

Melt Viscosity Reduction of Polycarbonate with Low Molar Mass Liquid Crystals

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ABSTRACT: The phase behavior and rheological behavior of low molar mass liquid crystal (LLC) and polycarbonate blends is firstly reported. The results of small angle light scattering (SALS) indicate that the LLC is miscible in the mixture for weight fractions of LLC less than 6%. Mixtures of two different liquid crystals with two different molecular weight of polycarbonate were prepared inside the miscible regime of the blends. Both the complex and steady shear viscosities of the blends were found to be significantly decreased upon addition of small amounts of liquid crystal (1% by weight). At low shear rate, the steady state shear viscosity was similar to the pure polycarbonate,

whilst, at higher shear rates, three further regimes of behavior, as has been described for liquid crystals and liquid crystal polymers, were found despite the low concentration of LLC; hence, the rheological properties of the blends can be significantly modified by small concentrations of LLC (as low as 1%). The decrease in melt viscosity of polycarbonate that we observe upon addition of LLC is not due to lubrication effects at the interfaces, as shown by reproducible oscillatory shear flow sweeps. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1108–1115, 2008

Key words: polycarbonate; viscosity; blends; liquid crystal

INTRODUCTION

Polycarbonate exhibits a high melt viscosity and requires a high processing temperature to reduce its melt viscosity for processing. However, a high processing temperature may result in deterioration of the properties due to thermal degradation. Hence, it is of interest to find a method to reduce the melt viscosity without subjecting the polymer to a high processing temperature. One attractive possibility is the usage of a low molar mass liquid crystal (LLC) as an additive.

Liquid crystal polymers (LCPs) have long been considered for improving rheological properties of polymers.^{1–8} Lin et al.⁹ studied the miscibility and viscoelastic properties of blends of a segmented block copolyester liquid crystal and poly(ethylene terephthalate). They found that the melt viscosity decreased exponentially with the LCP content. The addition of LCP also changed the distribution of the relaxation times of PET and broadened the zero-shear viscosity regime. However, there was no further significant reduction of viscosity, either as the LCP content exceeded 50 wt %, nor at low LCP con-

tent. Also, Hsieh et al.¹⁰ investigated the rheological properties of a thermotropic liquid crystalline polymer, HIQ45, blended with PC. The shear rate dependent behavior of the viscosities of the HIQ45 and PC blends differed from the shear thinning behavior of pure HIQ45. All blends showed Newtonian behavior even for the blend with a HIQ45 concentration of 75%. However, again there was no significant reduction of viscosity at low LCP content. A drawback of blending with LCPs is that they generally have a detrimental effect on the clarity of the final product because blends of high molecular weight polymers usually show some degree of immiscibility, which results in heterogeneity. This is particularly problematic since the reduction of melt viscosity only happens at high concentrations of LCP (up to 50%). This is in contrast to the addition of LLC described in this research, in which we report a significant reduction in melt viscosity even at low weight concentration of LLC (1%).

Low molar mass liquid crystal (LLCs) in polymer matrices constitute interesting systems from many points of view. Many studies concerning the phase behavior, miscibility, morphology, and properties have been reported for such blends.^{11–19} It has long been known that LLCs can reduce the melt viscosity of polymers,^{17,18} but the rheological responses and the effects on the melt viscosity of polycarbonate at different shear rates will be vividly shown in this

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article for the first time. Moreover the clarity of the polymer does not deteriorate because of the greater miscibility of LLC compared with LCP. Huh et al.¹⁷ studied the rheological and thermal properties of polystyrene (PS) with terephthal-bis-4-*n*-butylaniline (TBBA) and *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA) as plasticizers. Both are miscible with PS over a broad composition range and lead to a decreased glass transition temperature and melt viscosity. Watcharawichanant et al.¹⁹ studied the effects on molecular motion in poly(styrene-*co*-acrylonitrile) and poly(methylmethacrylate) blends after addition of LLC. The authors found that LLC increased the molecular mobility of the blends as observed through early stage phase separation via spinodal decomposition.

In the present work, blends of different molecular weight of PC and two types of LLC are studied in detail. The LLCs, derivatives of cyclohexylbiphenylcyclohexane, were chosen because the temperature range of their nematic regions correspond with the typical processing temperatures of polycarbonate.^{20,21} We explore the phase behavior and rheological properties of blends of LLC and polycarbonate. The melt rheological properties of these mixtures, inside the miscible regime, subjected to both steady and oscillatory shear flows are reported. The reproducibility of the oscillatory shear flows sweeps is also included as evidence that the effects we observe are not due to lubrication.

EXPERIMENTAL

Materials

Three different molecular weights of PC were used in this study, PC27K (number-average molecular weight, $\bar{M}_n = 16,440$ g/mol, polydispersity index, $\bar{M}_w/\bar{M}_n = 1.69$) supplied by Bayer Polymer Co. PC24K ($\bar{M}_n = 13,666$ g/mol, $\bar{M}_w/\bar{M}_n = 1.81$) and PC39K ($\bar{M}_n = 25,258$ g/mol, $\bar{M}_w/\bar{M}_n = 1.57$) from Aldrich Chemical Company. Molecular weights were determined via gel permeation chromatography using chloroform as the solvent. The LLCs used in this study were obtained from Merck Co. as CBC33 and CBC53 in the form of white powders.

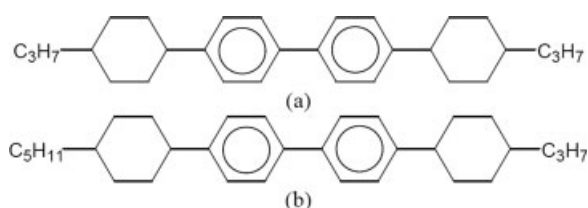


Figure 1 The chemical formulas of low molar mass liquid crystal (a) CBC33 (b) CBC53.

TABLE I
Properties of Low Molar Mass Liquid Crystals

Property	CBC33	CBC53
Melting point/°C	158	164
Smectic-nematic temperature/°C	223	250
Clearing temperature/°C	327	317
Molecular weight/g mol ⁻¹	403	431

The chemical formulas of the LLCs are shown in Figure 1 and their molecular weight characteristics, transition temperature and other physical properties are summarized in Table I.

Small angle light scattering

Blends of various compositions were prepared by solution casting. Thin as-cast films of the blends were completely transparent for weight fractions of LLC less than 10%. More quantitative studies of the miscibility were carried out using small angle laser light scattering (SALS) for liquid crystals contents of 1, 2, 4, 6, 8, and 10% by weight. The desired amounts of PC and LLC were dissolved in chloroform and stirred for 4 h. The samples were dried in a vacuum oven at 40°C for 24 h. A 5 mW He/Ne laser ($\lambda = 632.8$ nm) was used as the incident light source. Samples with a thickness ~ 0.1 mm were placed on a LINKAM hot stage, and heated at a rate of 3°C/min from 50–350°C. The SALS pattern was captured by a CCD camera, mounted on an arc between 7° and 42°, which corresponds to scattering vectors ranging from $q = 2.08 \times 10^{-4} \text{ \AA}^{-1}$ to $1.11 \times 10^{-3} \text{ \AA}^{-1}$. The data were analysed using Image-Pro Plus 3.0.

Rheological measurements

The samples for rheology measurements were prepared by solution casting in a common solvent. The amounts of LLCs used in the blends were 1, 2, and 5% by weight. Note that, as will be discussed in the following section, these compositions are inside the miscible regime from the light scattering results. The PC and LLC were dissolved in chloroform at 14% w/v. and stirred for 4 h. The solvent was then slowly evaporated at room temperature for 24 h. To remove residual solvent, the samples were further dried in a vacuum oven at 40°C for 3 days. The blends were prepared as 1 mm thick discs by compression moulding at 255°C. The samples were removed from the stainless mould prior to the rheological measurements.

The rheological properties of pure polycarbonate and blends were firstly measured using a TA Instruments AR2000. Parallel plates with a diameter of 25 mm were used to measure the shear viscosity as

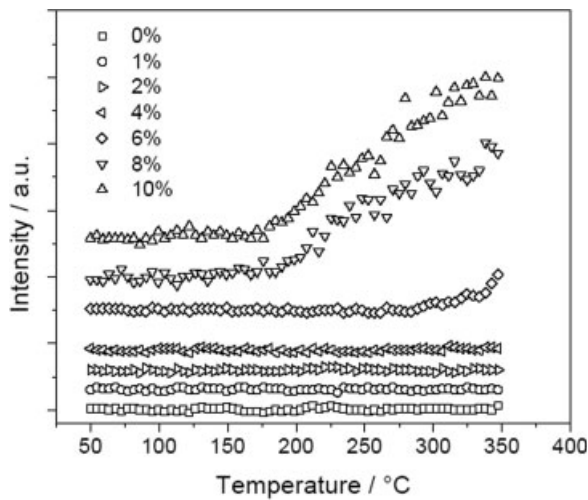


Figure 2 Temperature dependence of the intensity for PC/CBC33 blends, with varying CBC33 compositions by weight (see legend), at $q = 0.000950 \text{ \AA}^{-1}$ and a heating rate of $3.0^\circ\text{C}/\text{min}$. Each curve is shifted vertically for clarity.

function of shear rate and the oscillatory shear flow properties as a function of angular frequency. To confirm the viscosity behavior is real and reproduc-

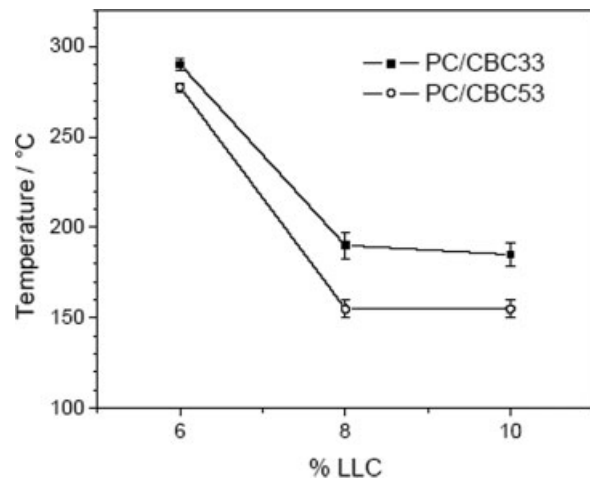


Figure 3 Cloud point curves of PC/LLC determined by small angle light scattering technique.

ble, a HAAKE Rheostress 600 was chosen to measure the blend viscosity. Parallel plates with a 20 mm diameter were used to measure the oscillatory shear flow with increased and then decreased angular frequency on the same specimen.

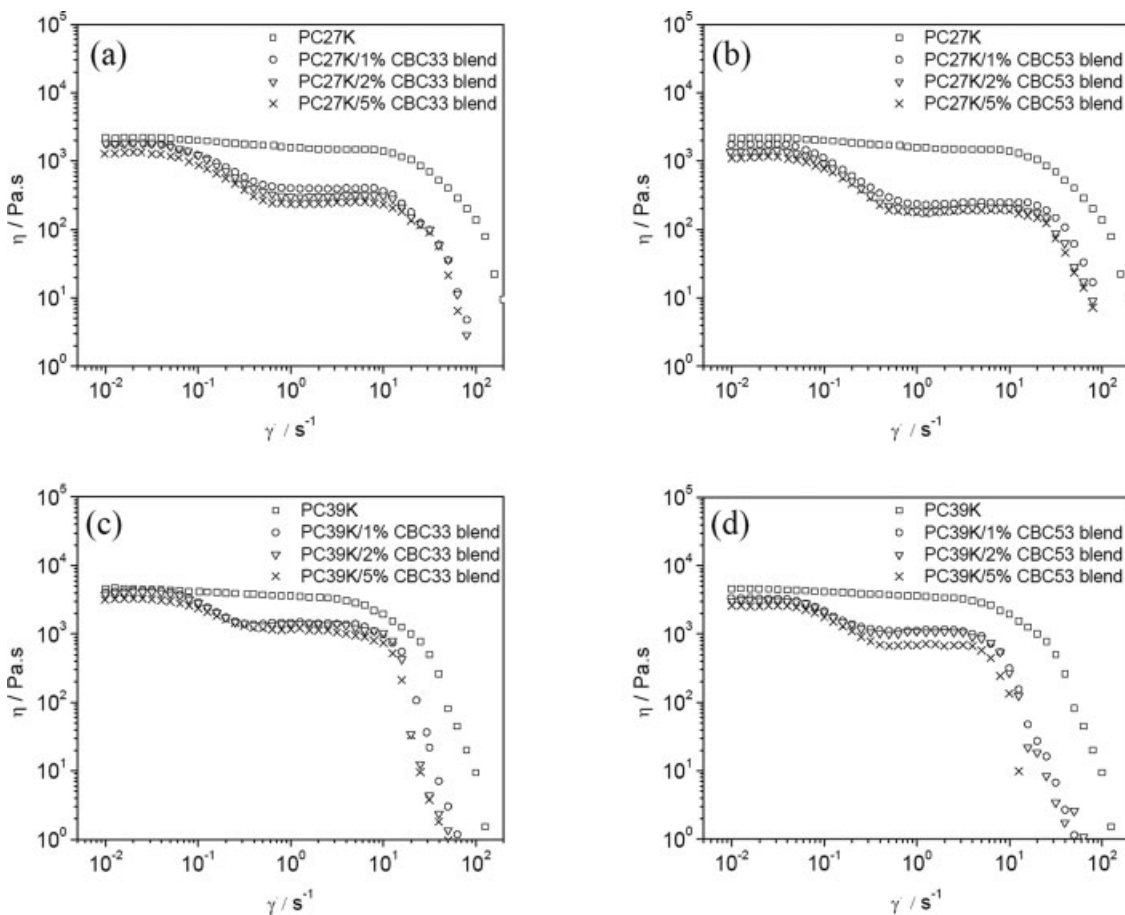


Figure 4 Steady shear viscosity of (a) PC27K/CBC33 blends, (b) PC27K/CBC53 blends, (c) PC39K/CBC33 blends, (d) PC39K/CBC53 blends, all measured at 255°C .

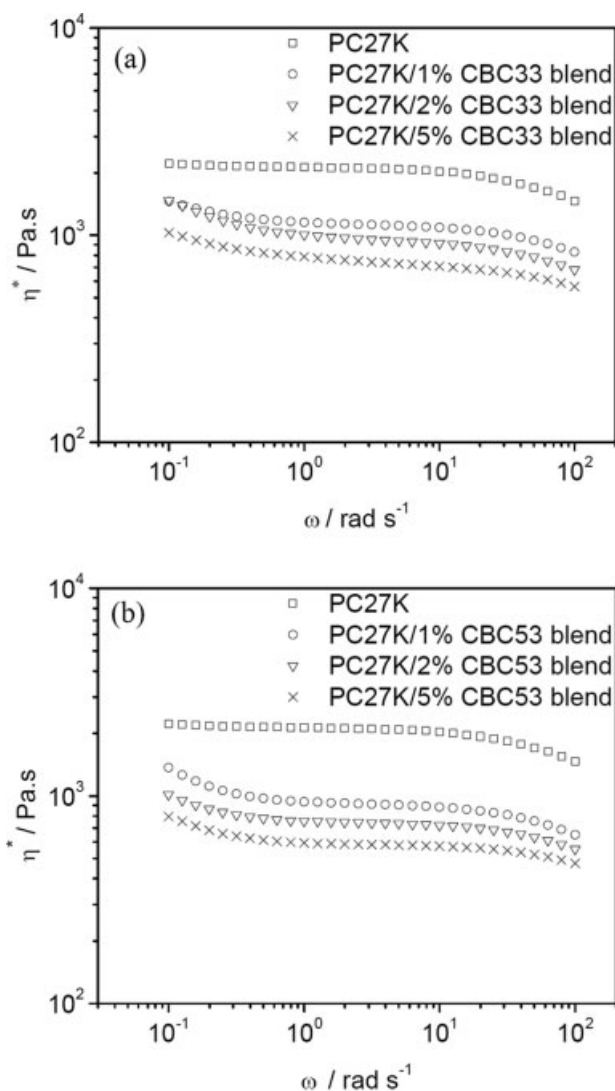


Figure 5 Complex viscosity of (a) PC27K/CBC33 blends, (b) PC27K/CBC53 blends at 255°C.

RESULTS AND DISCUSSION

Phase behavior

The intensity of the scattered light as a function of temperature indicate that the PC/LLC blends are miscible for weight fractions of LLC less than 6% over the entire observed temperature range. In contrast, LLC weight fractions of 6, 8, and 10% show partial miscibility with the PC. When phase separation occurs, if the two different phases have different refractive indices, there is an increase in the scattered intensity. The partially miscible blends, which are initially clear, become cloudy after heating, indicating lower critical solution temperature (LCST) behavior. The temperature at which the scattered intensities start to increase, as shown in Figure 2 for the scattering vector, $q = 9.5 \times 10^{-4} \text{ \AA}^{-1}$, is defined as the cloud point, T_c . Normally, the observed cloud

point temperatures are dependent on the heating rate. The faster the heating rate, the higher the apparent cloud point temperature is observed. However, our phase separation study is aimed to find the concentration limit of LLC that is miscible with the polycarbonate. The heating rate applied in this study is enough for this purpose. From the implication we are confident that at the temperatures and concentrations of interest to us, the blends are miscible. The resultant cloud point curves for LLC/PC blends are shown in Figure 3.

Rheological behavior

The shear viscosity, η , as a function of shear rate, $\dot{\gamma}$, for the three blends and for the pure PC at a fixed temperature of 255°C and the range of shear rates employed, from 1×10^{-2} to $1 \times 10^2 \text{ s}^{-1}$, are shown in Figure 4. It can be seen that all the blends exhibit

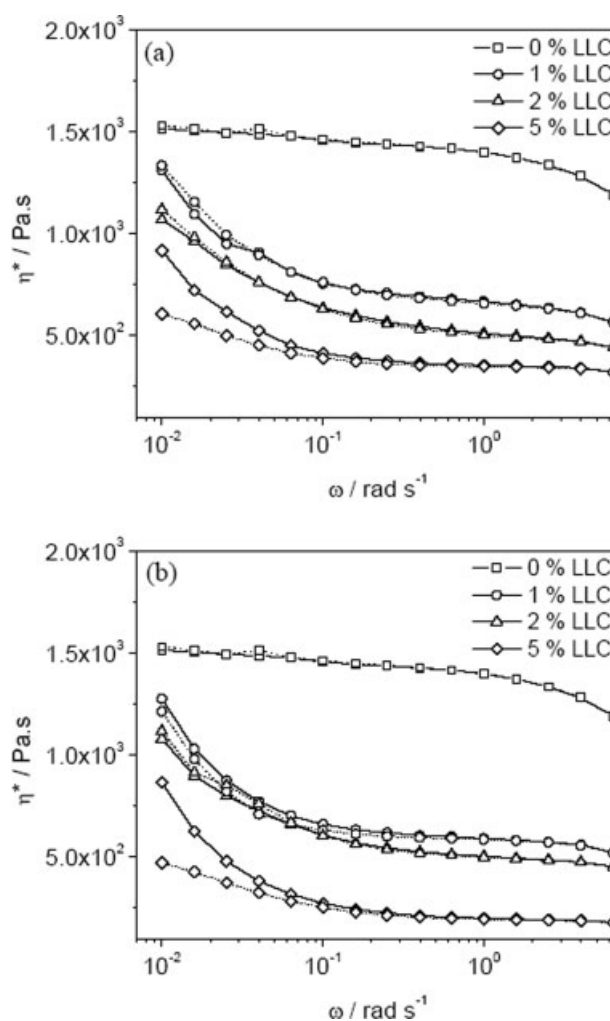


Figure 6 Complex viscosity of (a) PC24K/CBC33 blends, (b) PC24K/CBC53 blends at 255°C. Straight lines represent increased angular frequency, and dash lines represent decreased angular frequency.

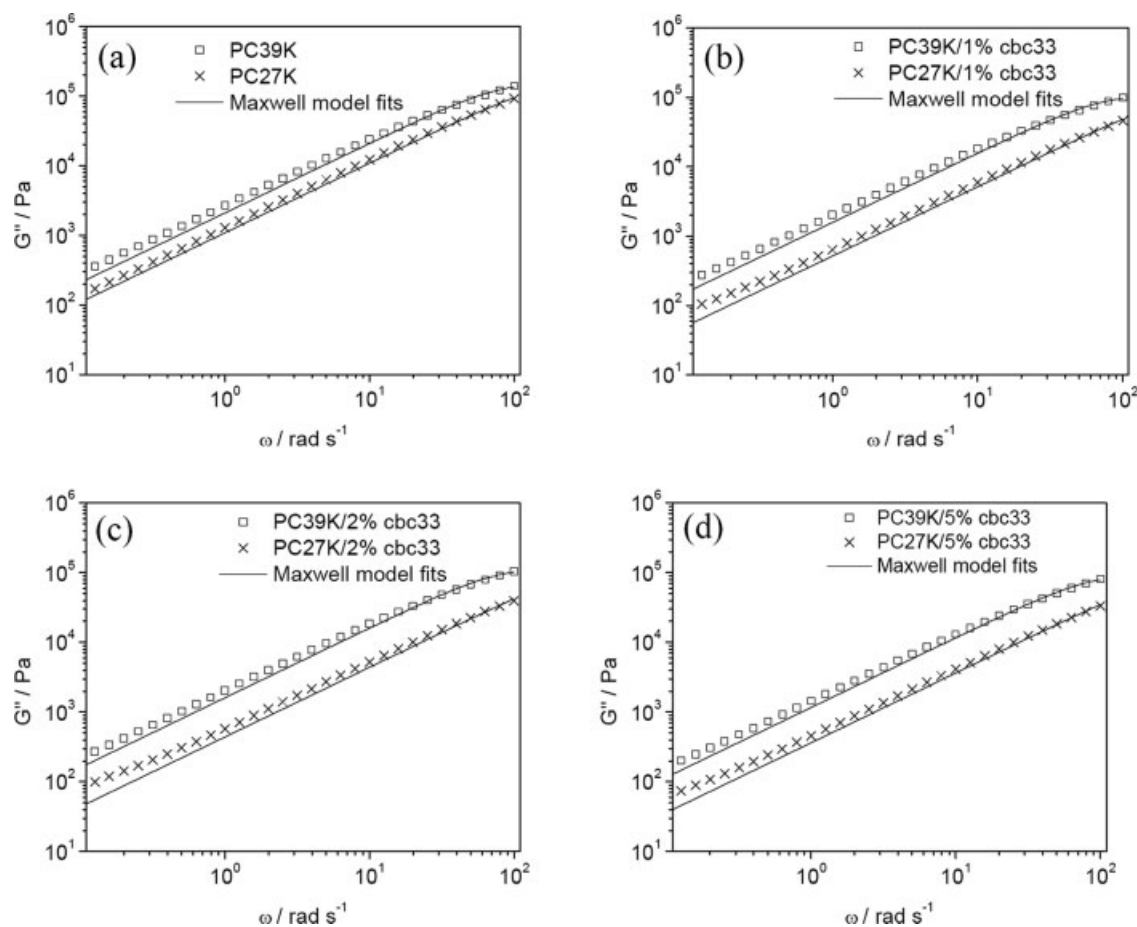


Figure 7 Loss modulus plotted and Maxwell model fits of (a) PC39K, PC27K (b) PC39K/1%CBC33, PC27K/1%CBC33 (c) PC39K/2%CBC33, PC27K/2%CBC33 (d) PC39K/5%CBC33, PC27K/5%CBC33 at 265°C.

four regions of viscosity behavior. At low shear rates, from $1 \times 10^{-2} \text{ s}^{-1}$ to $\sim 5 \times 10^{-2} \text{ s}^{-1}$, the melt viscosity of pure PC and the blends are very similar. At higher shear rates, all blends undergo clear shear-thinning, presumably as a consequence of the alignment and resultant anisotropic properties as Onogi and Asada described for liquid crystals and LCPs.²² The pure PC only exhibits two rheological regimes, as expected for entangled polymer melts. An abrupt reduction in shear viscosity of the blends was observed with only 1% by weight LLC, whilst the 2% and 5% LLC blends show a smaller decrease compared with the impact of 1% LLC, relative to the LLC content increase. As can be seen from comparison of Figure 4(a,c) and 4(b,d), the LLCs have a greater impact on the viscosity of the lower molecular weight PC. Similar characteristics were found for both types of LLC. However, CBC53 decreases the melt viscosity of the blends slightly more than the CBC33. This may be due to a tendency of the CBC53 to undergo greater alignment in a shear flow, due to its slightly greater length.

The storage modulus, G' , loss modulus, G'' , and dynamic complex viscosity, η^* , were measured as a

function of angular frequency, ω , from 0.1 to 100 rad/s at three different temperatures, 255, 260, and 265°C. Examples of η^* versus ω for pure PC and the blends are shown in Figure 5. The influence of LLC on the complex viscosities of the blends was similar to the influence on the steady shear viscosity, with the frequency dependent viscosity decreasing as LLC concentration increased. The frequency dependency of the complex viscosity of each of the blends is clearly different from that of pure PC, due to the induced alignment of the LLC. CBC53 decreased the complex viscosity of the blends by more than the CBC33, and the most pronounced decrease in viscosity was observed upon addition of only 1% by weight LLC. Further increases in LLC content further reduced the viscosity but again by a lesser relative extent.

From these results, we deduce that the orientation of the LLC, which is isotropic in the quiescent blend, becomes anisotropic under shear. From observation there is no migration to the surface of the melt polymer: the blends remain transparent, implying miscibility at a molecular level.²³ This is in contrast with normal lubricants, which are likely to phase separate

at the molecular level. This conclusion is further supported by the increase in mobility with LLC content observed in phase separation experiments.¹⁹

To confirm that it is the orientation of the LLC that causes viscosity reduction, and not the migration of LLC to lubricate the metal, angular frequency sweeps (increased and then decreased angular frequency experiments) in the oscillatory shear mode were performed. At a fixed temperature of 255°C, the angular frequency was increased from 1×10^{-2} to 10 rad/s, then after a hold (no oscillation) for 3 min, the angular frequency was decreased from 10 to 1×10^{-2} rad/s. Figure 6 shows the complex viscosity of the blends during both increasing and decreasing angular frequency sweeps. Pure PC, 1% and 2% LLC blends show completely reproducible behavior over the entire angular frequency range. In the case of 5% LLC blends the complex viscosity below 1×10^{-1} rad/s does not return to the original viscosity although above the frequency 1×10^{-1} rad/s, the viscosity shows perfect recovery. This behavior confirms our claim that it is the orientation of the LLC that is responsible for the decrease in viscosity, at least for the 1% and 2% LLC blends. If the LLC is lubricating the metal plates at the higher frequencies at which we observe the viscosity reduction in the blends, then we would expect that the two curves would not overlay each other since the lubrication effect would remain. Whilst there may be some lubrication effects for the 5% LLC, we note that the dramatic decrease in viscosity is observed already for the lower concentration LLCs.

The shear modulus of the PC and the blends was estimated by fitting the loss modulus and storage modulus to a single relaxation time Maxwell model,^{24,25}

$$G' = \frac{G_0 \omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (1)$$

and,

$$G'' = \frac{G_0 \omega \tau}{1 + \omega^2 \tau^2} \quad (2)$$

The loss modulus along with the fits to the Maxwell model for PC39K, PC27K, and their blends with CBC33 are shown in Figure 7. The lower molecular weight PC has a lower loss modulus than the high molecular weight, as would be expected. The Maxwell model fits the results reasonably well, enabling a simple qualitative comparison between blends with different LLC concentrations. It is not too surprising that the Maxwell model provides a reasonable description of the low frequency data, since PC has a very low entanglement molecular weight²⁶ of ~ 2000 g/mol, and hence the polymers studied in

this work are highly entangled. The reptation model²² predicts that the relaxation of stress is well described by a single relaxation time process, which is the basis of the phenomenological Maxwell model. The shear modulus estimated from Maxwell model for PC and PC/LLC blends at 1, 2, and 5% LLC concentration at various temperatures is shown in Figure 8. It can be seen that the shear modulus of the blends decreases with increasing LLC concentration and temperature. The most sensitive change in the shear modulus was upon addition of 1% LLC. The properties at various temperatures of different LLC types showed the same trend. The CBC53 blends have a lower shear modulus than the CBC33 blend, which corresponds to the viscosity results as shown in Figure 4. It is clear that CBC53 has a higher potential to reduce the viscosity in the plateau region at the intermediate shear rates than CBC33. Figure 9 shows the relaxation time of PC and PC/LLC blends. It can be seen that LLC has a more significant effect on the relaxation time of the low

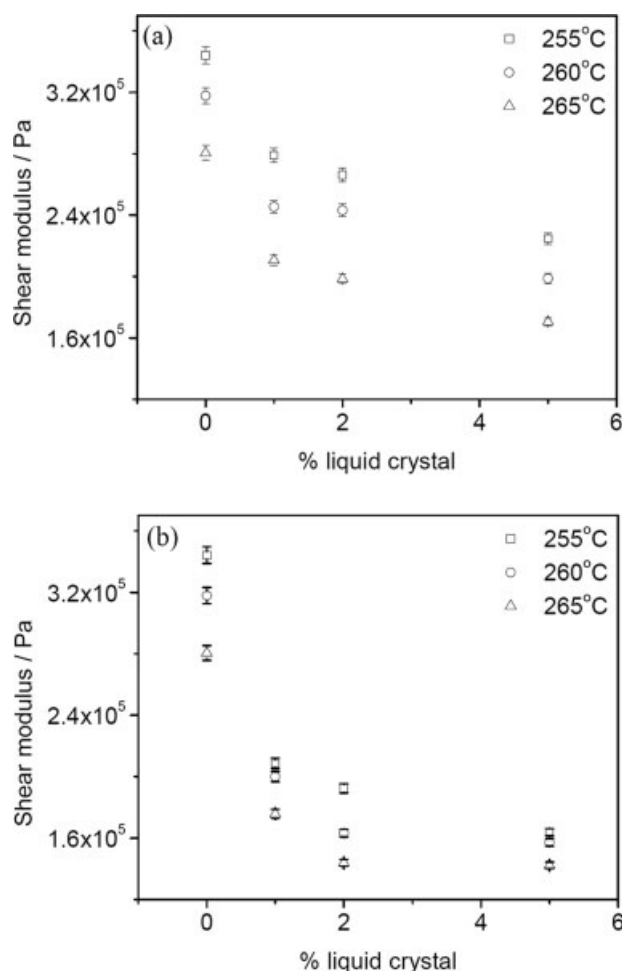


Figure 8 The shear modulus of (a) PC and PC/CBC33 blends, (b) PC and PC/CBC53 blends at 1, 2, and 5% liquid crystal concentration.

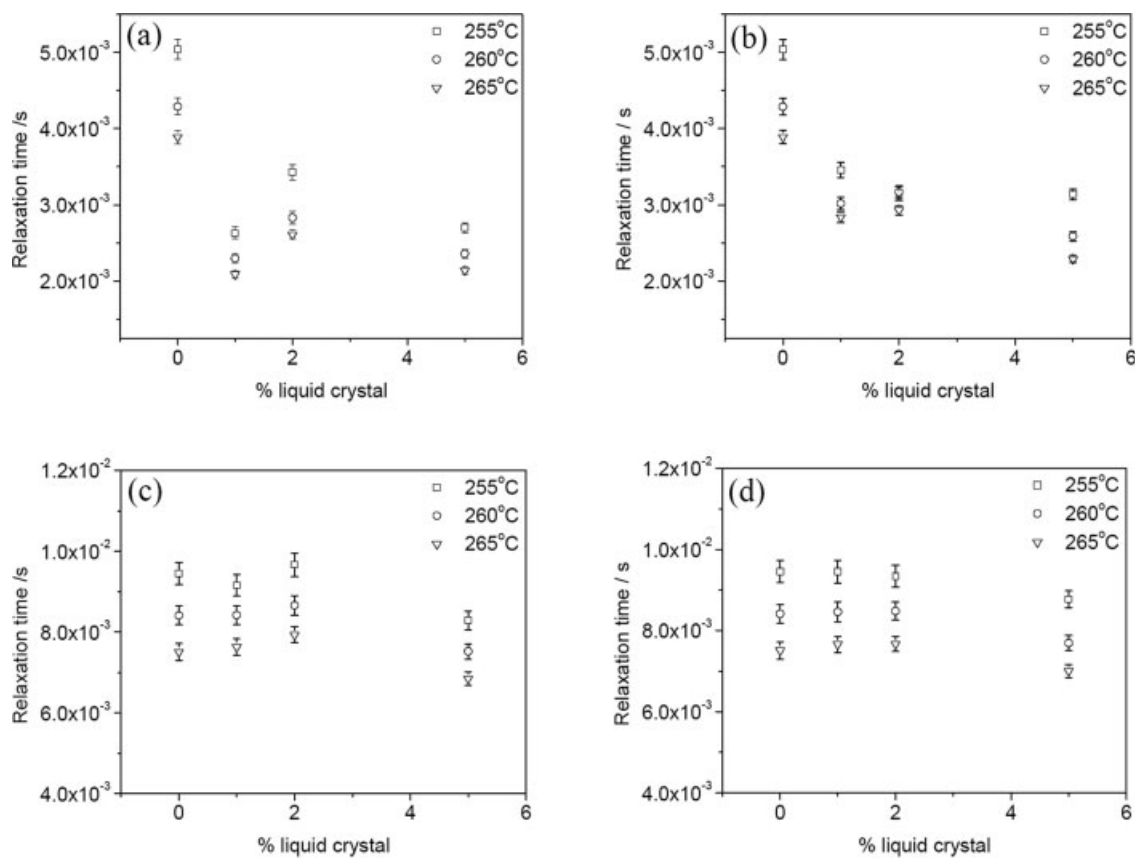


Figure 9 The relaxation time of (a) PC27K/CBC33 blends, (b) PC27K/CBC53 blends, (c) PC39K/CBC33 blends, (d) PC39K/CBC53 blends, at 1, 2, and 5% liquid crystal concentration.

molecular weight PC than the high molecular weight PC. For the lower molecular weight PC, the relaxation time decreases with LLC concentration, whilst, apart from a slight decrease at the highest LLC concentration, there is no clear dependence of the relaxation time on LLC concentration for the higher molecular weight PC. This can be explained on the basis of the modified form of the reptation model for mixtures²⁷; the greater the difference between the relaxation times of the individual components (polymer and LLC), the smaller the impact of the diluent on the apparent longest relaxation time, so for the higher molecular weight polycarbonate, the only observable impact of the diluent on the frequency spectrum, at the frequencies we are able to access, is upon the modulus, as observed.

CONCLUSIONS

We have shown that the addition of low molar mass liquid crystal to polycarbonate inside the miscible regime beneficially affects, from the viewpoint of processing, the rheological behavior. Even a very small concentration of LLCs in the polymer is sufficient to cause viscosity reduction in both shear flow

and oscillatory experiments. From the results it can be seen that LLCs have a greater impact on the rheological properties of the lower molecular weight PC than the high molecular weight PC. Indeed the most dramatic impact on the flow properties is observed upon addition of only 1% by weight liquid crystal. This is a consequence of the anisotropy of the LLC in the presence of flow. Thus, the melt viscosity of the blends can be decreased at low concentration of LLCs. The angular oscillatory shear loops of the blends show the reproducibility of the viscosity as the frequency is increased and then decreased. Thus, the anisotropy of the LLC is believed to be responsible for the decrease in the melt viscosity of polycarbonate, rather than lubrication at metal interface as can be found upon addition of typical small lubricant molecules.

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