (0.05, 0.1,

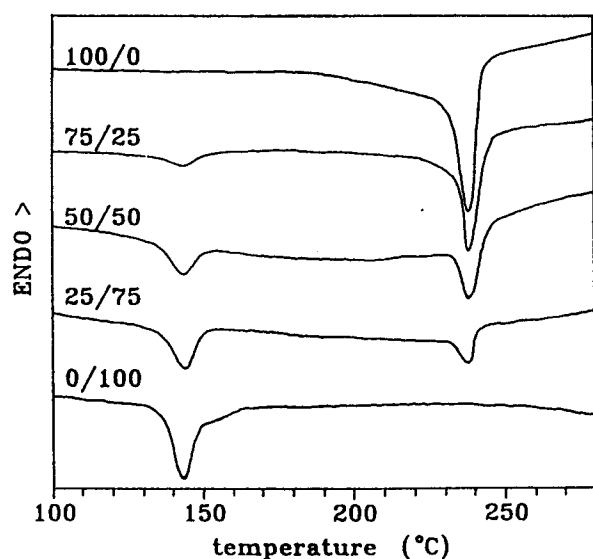


Fig. 1. DSC cooling from 320°C and at a rate of 20 K/min, parameter is the weight ratio: (Vectra A900)/(PET/60HBA).

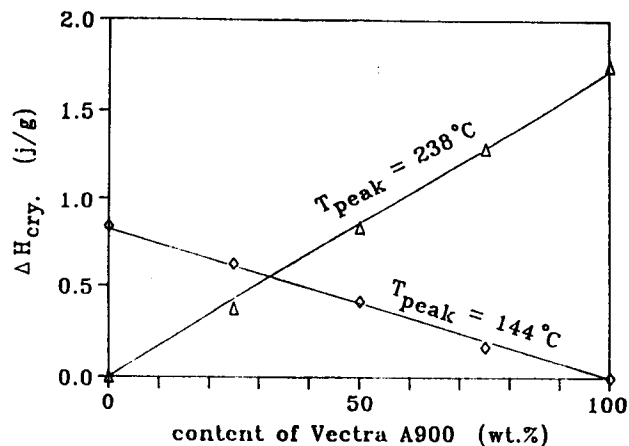


Fig. 2. Enthalpic changes of crystallizations at 144°C and 238°C vs. the weight fraction of Vectra A900.

0.2, or 0.4 s⁻¹). The shear stress, τ , increases until it reaches a maximum at about 2 shear units, then gradually decreases and levels off to a plateau from which the steady shear viscosity can be calculated. The first normal stress difference, N_1 , grows within a very short initial time then decays and may level off to a negative value for some compositions. Figure 3 shows an example.

The viscosity of the blends is lower than the viscosity of either one component (Fig. 4). At shear rates below 0.2 s⁻¹, the blend containing 90% Vectra A900 exhibits the lowest viscosity, which is about one-fourth the viscosity of pure Vectra A900. The steady first normal stress difference, N_1 , measured at various shear rates, is shown in Fig. 5. At shear rates 0.05 and 0.1 s⁻¹, pure Vectra A900 exhibits a negative N_1 close to 1000 Pa, whereas pure PET/60HBA shows a small negative N_1 . Negative N_1 of the blends grows with increasing weight fraction of Vectra A900. At the shear rate of 0.4 s⁻¹, N_1 is positive for both pure components, while intermediate blend compositions show a negative N_1 .

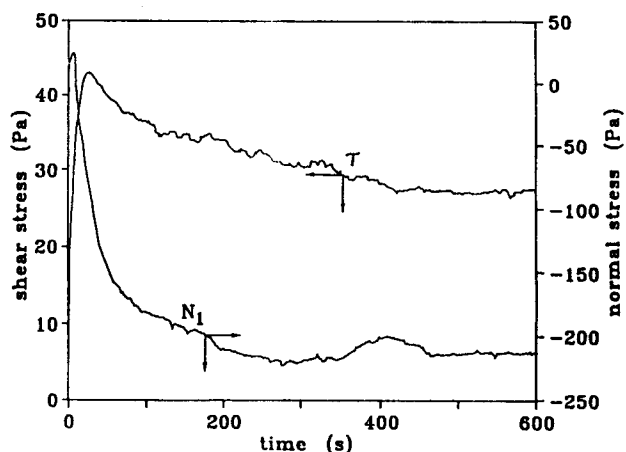


Fig. 3. Stress growth curves of the 50/50 blend sheared at 290°C and at a constant rate of 0.05 s⁻¹.

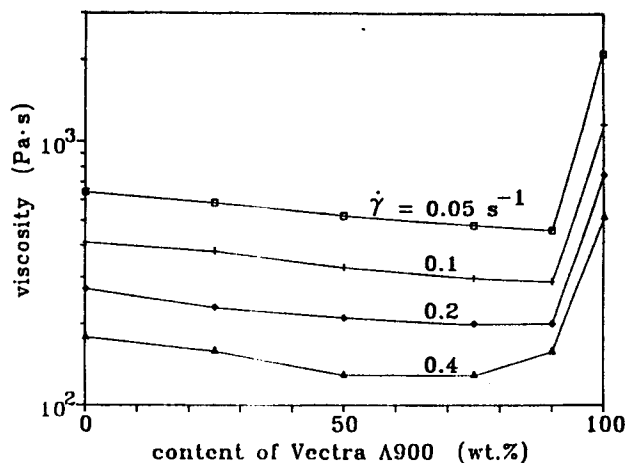


Fig. 4. Viscosity measured at 290°C and the indicated rates vs. the weight fraction of Vectra A900.

Oscillatory Shear Flow Measurements

Oscillatory shear flow measurements were performed in frequency sweep mode at 290°C and strain amplitudes smaller than 0.1 shear units, which is about the upper limit of linear viscoelastic regime for both Vectra A900 (10) and PET/60HBA (6). Vectra A900 exhibits elasticity-dominant behavior at low frequencies, where the storage modulus G' is higher than the loss modulus G'' and seems to level off with decreasing frequency (Fig. 6). The terminal zone of the dynamic modulus is at extremely low frequencies, outside the experimental frequency window. This indicates that there is a relatively strong intermolecular association in the nematic melt of Vectra A900. PET/60HBA does not show such elasticity-dominant properties in the whole frequency range of measurement, and the spectrum is very similar to one of a linear amorphous polymer (Fig. 7). The spectrum of the blend containing 90% Vectra A900 (Fig. 8) is significantly different from

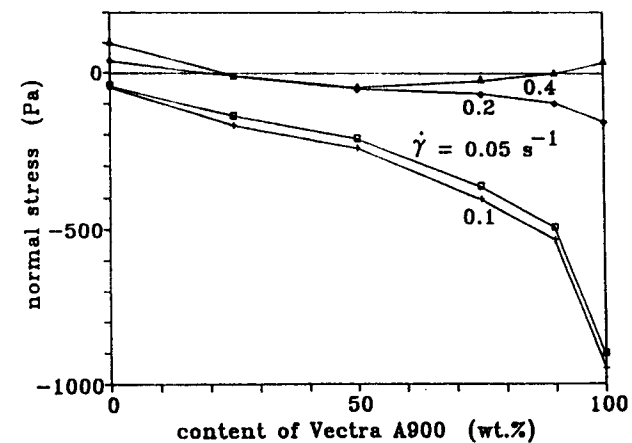


Fig. 5. First normal stress difference, N_1 , measured at 290°C and the indicated shear rates vs. the weight fraction of Vectra A900.

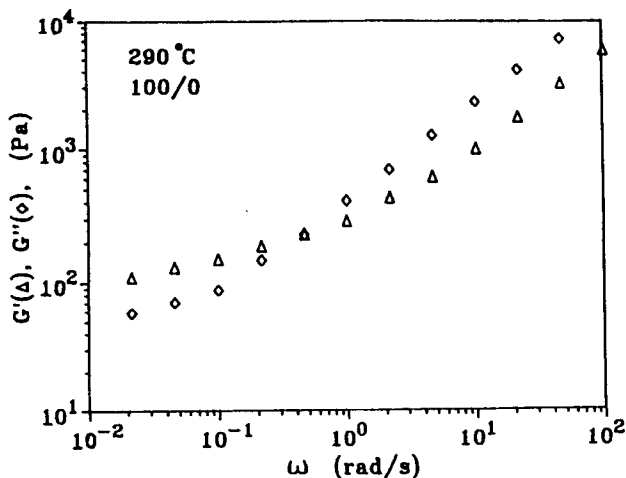


Fig. 6. Storage modulus G' and loss modulus G'' of pure Vectra A900 measured at 290°C vs. frequency.

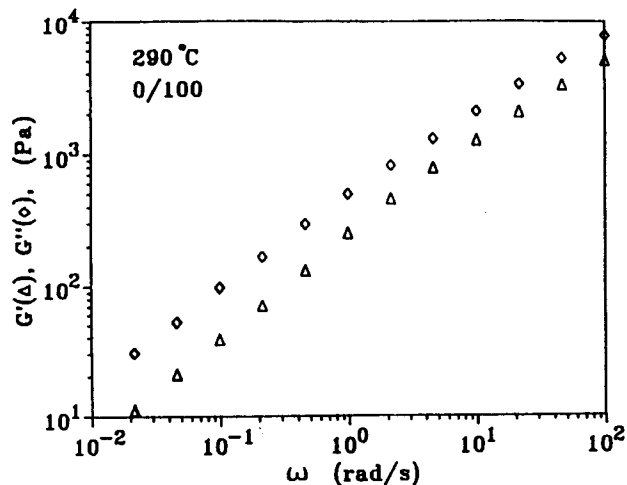


Fig. 7. Dynamic moduli of pure PET/60HBA measured at 290°C vs. frequency.

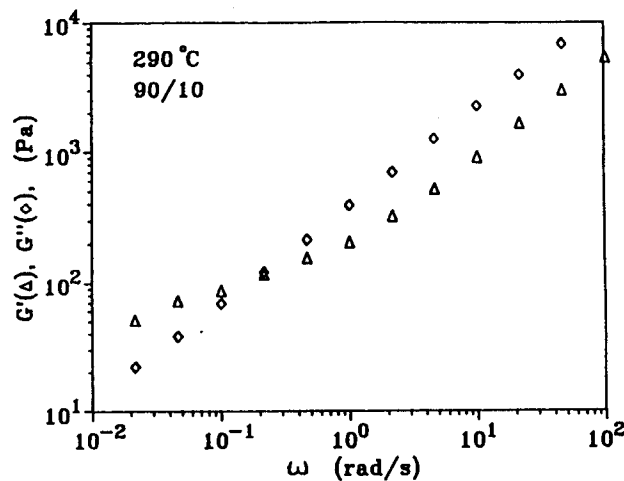


Fig. 8. Dynamic moduli of the 10/90 blend measured at 290°C vs. frequency.

that of pure Vectra A900, as shown by much reduced dynamic moduli and shrunken elasticity-dominant regime at low frequencies.

DISCUSSION

DSC results indicate that no significant transesterification occurs during the melt blending process and that the blends have a high degree of phase separation. If transesterification would take place or if the two components would be compatible in the molten state, the crystallization temperatures would be shifted and the enthalpic change of each crystallization transition would not show the linear composition dependence.

It is an interesting and potentially useful phenomenon that the immiscible LCP blends, especially the blend containing 10% PET/60HBA, exhibit much reduced viscosity. In comparison, the apparent viscosity of blends has been modeled by linear

interpolations of the type

$$\lg \eta_{BL} = W_a \lg \eta_a + W_b \lg \eta_b, \text{ for single phase (11)}$$

or

$$1/\eta_{BL} = W_a/\eta_a + W_b/\eta_b, \text{ for phase separated blends (1)}$$

where η_{BL} is the zero shear viscosity of the blend, and η and W are the viscosity and the weight fraction of individual components, respectively. This implies that η_{BL} should be between η_a and η_b . The present study, however, shows that these models cannot be applied to the immiscible LCP blends. Slippage at the Vectra A900 and PET/60HBA interface might possibly explain this phenomenon.

It is generally understood that negative N_1 is accompanied by the shear flow of heterogeneous polymeric melts. Compared with the individual components, the immiscible LCP blends show negative N_1 up to higher shear rates (Fig. 4). This implies that the blends may have increased heterogeneity.

Shear flow at higher rates could not be studied because of the fact that samples flow out from the gap between the cone and plate fixtures. The shear viscosity of pure Vectra A900 measured here is about 30% lower than that measured in an earlier study (10). This is attributed to differences in sample history and measuring method. With that in mind, the two sets of data are still in a reasonable agreement.

Oscillatory shear experiments, low-frequency properties are closely related to large-scale structure. Interface slippage might be responsible for the decay in low-frequency moduli of the melted blend containing 10% PET/60HBA (Fig. 8).

The steady shear viscosity of most flexible linear homopolymers follows the Cox-Merz rule (12):

$$\eta(\dot{\gamma}) = \eta^*(\omega) |_{\omega=\dot{\gamma}}$$

where $\eta(\dot{\gamma})$ is the shear rate dependent shear viscosity, and $\eta^*(\omega)$ is the frequency dependent complex viscosity. At the accessible shear rates, Vectra A900 follows the Cox-Merz reasonably well, but PET/60HBA and the blends do not (Fig. 9). For PET/60HBA and the blends, the relatively low $\eta(\dot{\gamma})$ indicates that for a phase separated system, steady shear may more effectively align the phase separated domains in the flow direction than oscillatory shear.

CONCLUSIONS

The experiments strongly suggest that the blends of Vectra A900 and PET/60HBA are completely phase separated in the entire range of composition. There is no evidence for transestification at the interface. The shear viscosity of these phase separated LCP blends, surprisingly, is significantly lower than

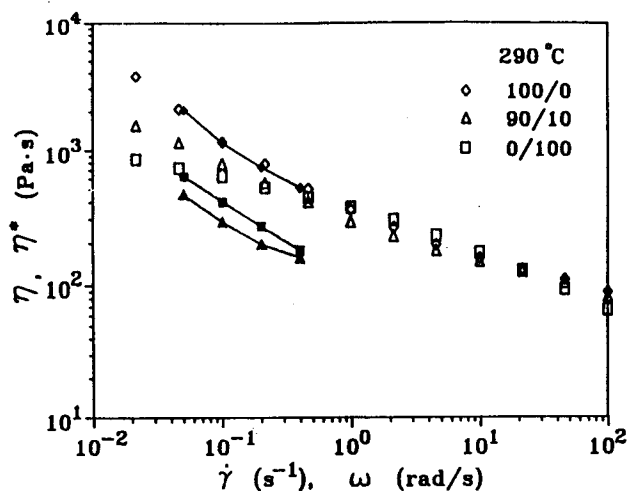


Fig. 9. Comparison of shear viscosity (filled symbols) with complex viscosity (open symbols).

the viscosity of individual components. Slippage might occur at the interface. Further studies of the morphology and the shear induced structural changes will help us better understand this unusual rheological behavior of phase separated LCP blends.

ACKNOWLEDGMENT

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