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A Study of the Miscibility and the Rheological Properties of Thermotropic Liquid Crystalline Polymers in Thermoplastic Matrix

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By using FTIR and DSC, the interfacial property of the polymer blends of engineering thermoplastics (TPs): polycarbonate (PC) and polyethersulfone (PES) with thermotropic liquid crystalline polymers (TLCPs) was studied. The TLCP/TP blend systems in this paper are mainly immiscible. The viscosity properties of the TLCP/TP blends were analyzed in detail. The mechanism of the viscosity variation of the blends was discussed. Based on the assumptions given in this paper, the reasoned theoretical formula of the blends' viscosity can express the abnormal variation of the viscosity of the TLCP/TP blends well. The variation regularity of the viscosity of TLCP/TP blends during processing was analyzed in theory.

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

INTRODUCTION

The new kind reinforcing polymer composites, thermotropic liquid crystalline polymer blends are paid a great attention now, due to their specific chemical structures, high strength, high modulus, low viscosities, good processability and other good mechanical properties. By blending TLCPs with some engineering thermoplastics, one can obtain so-called in-situ reinforced composites. These polymer composites overcome the defects of difficult processability and poor mechanical properties of classical composite materials. When processed with resin matrix at high temperature, TLCP's microdomains can be transformed and oriented to form microfibers in their matrix. When cooled, these microfibers behave as a reinforcing phase of the resin matrix.^{1,2}

The interfacial property of the two components—TLCP and TP—is the important factor which can affect the shear-induced fibrillation of TLCP phase during processing and their mechanical properties.^{6,7} It has been proved that the poor

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miscibility and proper viscosity ratio of the TLCPs and the matrix are the key factors to forming ideal TLCP microfibrers during processing.¹⁹ Generally, when blending thermoplastics with classical reinforcing fibers and fillers, the viscosity of the blends will increase. But when TLCPs are blended in this way, the viscosity of the blends will decrease. Viscosity will continue to decrease with increasing TLCP content and processing temperature. In most cases, the viscosity of TLCP/TP blends is lower than that of both pure components. So, by blending thermoplastics with TLCPs, one can notably decrease the processing temperature, improve the rheological property, reduce the loss of energy and avoid the polymer decomposition during processing.¹⁹⁻²³

EXPERIMENTAL

Materials

The thermotropic liquid crystalline polymers (TLCPs) (marked as KU9221 and KU9231) used in this study were supplied by Bayer Co. (Germany). The two experimentally used polycarbonates (PC), PC-A and PC-B, are domestic products with average molecular weights of 38,000 and 29,800, respectively. The polyethersulfone (PES) was supplied by Jilin Univ. (PRC) in the form of powders. 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 proper temperature before experiments.

Miscibility Analysis

1. FTIR was done by Fourier Transform Infrared Spectrometer NICOLE 5DX.
2. DSC experiment

We used Perkin Elmer Co. DSC-2C. Heating rate was 10 (20)°C/min, cooling

TABLE I
Mechanical Data of the Studied Polymers

	tensile		bending	
	E_p (GPa)	σ_{bb} (MPa)	E_p (GPa)	σ_{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

rate was 10°C/min. The graduation was 5 mcal/s. The temperature range was 40–400°C. The experiment was done in the atmosphere of N₂. In the experiment we first tested the DSC heating curve with a heating rate of 10°C/min; second, the DSC cooling curve with a cooling rate of 10°C/min. Then the DSC heating curve was tested again with a heating rate of 20°C/min.

Rheological Measurements

Rheological properties were measured by the capillary rheometer of Instron 3211. Its diameter D is 1.27 mm, length L is 25.56 mm. The experimental shear rate is 3.5433–118.1 1/s. The experimental temperature for PES system is 310°C, for PC-A system is 240–310°C, for PC-B system is 240–270°C.

RESULTS AND DISCUSSION

1. Interfacial Property and Miscibility

Figure 1 shows the infrared (IR)-transmission spectra of pure polymer PC, PES and in blends of TLCP/TP. By removing the IR spectrum of pure TLCP from that of the blends, one obtains the IR spectrum of PC and PES in blended systems. Comparing the subtractively obtained IR spectrum of PC and PES with that of pure PC and PES, we found almost no difference between the two spectra, no new transmission peak, and no variation of peak form and peak position. This indicates that no chemical reaction takes place on the interface between PC, PES and TLCP, and their interfaces are almost immiscible.

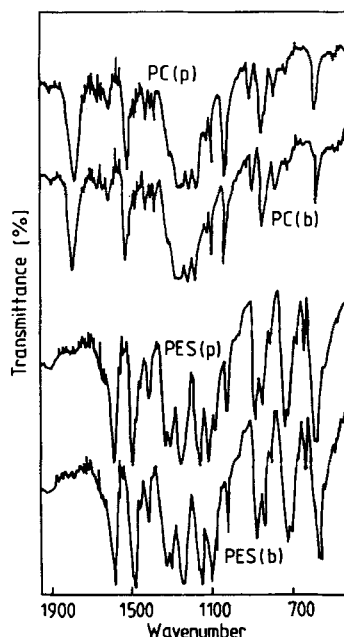


FIGURE 1 FTIR-transmittance of pure PC and PES compared with themselves in TLCP/TP blends.

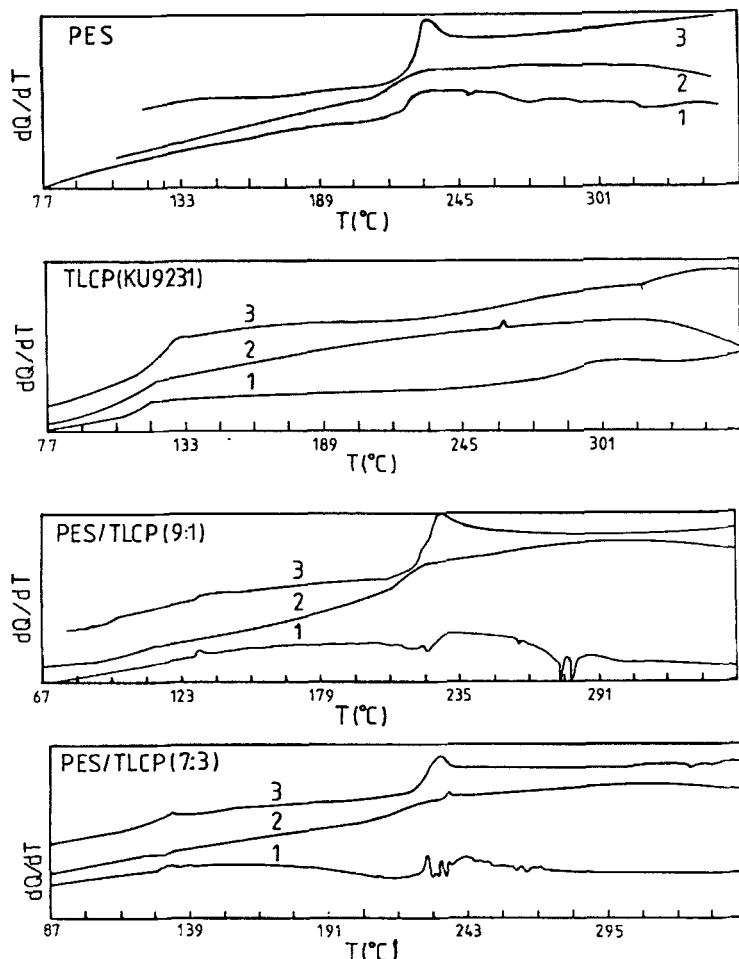


FIGURE 2 DSC thermogram of PES, TLCP(9231) and their blend: 1) heating 10°C/min; 2) cooling 10°C/min; and 3) heating 20°C/min.

The same conclusion can also be obtained by using the differential scanning calorimeter (DSC). Figure 2 gives the DSC thermogram of PES, TLCP(KU9231) and their blends. The measurements indicate that different thermo-history of materials results in different DSC thermogram.^{7,8} The glass transition temperature of PES is near 225°C; its endothermal peak appears near at 237°C. The glass transition temperature of TLCP is near 120°C and its endothermal peak shows smoothly between 267°C and 355°C. The blend TLCP/PES has two small endothermal peaks near 128°C and 229°C, respectively. The peak of higher temperature corresponds to the endothermal peak of PES, while the one of lower temperature corresponds to the T_g of TLCP. It indicates that the two components are mainly immiscible. But on their cooling and second heating curve, two glass transitions appear which are slightly below that of the pure (for system 9:1, they are near 97°C and 216°C; for system 7:3, they are near 117°C and 220°C). It indicates that there is still a slight miscibility of two components. But the miscibility will decrease with increasing

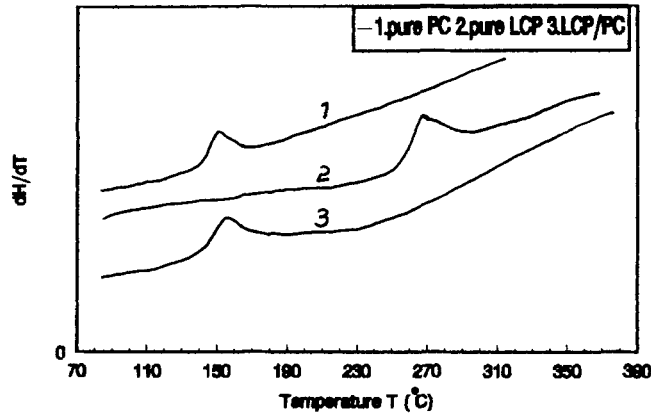


FIGURE 3 DSC thermogram of PC, TLCP(Ku9221) and their blend.

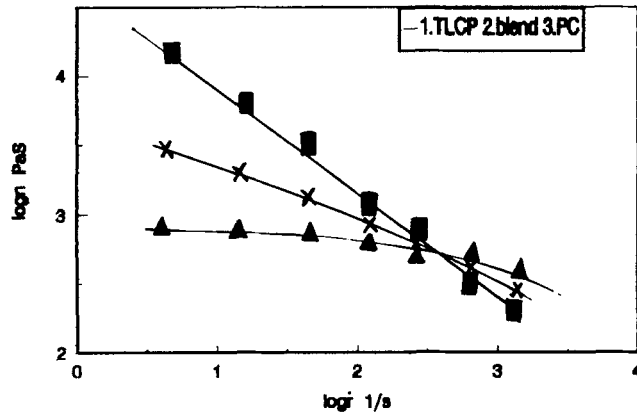


FIGURE 4 The rheological curve of melt PC, TLCP(Ku9221) and their blend.

the content of TLCP. The interfacial properties of the two components will also worsen.

Figure 3 shows the DSC thermogram of PC, TLCP(Ku9221) and their blend. The glass transition temperature of PC is near 155°C, the endothermic peak of TLCP is near 270°C. In this figure, the glass transition temperature of PC remains exactly at the same temperature as for the blend, whereas the endothermic peak of pure TLCP disappears in the DSC thermogram of the blend. This may also indicate that in the blend of TLCP/PC, the interface of two components is almost immiscible.

From the above analysis, it is tentatively concluded that the blend TLCP/PC and TLCP/PES are almost immiscible and it agrees with the basic condition of in-situ shear induced fibrillation during processing.

2. Rheological Properties and Variation Mechanism

Figure 4 gives the rheological curve of TLCP(Ku9221), PC and their blend. It shows that the viscosity of TLCP decreases linearly and markedly with increasing

shear rate. This indicates that the viscosity of TLCP is very sensitive to shear rate. Its macromolecular chains become likely to orientate along the flow direction with increasing shear rate, and its viscosity decreases strongly. The viscosity of the TLCP/PC blend is between that of the two pure components. The three curves intersect at $\dot{\gamma} = 10^3$. When $\dot{\gamma} < 10^3$, the viscosity of blend is higher than that of PC, but lower than that of TLCP, when $\dot{\gamma} > 10^3$, it is vice versa.

Figure 5 shows the viscosity of blend TLCP/PC as a function of the reciprocal of temperature under the different shear rate, $\dot{\gamma}$ from 1 to 10^4 l/s. These curves are parallel to each other and decrease linearly with increasing temperature. It agrees with Arrhenius equation: $\eta = \eta_0 \cdot \exp(-\Delta E/RT)$. The calculated flowing active energy is about 70 KJ/mol.

Figure 6 shows the rheological curve of TLCP(Ku9231), PES and their blend at 310°C . Figure 7 shows the viscosity of TLCP/PES as a function of TLCP's content under different shear rate. Figure 6 indicates that the viscosity of TLCP decreases strongly with increasing shear rate, but that of PES decreases smoothly. The two curves intersect at $\dot{\gamma} = 20$ l/s. The viscosity property of the blend TLCP/PES is different from that of the above discussed TLCP/PC system in that it does not agree with additive law. At the same condition, the viscosity of the blend TLCP/

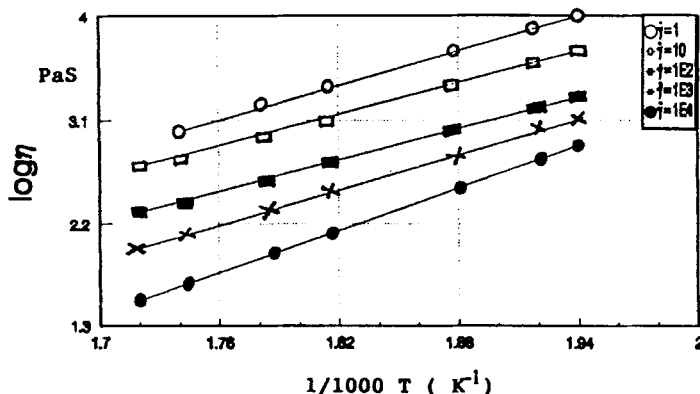


FIGURE 5 The viscosity of melt PC/TLCP(Ku9221) as a function of temperature under different shear rate.

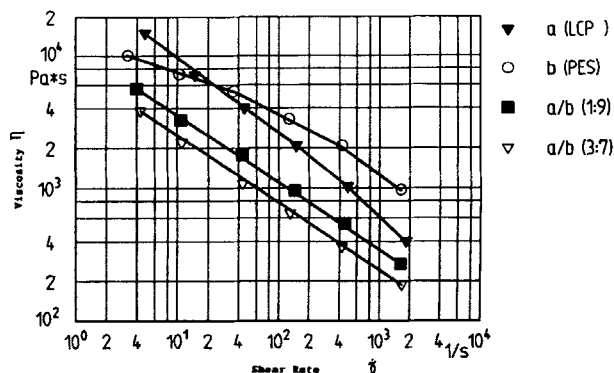


FIGURE 6 The rheological curve of melt PES, TLCP(Ku9231) and their blend.

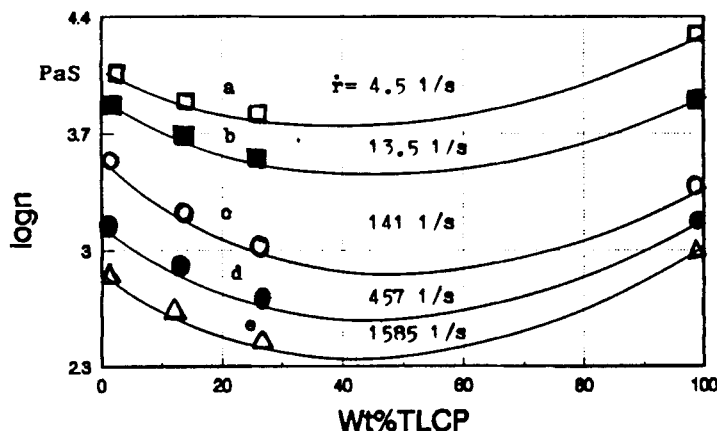


FIGURE 7 The viscosity of TLCP/PES blend as a function of TLCP content under different shear rate.

PES is notably lower than that of both pure components. This shows that by blending PES with a little TLCP, one can decrease the viscosity of the blend effectively. Zhuang, *et al.*¹⁶ thought it was caused by the effect of TLCP's liquid crystalline state at high temperature. Kulichiklin, *et al.*^{24,25} thought it was due to the fact that abnormal velocity distribution of the blend's flowing in capillary resulted in the volume expansion and the decrease of the viscosity. But the two interpretations do not well explain the different rheological characteristics of the two blend system TLCP/PC and TLCP/PES. We think the main cause of the abnormal variation of the viscosity of the blend is the internal lubrication of TLCP. Because the interface of TLCP phase and PES phase is only a little miscible, TLCP phase can be distributed well in the PES matrix, the TLCP molecular chains can be interwoven between the PES molecular chains. Under the effect of the flowing field, TLCP is liable to orientate and to form microfibrils or microdomains. They can isolate PES molecular chains and reduce the interaction between PES chains. They also reduce the internal friction between PES molecular chains when PES melt is deformed. So the viscosity of TLCP/PES blends decreases notably. It means that TLCP works as internal lubricant in the PES matrix. But why is the viscosity of blend TLCP/PC not lower than that of both pure components? We calculated the difference of the solubility parameters of the two blend systems TLCP/PES and TLCP/PC; the difference of solubility parameter of TLCP(Ku9231)/PES is 2.1, while that of TLCP(Ku9221)/PC is 4.0. This means that, although the both blend systems are immiscible, the blend system TLCP/PC proves more immiscible than TLCP/PES. So TLCP can not be distributed well in PC matrix, and cannot work well as an internal lubricant. But it does not mean that any TLCP/PC system cannot show the abnormal variation of viscosity, because the difference of solubility parameter is dependent upon the molecular structure of the two components. If a different kind of PC were used, one could also observe the abnormal viscosity variation. Acierio *et al.*²⁶ reported that the viscosity of the TLCP60(50%)/PC(50%) system was lower than that of both pure components. It is due to the fact that when the TLCP content increases, TLCP phase forms larger TLCP microdomains

and, under the effect of flowing field, they can connect with each other and form lubricant layer in PC matrix which decreases the viscosity of the blend. Its mechanism can also be attributed to the internal lubrication.

3. The Rheological Model of TLCP/TP Blends

The mechanism of abnormal variation of viscosities is attributed to the internal lubrication of microfibers and microdomains of TLCPs. In this work, based on the study of the flowing model in capillary, we devised an approximate theoretical formula that can be used to express the viscosity variation of TLCP/TP blend.

At first, we formulated two basic concepts: 1. critical shear stress (τ_c): the critical shear stress on interfaces that results in the relative slide of the interfaces of two phase. 2. the damping coefficient of relative motion (a): strength of slowing effect on unit area of two interfaces sliding with different velocity ($\Delta V > 0$).

We assumed ψ was the volume content of TLCP in blends; a and ψ have this relationship:

$$a = a_0 * \psi^{-\lambda} / (1 - \psi) \quad (1)$$

Under the condition of steady flow in the capillary, with the assumption that the microfibers do not affect the distribution of shear stress, we have the following formula:

$$\Delta V * a * \eta_0 = \tau_w * 2r/D_0 - \tau_c \quad (2)$$

r = distance between the center of the capillary and the microdomain of TLCP.

D_0 = diameter of the capillary.

τ_w = shear rate on the capillary wall.

η_0 = viscosity of the matrix.

In fact, the diameters of TLCP microdomains are about 1 nm–10 μ m, and are much less than D_0 , so the TLCP microdomains can be treated as the microunits which distribute regularly in the matrix; assumed as a continuous phase. For a newtonian fluid, assuming the viscosity of matrix is η_0 , the viscosity of TLCP is η_1 , ratio $\delta = \eta_1/\eta_0$, total flow of pure matrix under iso-pressure is Q ; then the contribution of lubrication of TLCP's microfibers to the total flow is:

$$\Delta Q = Q[32d\psi^\lambda(1 - \psi) * (1 - \lambda)/a_0 * D_0^2] \quad (3)$$

$\lambda = \tau_c/\tau_w$

Q = total flow

d = diameter of TLCP's microdomain

The precondition of using this formula is that $\lambda < 1$, and that TLCP content is not too high and under the condition of iso-pressure or iso-shear stress. Assuming $K = 8/13 a_0 * D_0$, then based on the above assumptions, the viscosity of blends η_c is:

$$\eta_0/\eta_c = 1 - \psi + \psi/\delta + K * \psi^\lambda * (1 - \psi) * (1 - \lambda) \quad (4)$$

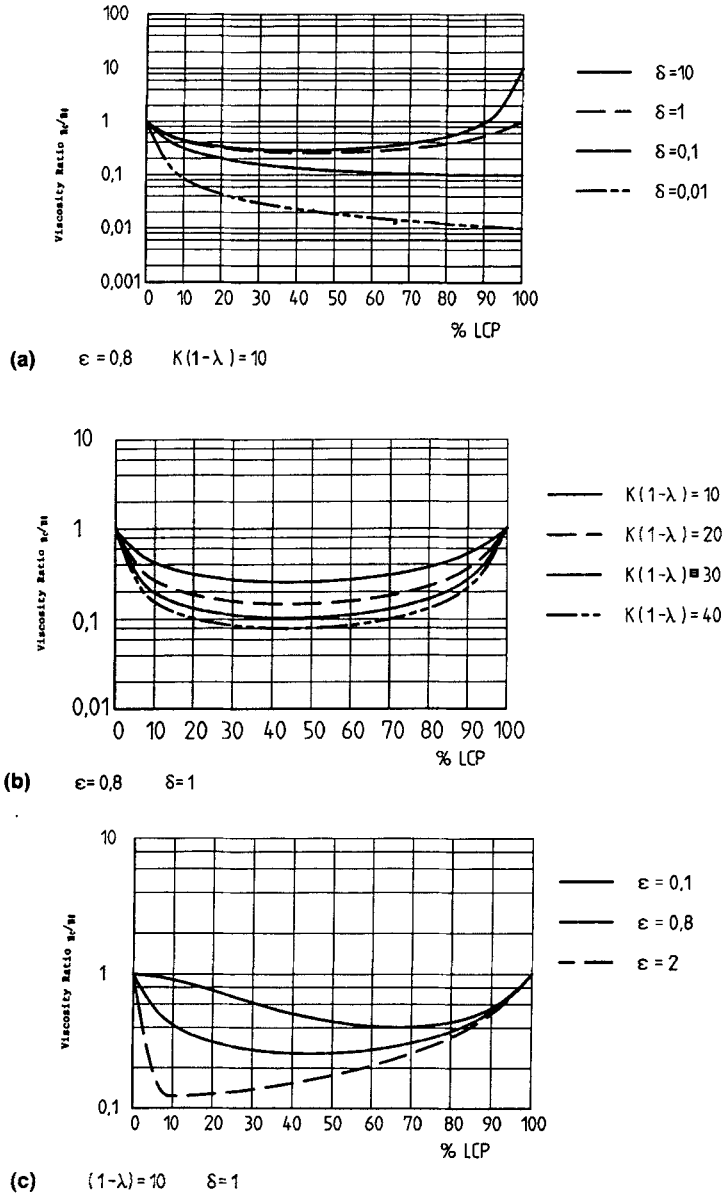


FIGURE 8 The theoretical viscosity of the blends at different parameters as a function of TLCP content.

Figure 8 shows the theoretical viscosity of blend as a function of TLCP content at different parameters. Figure 9 gives the calculated viscosity of TLCP(Ku9231)/PES blend system by formula (4) compared with experimental results. It shows that the calculated results agree with the experimental results well. This means formula (4.) not only can be used to explain the abnormal variation of viscosity of TLCP/TP blends, but also can be used to estimate the viscosity of these blends.

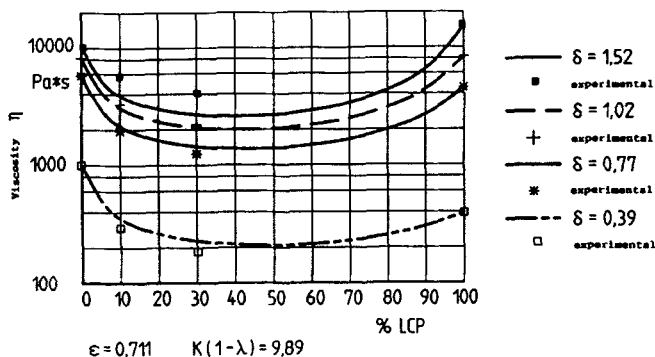


FIGURE 9 The viscosity of TLCP/PES blend as a function of TLCP content under different shear rate (experimental and calculated).

CONCLUSIONS

The FTIR and DSC experiment indicates that the miscibility of two components in system PES/TLCP and PC/TLCP are poor; it agrees with the basic condition of TLCP in-situ shear induced fibrillation in thermoplastic matrix during processing.

Due to the internal lubrication of TLCP in TP matrix, the viscosity of the blends varies abnormally. It can be strongly lower than that of both pure components. This does not agree with the general additive law. By blending thermoplastics with TLCPs, the processability of the blend can be improved notably.

The theoretical formula which expresses the variation of blends viscosity shows that the calculated results agree well with the experimental results. This means that this formula not only can be used to explain the abnormal variation of viscosity of TLCP/TP blends, but can also be used to estimate the viscosity of these blends.

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