

Rheology of Rigid-Flexible Liquid Crystalline Polymer/Poly(methyl methacrylate) Blends

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SYNOPSIS

The random liquid crystalline copolymer poly(4,4'-biphenylene azelate)-*co*-(2-methyl-1,4-phenylene azelate), synthesized by condensation polymerization, was found to be soluble in chloroform and methylene chloride. DSC, rheology, and optical microscopy indicated that this LCP broadly melts at *ca.* 160°C to a weakly birefringent melt that becomes isotropic at approximately 180°C. DSC and optical microscopy of blends with poly(methyl methacrylate) (PMMA) at $w_{LCP} = 0.06, 0.16, 0.34,$ and 0.69 , indicated little compatibility between the polymers at middle compositions. Dynamic and steady shear flow rheological measurements, using cone/plate geometry, showed the PMMA-rich (6 wt % LCP) and LCP-rich (69 wt % LCP) blends to be essentially homogeneous, and dominated by the properties of the major component. However, at 16 wt % and 34 wt %, the resulting phase separation led to lower dynamic moduli (than either LCP or PMMA separately), and increased shear thinning. This behavior supports the notion that the LCP acts as a lubricant by promoting the flow of the non-LCP. The results reported in this article show that these rheological effects, which were previously observed in blends of insoluble, rigid LCPs and engineering thermoplastics, still exist with a much less rodlike LCP mixed with a commodity polymer.

INTRODUCTION

Research on liquid crystalline polymer (LCP) blends has been recently reviewed.¹⁻² In general, marginal miscibility is observed between liquid crystalline polymers (LCPs) and flexible polymers. Measured mechanical and rheological properties deviate from simple linear averages between the component polymers¹⁻³ and are complex functions of composition. Of particular interest are rheological studies. It has been observed that under certain conditions, at very low LCP content (ranging between 5 and 20 wt %), blends often possess lower viscosities and greater shear thinning than the parent polymers.³⁻⁶

However, these studies³⁻⁶ typically involve insoluble, rigid "Vectra"-type⁴⁻⁵ LCPs, with high transition temperatures ($>200^{\circ}\text{C}$). The non-LCP component, therefore, had to be an engineering thermoplastic, such as a polysulfone³ or polyamide^{4,6}; alternatively, the LCP polymer could be blended in

the supercooled state. Work at Polaroid has focused on soluble, low transition temperature LCPs and blends.⁷ It is of interest to explore the rheological properties of copolymers comprising alternating rigid-flexible units blended with thermoplastics for a variety of commercial applications, including processing aids.⁵ In this initial study, we have directed our attention to blends of an LCP with poly(methyl methacrylate) (PMMA), a typical commodity polymer. From both a theoretical and commercial perspective, it would be significant if the above rheological effects could be demonstrated at lower temperatures with polymers that are better known as commodities rather than as "high performance" materials.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) was purchased from Polysciences (Catalog #4553, lot #33672) and was used as received. The molecular

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weight distribution was determined by GPC (Waters 150-C ALC/GPC, 2×10 micron Polymer Labs mixed columns, chloroform): $\bar{M}_n = 35,400$; $\bar{M}_w = 133,5000$; PD = 3.8. Methylene chloride, chloroform, and methanol (Certified ACS) were used as received from Fisher Scientific Company. 4,4'-biphenol, methylhydroquinone, azelaoyl chloride, and triethylamine were all obtained from Aldrich Chemical Company.

Synthesis of LCP

A ten gallon reactor was dried by heating overnight. The reactor was purged with dry nitrogen during the drying of the vessel and throughout the reaction. At ambient temperature, the reactor was charged with 18 kg of methylene chloride, 0.929 kg of 4,4'-biphenol, 0.619 kg of methylhydroquinone, and 2.937 kg of triethylamine. The reactants were stirred at 200 rpm at 25°C for 30 min, then were cooled to 12°C over a 1 h period.

The addition of azelaoyl chloride (1.669 kg), at a rate of 1.113 kg/h, reduced coagulation and minimized the endotherm (temperature kept below 15°C). Upon completion of the addition, the addition vessel and transfer lines were rinsed with 1.2 kg methylene chloride.

The reaction vessel was warmed to 24°C in 60 min by raising the jacket temperature by 2°C every 10 min. After 1 h at 24°C, the reaction vessel contents were transferred over a 15 min period to a 50 gallon vessel containing 102 kg methanol. The 10 gallon reactor was rinsed with 23 kg methanol, which was then transferred to the 50 gallon vessel. After stirring the quenched reaction for 1 h, the product was filtered through a Niagara filter, collected, and slurried in 15 gallons of water for another hour. It was filtered again and washed with 15 more gallons of water. The product was collected and vacuum dried at 50°C to yield 2.07 kg (91%) of colorless solid. The inherent viscosity (chloroform, 0.5 g/mL 30°C) was 0.26. NMR (^1H , 300 MHz Bruker) δ (ppm): 7.54 (*d*), 7.26 (*s*), 7.13 (*d*), 6.97 (*m*), 2.58 (*m*), 2.16 (*m*), 1.79 (broad *s*), 1.40–1.60 (broad *m*). The ratio of biphenol to methylhydroquinone in the copolymer was 1.4: 1, determined from the ratio of the farthest downfield aromatic protons (4 @ 7.54 ppm) of biphenol to the methyl (3 @ 2.16 ppm) protons of methylhydroquinone. Molecular weight of the LCP was determined by GPC (as above): $\bar{M}_n = 4,870$; $\bar{M}_w = 13,300$; PD = 2.7. Samples were further purified by dissolving polymer in chloroform (5 wt %), precipitating in a large excess of methanol, and redrying (yield = 63%). A negligible change in

molecular weight by GPC was observed since MW = 580 was the cutoff value. However, HPLC (with an HP 1090 LC) on methanol extracts of the LCP show far fewer peaks (indicative of oligomers and residual monomer) after purification as compared with the crude product.

Rheology

All samples were prepared by weighing PMMA and/or LCP directly into vials and mixing by slurrying 5 g (total sample) in 10 mL methylene chloride for one day, then vacuum drying at 90°C for four days. The samples were then molded by melt pressing into plates at 180°C. Both dynamic and steady state shear flow measurements were performed on a Rheometrics Mechanical Spectrometer (RMS – 800), using cone/plate geometry, with the radius = 12.5 mm and a cone angle of 0.1 radians. In the rheometer, a molded sample was first heated to 200°C for molding between the cone and plate, cooled to 130°C for crystallization, and then was heated to the desired temperature for rheological measurements. Other details of the measurements (strain rate, amplitude, heating rate) are described in the relevant figure captions.

DSC

Samples were taken from those used in rheological studies. In a Perkin–Elmer DSC7 system, samples were typically heated from 25 to 200°C at a heating rate of 20°C/min, and then were immediately cooled at a rate of 10°C/min. Transition temperatures reported are those on the first cooling scan.

Optical Microscopy

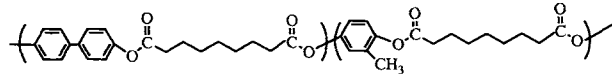
Samples, sandwiched between glass slides, were examined under 100 \times magnification between cross-polars, using a Zeiss, hot stage microscope. They were heated from 20–200°C using a current of 2.4 A.

RESULTS AND DISCUSSION

Liquid Crystalline Polymer

The structure of the liquid crystalline polyester synthesized for our studies, the random copolymer poly(4,4'-biphenylene azelate)-*co*-(2-methyl-1,4-phenylene azelate) is shown below. It was synthesized by a condensation polymerization of the two

corresponding aromatic diols with the aliphatic acid dichloride in methylene chloride with triethylamine.



As a result of the stoichiometry (3 : 2, diol : diacid), the molecular weight of the polymer ($\bar{M}_n = 4,870$; $\bar{M}_w = 13,300$; PD = 2.7) is low. It is soluble in chloroform (ca. 7 wt %) and methylene chloride (ca. 5 wt %).

Measurements using optical microscopy detect the LCP softening at approximately 145–150°C to form a birefringent melt (observed between cross-polars), and clearing at a temperature of 185–190°C. Differential scanning calorimetry (DSC) exhibits a weak broad transition, centered near 160°C, upon heating. A much more distinct exotherm (153.6°C, 5.0 J/g) is observed on the cooling scan. These results are unlike the strong transition peaks typically observed for LCPs⁸ and are probably due to the random nature of the polymer. Indeed, for segmented LCPs such as ours, the melting (DSC) transition is usually strong, whereas the nematic/isotropic is broad and weak. Thus the DSC result seen here, although not uncommon, does not typify the behavior observed for this class of LCPs.⁹

Dynamical shear measurements indicate that the LCP has a melting transition at about 168°C as the storage modulus G' and the loss modulus G'' decay by several orders of magnitude (Fig. 1). The nematic/isotropic transition, however, can not be detected, due to extremely low dynamic moduli. Steady

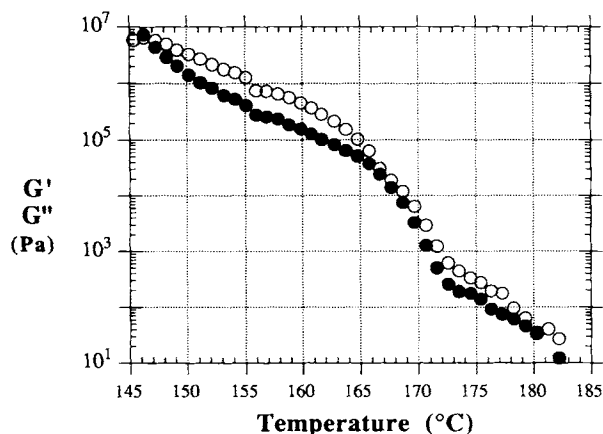


Figure 1 Storage modulus (○) G' and loss modulus (●) G'' of the LCP measured at 1 rad/s and strain amplitudes within the linear elastic regime. The heating rate was 1°C/min.

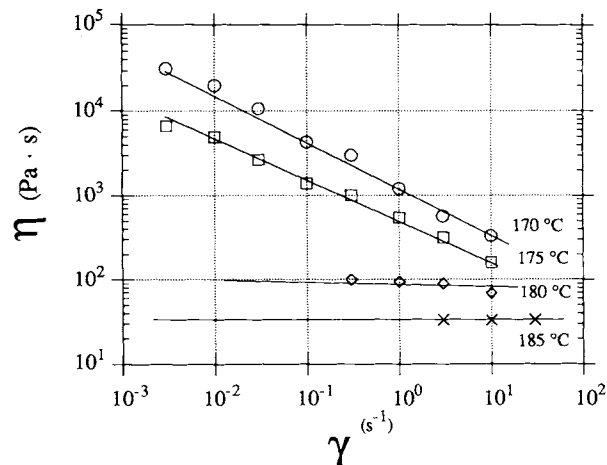


Figure 2 Steady shear viscosities of the LCP as a function of shear rate at the indicated temperatures.

shear measurements (Fig. 2), though, show that shear thinning behavior is observed only below 180°C. Above 180°C, the polymer behaves as a typical low molecular weight liquid. This result implies that a nematic/isotropic transition appears to exist between 175°C and 180°C. These measurements were not made below the melting temperature due to slippage of sample on the fixture surface.

Thus the three methods (DSC, Rheology, Optical Microscopy) all generally agree that this LCP melts in the 160s°C to a weakly birefringent melt that converts to the isotropic phase around 180°C.

Blends

DSC

The glass transition temperature (T_g) of PMMA was observed at 102°C, in accord with literature reports. As mentioned above, transitions of the LCP are not clear on a first or second heating. Therefore, transitions were taken from cooling scans. With this approach, a single exotherm is evident in the DSC of the LCP at 154°C, as mentioned above.

At high PMMA content ($W_{LCP} = 0.06$ w/w), the only transition observed is the PMMA T_g at a slightly perturbed value of 106°C. At high LCP content ($W_{LCP} = 0.69$), a single exotherm is observed at 156°C, barely perturbed from that of the LCP measured by itself. At $W_{LCP} = 0.16$, both the heating and the cooling scans are very broad, with little indication of any abrupt thermodynamic transitions. The cooling scan at $W_{LCP} = 0.34$ gives two broadened transitions, one each at approximately at the transitions seen in the pure PMMA and in pure LCP.

Thus, DSC is not very informative, but appears to indicate that little compatibility exists between LCP and PMMA at the middle compositions, since two transitions with negligible shift from the pure component values are apparent in the scans.

Optical Microscopy

Whereas PMMA simply softens near its T_g , the blends all form birefringent melts between 145–150°C. These become isotropic between 185–190°C. Thus, since little perturbation of the LCP transition exists, it again appears that the PMMA is in a separate phase. Results with the $W_{LCP} = 0.06$ sample are somewhat ambiguous; the sample becomes birefringent only when deformed under pressure. Again, these results would seem to indicate a separate LC phase at low composition.

Rheology

Dynamical Shear Measurements detect an essentially unperturbed thermal transition at 168°C for LCP in the blends containing 69 wt % and 34 wt % LCP. This result is similar to that illustrated in Figure 1 for LCP alone, but is lower in magnitude. This means that the LCP is essentially phase separated from the PMMA in these two blends. The blend containing 16 wt % LCP has a very small melting transition (Fig. 3); at this concentration one might expect the properties of the PMMA to dominate, since it is the major component. The blend containing 6 wt % LCP does not show any melting transition, just as the scan of PMMA alone, implying that the LCP might be miscible with PMMA below a

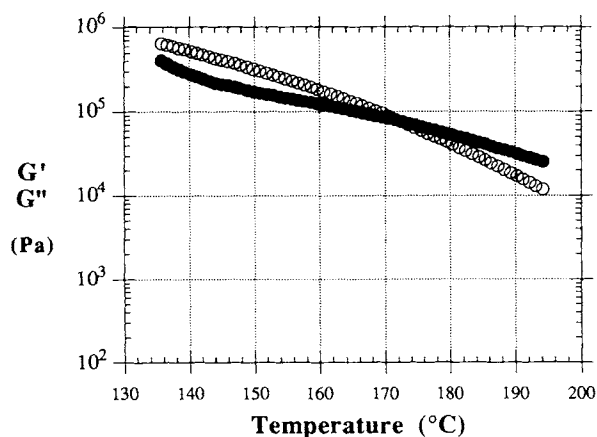


Figure 3 Dynamical moduli G' (○) G'' (●) of the blend LCP/PMMA (16/84), measured at 1 rad/s and a small strain amplitude $\gamma_0 = 0.5\%$. The heating rate was 1°C/min.

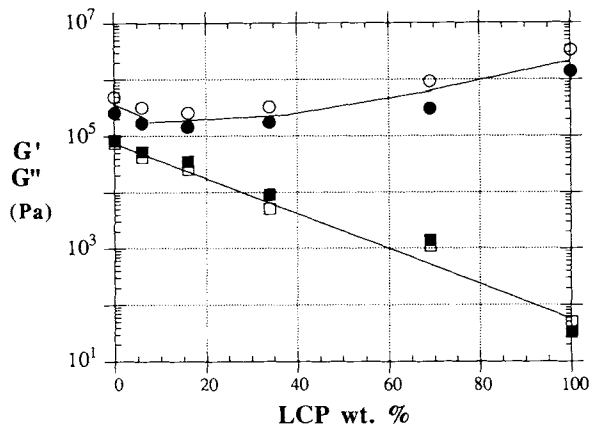


Figure 4 Dynamical moduli measured at 1 rad/s and strain amplitudes within the linear viscoelastic regime plotted as a function of LCP content in the blends: 150°C, (○) G' (●) G'' ; 180°C, (□) G' (■) G'' .

certain weight fraction. Similar results were found with an all-aromatic, rodlike polyester blended with polysulfone.^{7c}

At 150°C, the dynamic moduli, G' and G'' decrease with the LCP content until they reach minima between 6 wt % and 16 wt %; this is followed by very small moduli increases as the LCP content increases to 34% LCP (Fig. 4, circles). This observation might imply that below 6%, the LCP is miscible with PMMA and acts as a plasticizer. Moreover, we would not expect the LCP to be able to crystallize at such a low concentration. As the LCP content exceeds the saturation limit (6%), the excess LCP molecules begin to phase separate into soft, noncrystalline domains, which impart nearly constant moduli up to 34%. This implies that, in this broad concentration range, the LCP acts a “lubricant” for the phase separated PMMA. Above 34%, the moduli increase as the rheological properties of the LCP dominate the mixture. However, this is only a hypothesis. One could alternatively argue that the nearly constant moduli result from a balance of two opposing effects; whereas an increase in the volume fraction of LCP particles increases the moduli, the increase in the concentration of the LCP in the PMMA-rich phase decreases the moduli.

Above the melting temperature (180°C), the dynamic moduli monotonically decrease in a linear fashion with greater LCP content (Fig. 4, squares), which is a consequence of the conversion of the LCP to its lower modulus isotropic phase. Previous investigators³⁻⁵ have made observations in agreement with our results. In two cases,^{3,5} electron microscopy was performed to attempt to correlate morphology to rheology; still, it was difficult to ex-

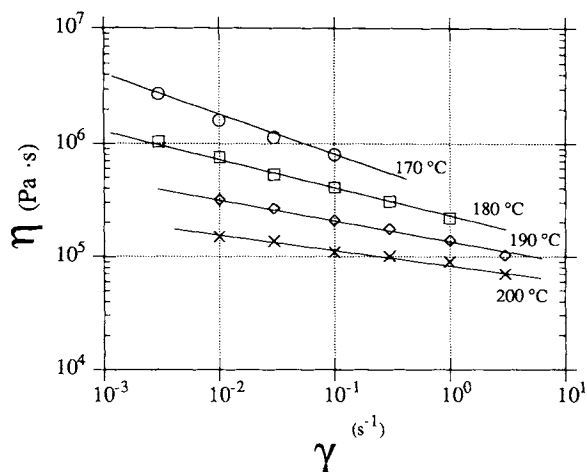


Figure 5 Steady shear viscosities of the blend LCP/PMMA (16/84) as a function of shear rate at the indicated temperatures.

plain all aspects in the systems.⁵ As we have not done such measurements, we can only speculate that the depressed G' and G'' observed are a result of similar effects. That we detect the minima at 150°C, when the LCP is in its liquid crystalline state, and not at 180°C, when the LCP is isotropic, clearly demonstrates that liquid crystallinity is the cause of the phenomena.

As mentioned above, the pure LCP is shear thinning until 180°C (Fig. 2), and blends containing 69 wt % LCP show similar behavior. As expected, neither the pure PMMA nor the 6 wt % LCP blend exhibit shear thinning, indicating that shear viscosity is not a function of shear rate. Thus, plots for these samples, such as in Fig. 2, are horizontal curves for all temperatures investigated. This again indicates that no phase separation exists in these blends (6 and 69% LCP). However, the blends containing 34 wt % and 16 wt % LCP show a broadened temperature range of shear thinning. As shown for the 16 wt % LCP sample in Figure 5, shear thinning occurs even at 200°C, well above the nematic/isotropic transition of LCP. Thus the effect of enhanced shear thinning that previous investigators observed,⁴⁻⁵ with blends of more rodlike LCPs and specialty polymers, can be detected with less "rigorous" conditions.

CONCLUSIONS

Based on DSC and rheological measurements, the PMMA-rich (6 wt % LCP) and LCP-rich (69 wt %

LCP) blends are dominated by the properties of the major component. Thus, there appears to be some mutual solubility at the extremes of the phase diagram. However, at 16 wt % and 34 wt %, the resulting phase separation in the liquid crystalline state of the LCP (150°C) leads to lower dynamic moduli (than both LCP and PMMA), and increased shear thinning, characteristic of previous results,⁴⁻⁵ supportive of the LCP acting as a lubricant to promote the flow of the nonLCP. At higher amounts of LCP (69 wt %), it becomes the major phase and properties are then those of LCP itself.

We conclude that the rheological effects, previously observed in LCP/nonLCP blends,¹⁻⁶ still exist with much less rodlike LCPs mixed with commodity polymers. Consequently, this conclusion needs to be accounted for in theoretical simulations, and it suggests a greater range of applications of LCPs such as processing aids and rheological modifiers.

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