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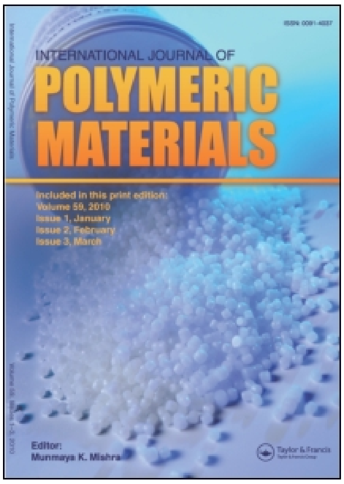

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Fang Shi[a]
[a] Department of Mat. Sci. & Engr., Zhejiang University, Hangzhou, P.R. of China

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# Miscibility and Rheology of In-situ Composite Materials of Thermoplastics with Thermotropic Liquid Crystalline Polymers II

FANG SHI

*Department of Mat. Sci. & Engr., Zhejiang University, Hangzhou, 310027, P.R. of China*

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The miscibility of the polymer blends of thermoplastics (TPs): polycarbonate (PC) and polyethersulfone (PES) with thermotropic liquid crystalline polymers (TLCPs): KU9221 and KU9231 was studied using the DSC experiment. Each TP/TLCP blending system in this paper is mainly immiscible. The viscosity properties of the TLCP blends were analyzed in detail.

KEY WORDS Viscosity, miscibility, polymer blends, liquid crystalline polymers.

## INTRODUCTION

Due to their specific chemical structures, high strength, high modulus, low viscosities, good processibility and other advantageous mechanical properties, the new generation reinforcing polymer composites—Thermotropic Liquid Crystalline Polymer Blends—are now paid a great deal of attention. By blending TLCPs with various engineering thermoplastics, one can obtain in-situ reinforcing composites. These polymer composites overcome the defects of the difficult processibility and poor mechanical properties of classic composite materials. When processed with resin matrix at high temperature, TLCP's microdomains can be transformed and oriented to form microfibers in the matrix. When cooled, these microfibers behave as the reinforcing phase of the resin matrix.[1,2] It has been proved that the proper miscibility and proper viscosity ratio of the TLCPs and the matrix is the key factor to form ideal TLCP microfibers during processing.[19] It is very important, therefore, to study interface property and the viscosity variation of the TLCP blends during processing.[19–23]

## EXPERIMENTAL

### Materials

The TLCPs (marked as KU9221 and KU9231) used in this study were supplied by Bayer (Germany). Two kinds of polycarbonate (PC) were used: PC-A and PC-B

TABLE I

Mechanical data of the studied polymers

| | tensile | | bending | |
|---|---|---|---|---|
| | $E_p$(GPa) | $\sigma_{bb}$(MPa) | $E_p$(GPa) | $\sigma_{bb}$(MPa) |
| PC-A | 2.2 | 55 | 2.0 | 80 |
| PC-B | / | 68 | / | 98 |
| PES | 2.5 | 70 | 2.3 | 100 |
| KU9221 | 20 | 200 | 10 | 180 |
| KU9231 | 17 | 160 | 12 | 150 |

(domestic products with average molecular weights of 38,000 and 29,800, respectively). The polyethersulfone (PES) in the form of powders was supplied by Jilin Univ. (PRC). Table I lists some important mechanical properties of these materials. In this work, KU9231 and PES were blended with a weight ratio of 1:9 and 3:7, KU9221/PC-A was 1:4, KU9221/PC-B was 1:9 and 1:4. All experimental materials were dried at the proper temperature before the experiments commenced.

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### DSC Analysis

We used Perkin Elmer Co. DSC-2C. The heating rate was 10 (20)°C/min and the cooling rate was 10°C/min. The graduation was 5 mcal/s. The temperature range was 40–400°C. The experiment was done under the condition of He atmosphere. We first obtained the DSC heating curve using heating rate of 10°C/min. We then determined the DSC cooling curve with cooling rate of 10°C/min, followed by a second determination of the DSC heating curve this time with a heating rate of 20°C/min.

### Rheological Measurements

Rheological properties were measured by the capillary rheometer of Instron 3211 and XLY-II (for PC-A/TLCP system only). The experimental shear rate was 3.5433–118.1 l/s. The experimental temperature for PES system was 310°C, for PC-A system is 240–310°C, for PC-B system was 240–270°C.

## RESULTS AND DISCUSSION

### 1. DSC Experiment

Figure 1 shows the DSC curves of PES, KU9231, PES/KU9231 (9:1), PES/KU9231 (7:3). The measurements indicated that different heating history of materials results

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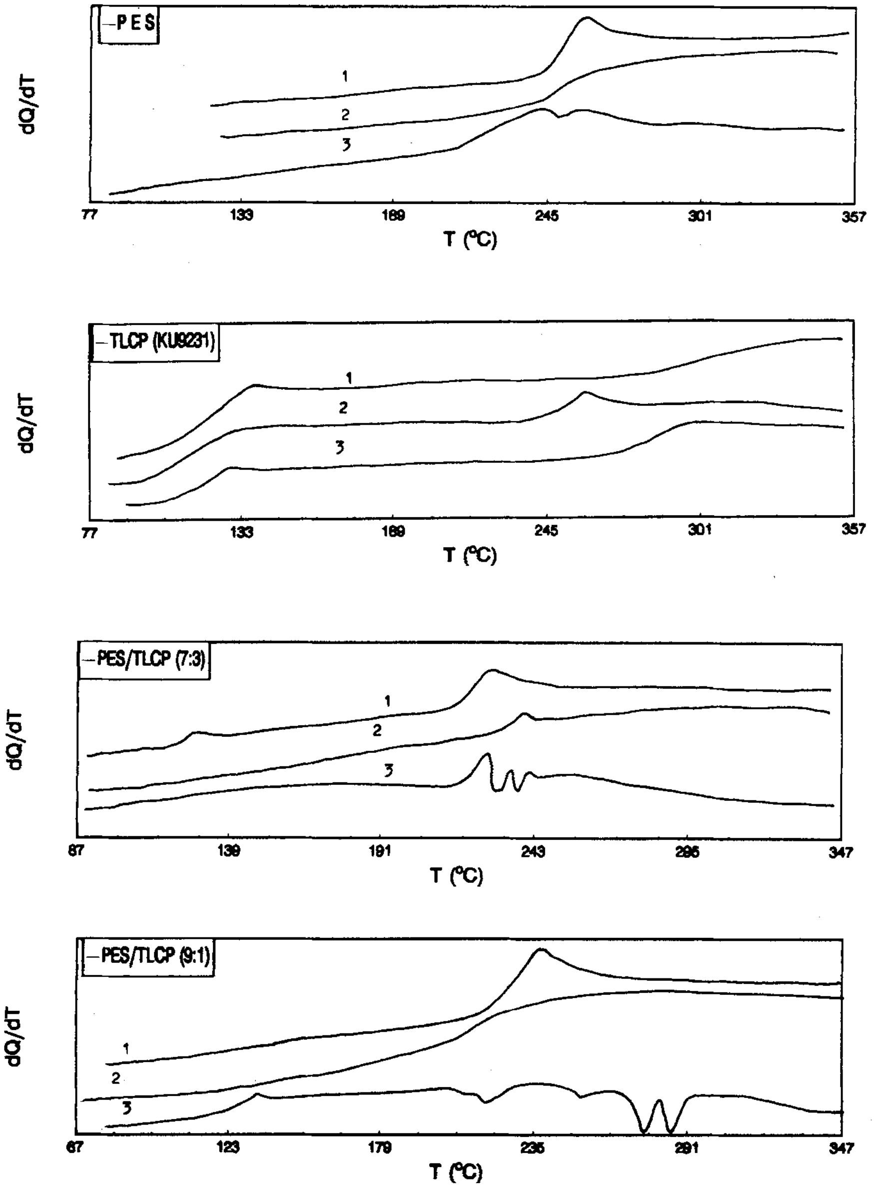

FIGURE 1 DSC curves: 1) heating 10°C/min, 2) cooling 10°C/min, 3) heating 20°C/min.

in different DSC curves.[7,8] The glass transition temperature of PES is near 225 ± 3°C and its absorptive peak appears near 233°C. The glass transition temperature of KU9231 is near 118 ± 3°C and its absorptive peak shows smoothly between 267°C and 355°C. Its melting point is 310°C.[9] The blend PES/KU9231 has two small peaks near 128 ± 2°C and 229 ± 3°C, respectively. The peak of higher temperature possibility corresponds to the absorptive peak of PES, but the one of lower temperature is very indistinct and, for the blend 9:1, there are two small joined

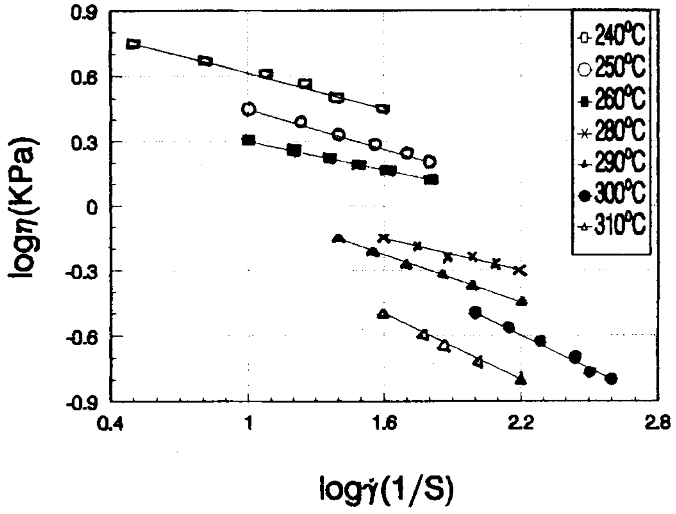

FIGURE 2 The rheological curve of melt PC-A/KU9221 (4:1).

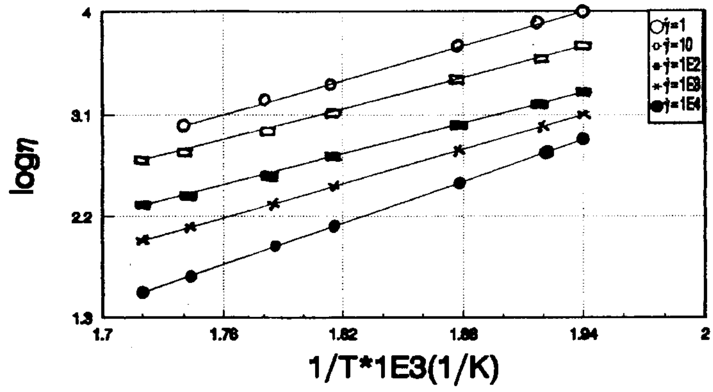

FIGURE 3 The viscosity of melt PC-A/KU9221 (4:1) under iso-shear rate as a function of the temperature.

exothermic peaks on its first heating curve. Unfortunately, the mechanism is not clear yet. On the first heating curves of the blends, only 225 ± 2°C corresponds to the glass transition temperature of PES. But on their cooling and second heating curve, two glass transitions appear which are slightly below the pure (for system 9:1, they are 97 ± 2°C and 210 ± 3°C; for system 7:3, they are 117 ± 5°C and 220 ± 5°C). This indicates that there is slight miscibility of two components. But the miscibility will decrease as the content of TLCP increases. The interface properties of the two components may also worsen.

## 2. Rheological Properties

Figures 2–11 show the results of the rheological measurements of the melts. Figures 2, 5, 7 and 10 indicate the melts belong to pseudo-plasticity. Under general testing

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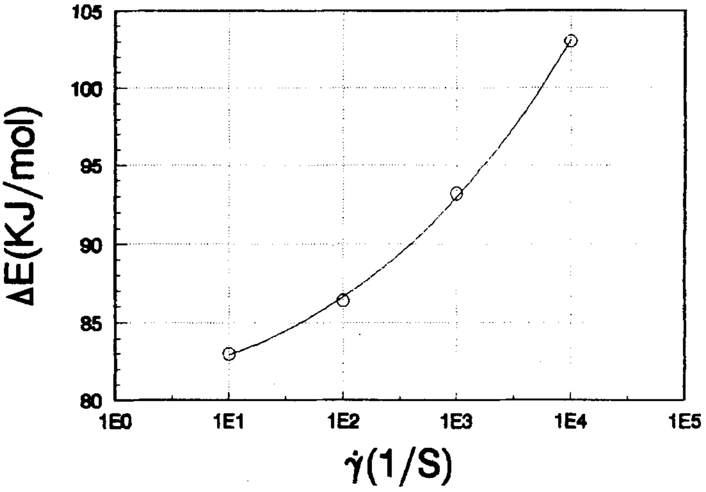

FIGURE 4 The flowing active energy of melt of PC-A/KU9221 (4:1) as a function of the shear rate.

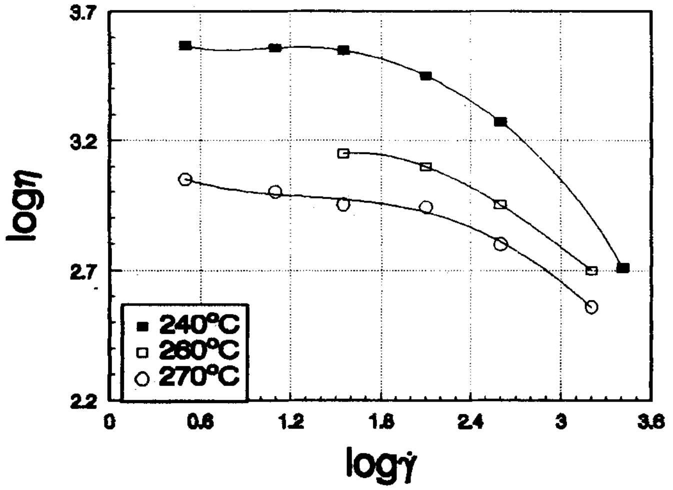

FIGURE 5 The rheological curve of melt PC-B.

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conditions, the melts of PC-A/KU9221 (4:1), KU9231, PES/KU9231 (9:1 and 7:3) tally with power law. Their exponents are 0.68 ± 0.04, 0.59 and 0.51 respectively. The other melts can be regarded as Newtonian fluid under lower shear rate range. The rheological curve of blend TLCP/PC-B is similar to that of pure PC, but the blend viscosity is lower and more sensitive to shearing. This result is in agreement with Reference 10. The rheological curve of blend TLCP/PES is similar to pure TLCP: the blend viscosity is also lower. However, while it is less sensitive to shearing than the blend, it is more sensitive than pure PES. Figures 3, 6 and 8 show the viscosity as a function of the reciprocity of temperature under the condition

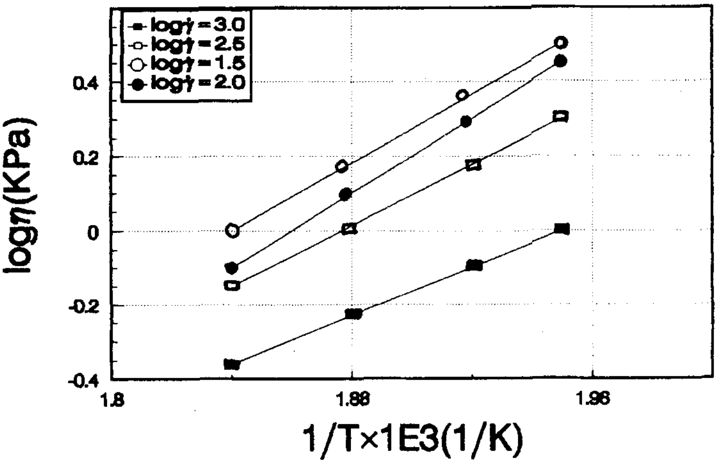

FIGURE 6 The viscosity of melt PC-B under iso-shear rate as a function of the temperature.

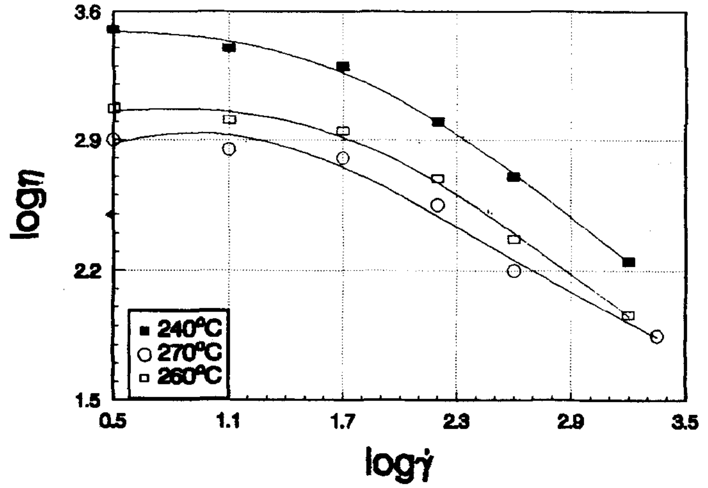

FIGURE 7 The rheological curve of melt PC-B/KU9221 (4:1).

of iso-shear rate. They indicate the viscosities of the melts of PC-A/KU9221 (4:1), PC-B and PC-B/KU9221 (4:1) decrease with the increase of temperature, corresponding to Arrhenius equation: $\eta = \eta_0^* \mathrm{EXP}(-\Delta E/RT)$.

Figures 4 and 9 show the relationship of $\Delta E$ and shear rate ($\Delta E$ is the flowing active energy of melts). They indicate $\Delta E$ is relative to shear rate. Figure 3 shows the $\Delta E$ of PC-A/KU9221 (4:1) decreases as the temperature is increased, contrary to the reaction of pure PC-B and PC-B/KU9221 (4:1).

According to Figures 5, 7, 10 and the results of Reference 11, when TLCPs are added to resin matrix the viscosities of the blends substantially decrease, even more than the viscosities of pure components. This does not agree with the general

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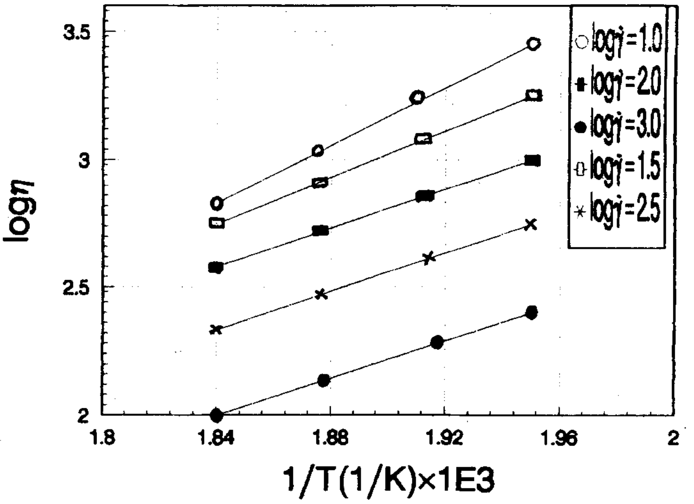

FIGURE 8 The viscosity of melt PC-B/KU9221 (4:1) under iso-shear rate as a function of the temperature.

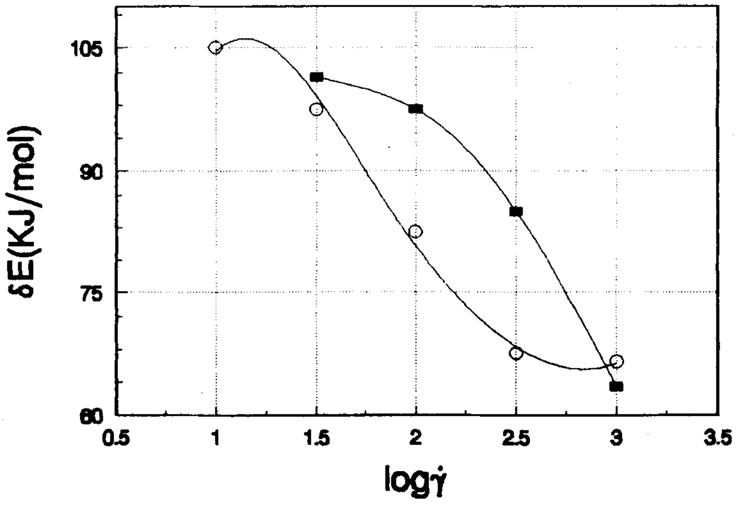

FIGURE 9 The flowing active energy as a function of shear rate of melt pure PC-B and PC-B/KU9221 (4:1).

additive law. In Figure 8, the viscosity of system PES/KU9231 decreases significantly when the shear rate is more than 16 l/sec at 310°C.[5]

Figure 12 indicates that the viscosities of blends decrease when the amount of TLCPs is increased, and are much lower than the viscosities of the two pure components. This result agrees with the system of PC/Veotral,[7] PES/TLCP,[11] PC/TLCP,[12] PEEK/TLCP[13] and PPO/TLCP.[14]

The abnormal change of viscosities was attributed to the lubrication of microfibers and microdomains of TLCPs.

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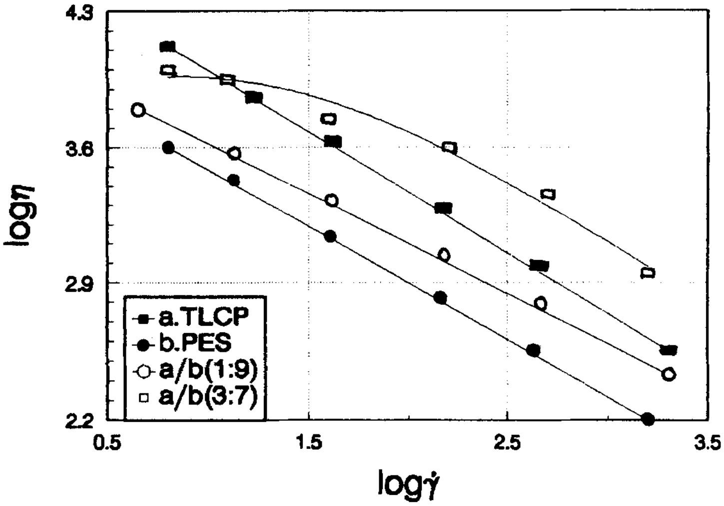

FIGURE 10 The rheological curve of melt PES/KU9231 system.

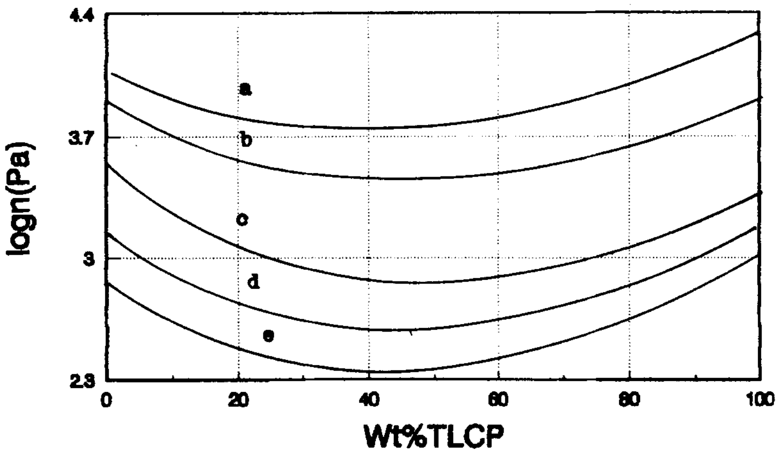

FIGURE 11 The viscosity and TLCP weight percent of melt PES/KU9231 under iso-shear rate.

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## CONCLUSIONS

1. The DSC experiment indicates that the two components in system PES/TLCP and PC/TLCP are not miscible.
2. The viscosities of melt KU9221 and KU9231 are very sensitive to shear rate and they are not typical Newtonian fluid. The viscosities of melt PC and PES barely change in the range of shear rate and they behave as Newtonian fluid.
3. The rheological curves of blend KU9221/PC-B and pure PC-B are similar, but KU9221/PC-B is more sensitive to shearing and its viscosity is lower than that of pure PC-B. When shear rate is over 16 l/sec, the viscosity of KU9231 is lower than that of PES. The rheological curves of blend KU9231/PES are similar to that

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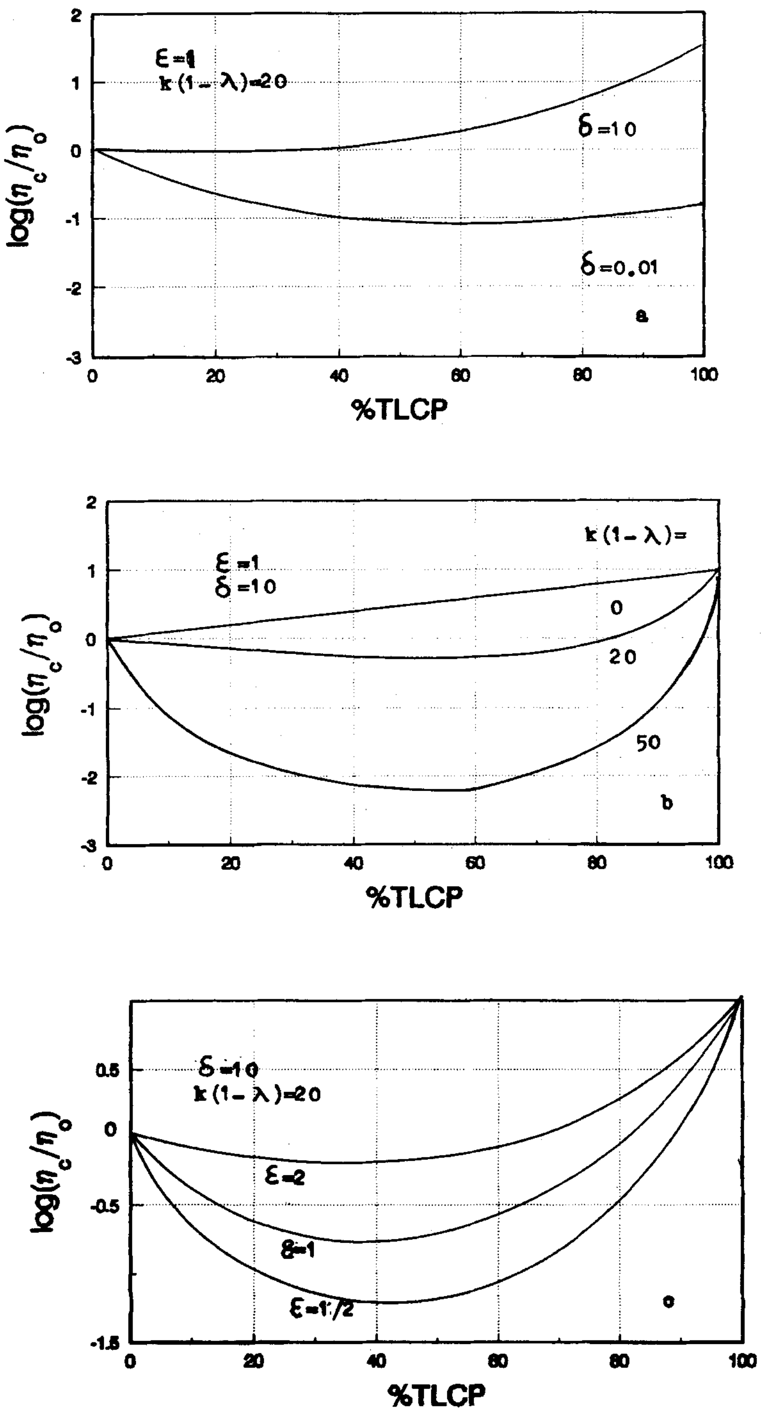

FIGURE 12 The viscosity of the blends at different parameters as a function of the volume content of TLCP.

of pure TLCP. The blend is less sensitive to shear rate than pure TLCP but more sensitive than pure PES. When the shear rate is increased, the viscosities of the two components will decrease, as will the ratio of the two viscosities.

4. In this work, the viscosities of blend PC-B/KU9221 and PES/KU9231 behave abnormally and are lower than that of the two pure components. The measurement indicates that the addition of TLCP to thermoplastics will effectively improve their processing properties.

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