A Viscosity Function for Thermoplastics Blended with a Thermotropic Liquid Crystalline Polymer

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SYNOPSIS

The capillary flow behavior of thermoplastic blends containing thermotropic liquid crystalline polymers (TLCP) was studied both theoretically and experimentally. Significant viscosity reductions were observed for a polyethersulfone (PES) blended with a TLCP at 10 and 30 wt %, respectively. A viscosity function was developed and tested to evaluate the relationship between the blend viscosity reduction and weight fraction including some property-related parameters: $\eta = \eta_0[1 - \varphi + \varphi/\delta + K(1 - \varphi)(1 - \lambda)\varphi^\epsilon]^{-1}$, where η and η_0 stand for blend and matrix viscosity, respectively. φ is the weight fraction; δ, the viscosity ratio of the two parent components; λ, the critical stress ratio; and ϵ, an exponent. Interfacial slippage in the blend has been suggested as the flow mechanism by which a substantial reduction in the melt viscosity takes place upon the addition of a small amount of TLCP. The fact that experimental data could be fitted to the viscosity function with satisfactory accuracy should make the function an acceptable way of modeling, analyzing, and parameterizing the experimental rheological data of these blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

One of the most attractive features of thermotropic liquid crystalline polymers (TLCPs) is their ability to alter the rheology of bulk thermoplastic (TP) polymers. A distinct viscosity reduction occurs as a small quantity of TLCP is added to a TP matrix. This negative deviation effect from the log-additivity rule has been widely reported in the literature. For example, Siegmann et al.[1] observed a steep viscosity drop when a TLCP was blended with an amorphous polyamide. The greatest reduction was seen at 5% TLCP loading. With the addition of more TLCP, the blend viscosity increased. In some cases, the viscosity of the pure TLCP was almost the same as that of the pure polyamide, yet with appropriate mixing the blend can achieve a viscosity nearly an order of magnitude lower. A review of this problem was written by Dutta et al.[2]

Nobile et al.[3] reported that viscosity of a polycarbonate/TLCP blend can increase or decrease in the same system at the same temperature, depending on the shear conditions. At a very low shear rate (e.g., 10^{-2} s^{-1}), the viscosity was found to increase with TLCP content, whereas at a high shear rate (e.g., 700 s^{-1}), a significant drop was observed, about a factor of 10 at 50% TLCP content. But in all the cases, the way in which TLCPs alter bulk polymer flow is not yet well understood.

The purpose of this study was to model the steady-state (capillary) flow behavior of TP/TLCP blends by a generalized mathematical function based on some shear-induced morphological features. The most important parameters impacting on the flow behavior are viscosities of the two virgin components and their viscosity ratio, the surface as well as the interfacial tension between the components, the presence or absence of interfacial agents, and the blending procedures. Our attention was primarily confined to incompatible systems. The shear viscosity vs. weight fraction was measured and the experimental data were then fitted by a computer program to the so-called viscosity function. By deriving and fitting some characteristics of this function, some parameters and their physical meanings were analyzed and discussed.

THEORETICAL ANALYSIS

To study the flow behavior of an incompatible TP/TLCP binary system through a capillary, we first summarize some experimental observations and theoretical assumptions:

1. There is a steady-state laminar flow of concentric layers in a capillary.
2. During a steady-state capillary flow, several shear-induced effects emerge on the blend morphology.[4-6] It is, for instance, frequently observed that TLCP domains form a fibrillar structure. The higher the shear rate, the higher the aspect ratio of the TLCP fibrils[7] (see Fig. 1). It is even possible that fibers coalesce to form platelets or interlayers.
3. Under steady-state flow conditions, there is an increasing tendency for this fiberlike structure to move toward the capillary wall as shear stress, flow flux, and radial position increase. In fact, we often obtained extrudates with a very thin TLCP-rich skin layer from the capillary test.[8]
4. It is believed that the thin TLCP-rich skin layer or interlayer may be responsible for a pluglike flow (i.e., a continuous velocity profile) due to a composition-dependent interfacial slippage,[9] and, therefore, for the improved fluidity of this binary system.

Starting from these observations and assumptions, we introduce two parameters:

1. Critical interface shear stress τ_c (Pa): This is a shear stress just causing a relative slide on the phase interface of the two components.
2. Interface slip factor α (m^{-1}): This factor is defined as a phenomenological parameter characterizing the lubrication behavior on the phase interface as a slide occurs.

Interfacial lubrication or slippage can be considered a composition-dependent phenomenon. Therefore, we postulate a relationship between α and the weight fraction φ:

$$\alpha = \frac{\alpha_0}{\varphi^\epsilon (1 - \varphi)} \quad (1)$$

where φ is the weight fraction of TLCP, the exponent ϵ depicts the influence of φ on the slip factor α, and α_0 is a proportional factor.

Because the interfacial slippage is assumed to be caused by the thin TLCP-rich interlayers, we can write a stress equilibrium relation as

$$\Delta V \alpha \eta_0 = \tau_w \frac{2r}{R_0} - \tau_c \quad (2)$$

where ΔV (m/s) represents the interface slide velocity; η_0 (Pas), the matrix viscosity; r (m), the distance of the TLCP-rich interlayer to the capillary axis; R_0 (m), the capillary radius; and τ_w (Pa), the shear stress on the capillary wall.

The shear-stress distribution is uneven in a capillary. Since interfacial slippage takes place only at a point where the shear stress exceeds a critical value, a critical radius r_c can be defined as
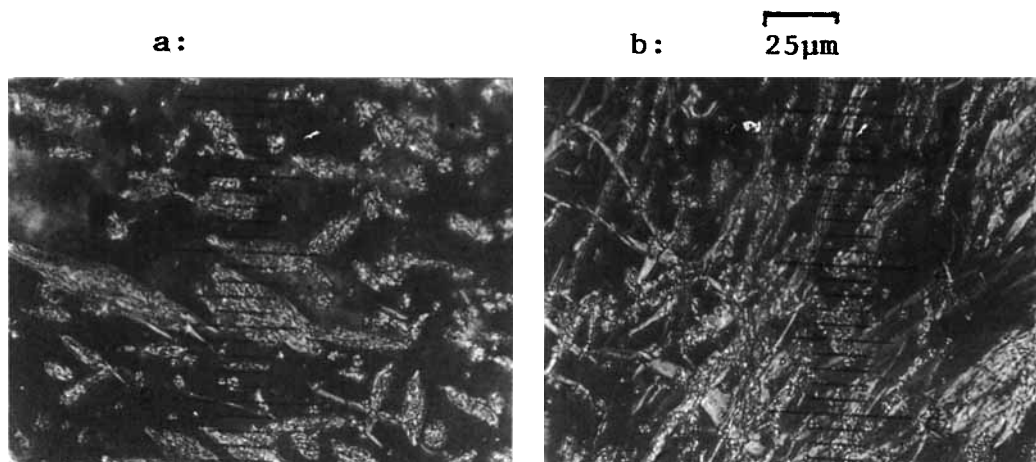
a: **b:**   25μm

Figure 1 Fibrillation of TLCP KU 9221 (Bayer) in a PC matrix at two shear rates: (a) 118 s^{-1} and (b) 1180 s^{-1}, during capillary flow.[7]

$$r_c = \frac{R_0}{2} \cdot \frac{\tau_c}{\tau_w} \qquad (3)$$

If $r < r_c$, there is no interfacial slippage. Thus, the improved fluidity, i.e., the increased volume flux under a constant pressure through a capillary, can be attributed only to the TLCP-rich interlayers formed in the area where $r \geq r_c$.

τ_c/τ_w in eq. (3) defines a critical stress ratio: $\lambda = \tau_c/\tau_w$. If $\lambda > 1.0$, the volume flux through the capillary should follow the values predicted by the simple additivity rule. On the opposite side, if $\lambda \leq 1.0$, there must be an additional volume flux of a quantity of ΔQ due to interfacial slippage and/or interfacial lubrication under constant capillary pressure.

A TLCP-rich interlayer can be visualized as being a layer consisting of numerous TLCP fibrils. The layer may have a thickness of d, which is assumed to be exactly equal to the average fibril diameter. The fibril number n within a layer can be calculated by the equation

$$n = 4\varphi \frac{R_0}{d} \qquad (4)$$

The flux increase should depend on the fibril number n. When each fibril causes a flux increase of ΔQ_1 of the TLCP component, an argument of continuity suggests that there must be also a flux contribution of $\Delta Q_1(1 - \varphi)/\varphi$ coming from the matrix component. Thus, the whole flux increase produced by each TLCP-rich interlayer is

$$\Delta Q_n = n\Delta Q_1/\varphi = 4\Delta Q_1 R_0/d = 4\Delta V \pi dR_0$$

$$= 4\pi dR_0(\tau_w - \tau_c)/(\alpha\eta_0)$$

$$= 4\pi dR_0\tau_w(1 - \lambda)\varphi^\epsilon(1 - \varphi)/(\alpha_0\eta_0)$$

$$= \frac{128 Q d\varphi^\epsilon(1 - \varphi)(1 - \lambda)}{\alpha_0 R_0^2} \qquad (5)$$

Furthermore, when m interlayers exist within a capillary flow, where $m = kR_0/d$ and k is a linear factor, the total flux increase of ΔQ caused by the slippage of these m interlayers can be written as

$$\Delta Q = 128kQ\varphi^\epsilon \frac{(1 - \varphi)(1 - \lambda)}{\alpha_0 R_0}$$

$$= KQ\varphi^\epsilon(1 - \varphi)(1 - \lambda)$$

$$K = 128 \frac{k}{\alpha_0 R_0} \qquad (6)$$

If TLCP is well dispersed and fibrillated, R_0/d in eq. (4) is larger than 10^3 for most cases. When $R_0 = 1$ mm and $\varphi = 25\%$, n will be more than 1000. These fibrils with their average diameter less than 1 μm may just form only one interlayer near the capillary wall or only one thin TLCP-rich skin layer mentioned above. This phenomenon has been observed by us[7,8] and reported by many other researchers.

Finally, a generalized viscosity function in the form of a weight fraction-dependent viscosity ratio η_0/η could be derived as follows:

$$\frac{\eta_0}{\eta} = 1 - \varphi + \frac{\varphi}{\delta} + K\varphi^\epsilon(1 - \varphi)(1 - \lambda) \qquad (7)$$

where η is the blend viscosity; δ, the viscosity ratio of η_1/η_0; and η_1, the TLCP viscosity.

When $\varphi = 0$, eq. (7) reduces to $\eta_0 = \eta$, while when $\varphi = 1$, it becomes $\eta_1 = \eta$. When K approaches 0, eq. (7) reduces to the inverse additivity rule as

$$\frac{1}{\eta} = \frac{1}{\eta_0} + \frac{1}{\eta_1} \qquad (8)$$

which often gives the lower bound of composite properties. K approaching 0 corresponds to a situation where $m = 0$, indicating that there exists no interlayer which promotes the blend melt flow.

When other parameters are fixed, the viscosity function (7) is a reducing function of the TLCP weight fraction. Figure 2 shows the patterns. Generally, the blend viscosities are lower than the matrix viscosity (i.e., $\eta/\eta_0 < 1.0$), even when a small amount of TLCP is added to the system and even when the TLCP itself has a viscosity higher than
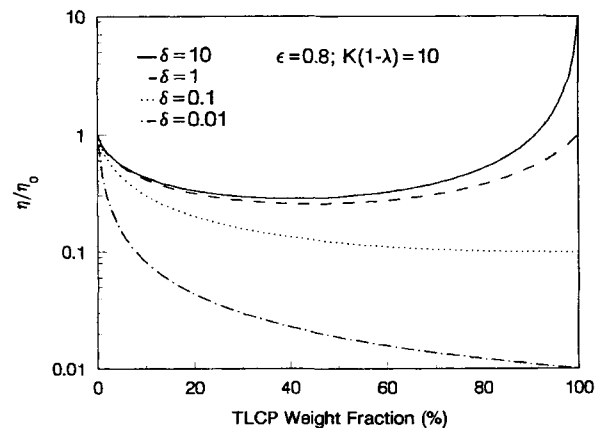

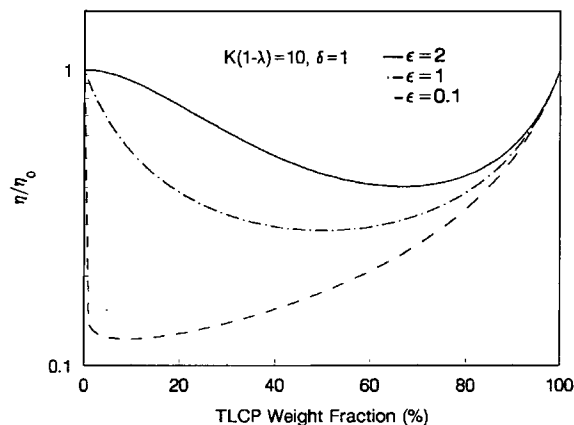**Figure 2** Theoretical viscosity function patterns by varying the viscosity ratio δ.

Figure 3 Theoretical viscosity function patterns by varying the exponent ϵ.

that of the matrix (e.g., when $\delta = 10$). The smaller the ratio δ of the TLCP viscosity η_1 to the matrix viscosity η_0, the lower their blend viscosity η.

The influence of the viscosity ratio δ on the flow behavior in a capillary was discussed by Rumscheidt and Mason.[10] They pointed out that when the viscosity ratio is small, the dispersed droplets are drawn out to great lengths but do not burst. When the viscosity ratio is of the order of unity, the extended droplets break up into smaller droplets. At very high viscosity ratios, the droplets undergo only very limited deformations. This mechanism can explain our observations and suggests our assumptions summarized above as points (2), (3), and (4).

Equation (7) is log-normal symmetric in weight fraction for $\epsilon = 1$ (see Fig. 3). In this case, it describes systems in which there is no concentration-dependent phase transition of any kind. In other words, eq. (7) should not be used for systems with partial solubility. This symmetric dependence of blend viscosity on the weight fraction was observed, for instance, on a PC/TLCP blend and reported in Ref. 3. Otherwise, when $\epsilon < 1$, eq. (7) describes the viscosity reduction, giving a minimum value particularly in the range of $\varphi < 50\%$, whereas when $\epsilon > 1$, the opposite is true. Incompatible systems, such as most TP/TLCP blends, belong to the first kind of flow behavior. But it has also been reported that some TP/TLCP blends have composition-dependent viscosity, indicating two minima below and above the 50 wt % of TLCP, caused by shear conditions. An example for this behavior was a polysulfone/TLCP blend, its flow curves being measured at 240°C.[9] This special kind of flow behavior must be also describable by applying eq. (7).

The viscosity drop becomes more pronounced in the whole range of φ (0% $< \varphi < 100\%$) when $K(1 -$

λ) increases, indicating that the value of parameter K considerably affects the flow behavior of the blend (Fig. 4). Note that $K(1 - \lambda)$ is related to the fibrillation and migration of the TLCP-rich interlayer.

As demonstrated, function (7) gives complete information on how the weight fraction influences the blend viscosity by taking into account the critical stress ratio λ, the viscosity ratio δ, and a parameter K which involves influences of the phenomenological interface slip factor α or α_0, the interlayer number m, and the d/R_0 ratio. It was also assumed in introducing this function that (1) the TLCP phase is well dispersed, fibrillated, and aligned and just forms an interlayer; (2) there is no elastic effect; (3) there is no phase inversion of any kind; (4) $\lambda < 1.0$; and (5) there is a steady-state capillary flow under a constant pressure or a constant wall shear stress. The applicability of this function to describe the composition-dependent viscosity reduction will be tested.

EXPERIMENTAL

The TLCP used was KU 9231 produced by Bayer AG, Germany. The matrix material was an engineering plastic polyethersulfone (PES) manufactured by Jilin University, China. All the materials were dried in a vacuum oven at 115°C for 24 h. They were then melt-blended using a domestic twin-screw extruder (ϕ35). The weight ratios of PES : TLCP were 90 : 10 and 70 : 30, respectively.[11]

Rheological experiments were conducted on an Instron capillary rheometer, Model 3211, ICR. The data were systematically corrected according to the Bagley and Rabinowitsch procedures. The test temperature was 310°C. Prior to testing, the blended
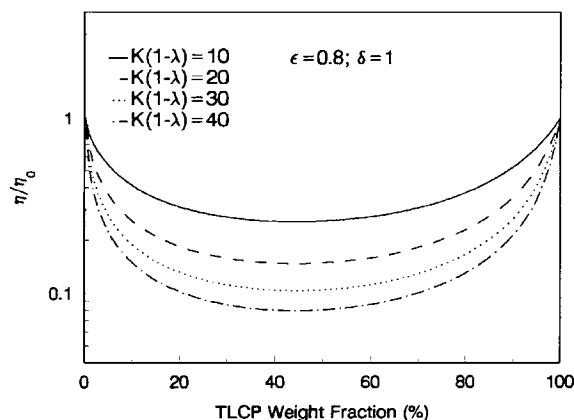

Figure 4 Theoretical viscosity function patterns by varying the parameter $K(1 - \lambda)$.
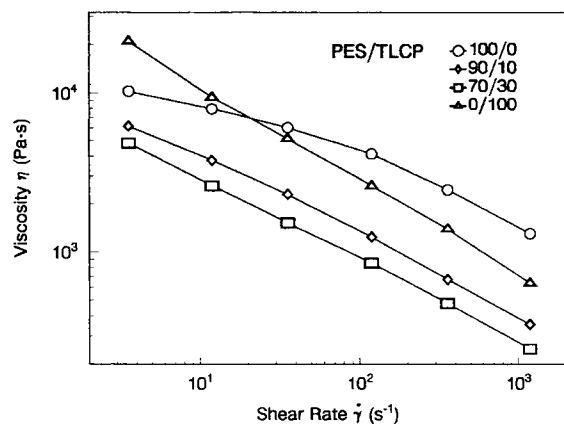
Figure 5 Experimental viscosity curves of PES, TLCP, and their blends with two weight ratios.

materials were dried again in the vacuum at 125°C for 4 h.

RESULTS AND DISCUSSION

In an earlier article[12] we reported that KU 9231 was incompatible with the PES used in this study. Figure 5 reports the viscosity vs. shear rate results for the two original components TLCP and PES and their blends, respectively. The viscosity curves of the two pure components crossed each other at a shear rate about 25 s^{-1}, i.e., at this point, the viscosity ratio was 1. As mentioned previously and as can be expected, the mixtures containing a TLCP component exhibited, in fact, shear viscosities lower than those of their original components, whether the TLCP weight fraction was 10 or 30%. The higher the TLCP weight fraction, the lower the blend viscosity.

The effect of the blending ratio on the melt viscosity of the two-phase system can best be seen from the cross plots at different shear stress. For this purpose, the rheological data were first fitted to eq. (7) by a computer program, and, then, for $\tau = \eta\dot{\gamma}$ being fixed, the theoretical blend viscosity curves and the experimental values were plotted against the TLCP weight fraction, respectively (Fig. 6). It was found that the computer-fitted curves ran perfectly through the experimental data points. The calculated parameter $K(1 - \lambda)$, ϵ, and δ are listed in Table I in their dependence on the shear stress.

It is obvious that all values of $K(1 - \lambda)$ were found to be larger than 30. They increased with increase of the shear stress (i.e., shear rate), and it is well known that high shear stress leads necessarily to dispersed TLCP fibril formation with a higher aspect ratio. Experimental evidence is given for the
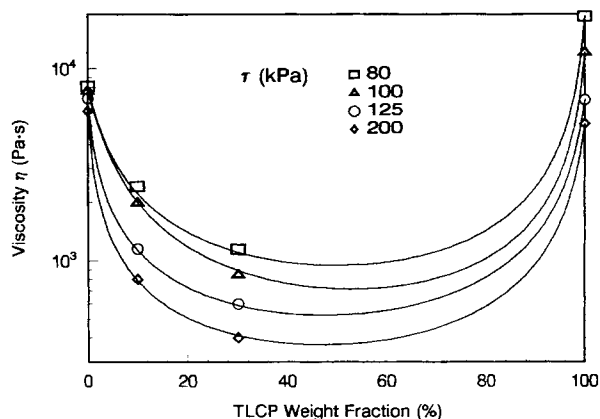

Figure 6 Comparison of theoretical viscosity curves with experimental value points for fixed shear stresses.

same PES/TLCP system in Ref. 7, where a larger average fibril aspect ratio was microphotographed at a higher shear rate. The average value of the exponent was approximately $\epsilon = 1$, indicating that the viscosity curves are nearly symmetric.

The shear-induced fibrillation and migration effects of TP/TLCP blends have been also theoretically analyzed elsewhere in terms of the viscosity ratio, Weber number, and the critical burst time.[13] This more detailed study has pointed out that under certain conditions a higher fibril aspect ratio comes into existence when the viscosity ratio δ lies in the range between 0.1 and 1.0. As reported in Table I, when $\tau \geq 125$ kPa, the viscosity ratio indeed decreases to the range of $\delta < 1.0$.

The influence of the viscosity ratio δ on blend viscosity reduction can be described by eq. (7). As an example of $\epsilon < 1$, it is seen from Figure 7 that the theoretical viscosity curves have two ranges, both completely below the order of unity. In the range of δ smaller than 1, particularly smaller than 0.1, there is a considerable increasing tendency of η/η_0 against δ, suggesting that the lower viscosity component (TLCP) may migrate to the capillary wall, controlling the flow behavior of the blends. The higher the shear stress and rate, the stronger this viscosity re-

Table I Parameters Provided by Fitting the Experimental Data to Eq. (7) for PES/TLCP Blends

τ (kPa)	K $(1 - \lambda)$	ϵ	δ
80	32.13	1.03	2.259
100	43.43	1.14	1.583
125	45.94	0.90	0.962
200	55.78	0.88	0.838
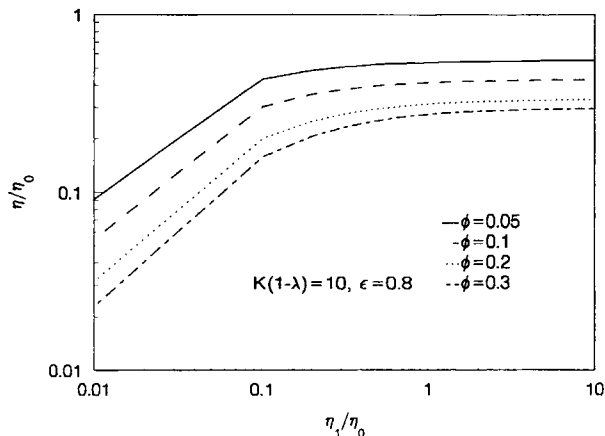
Figure 7   Theoretical viscosity function vs. viscosity ratio δ at different blending ratios.

Figure 9   Comparison of theoretical viscosity curves with experimental value points for fixed shear stresses.

duction effect. At higher δ ratios than 1, i.e., at lower shear stress, the matrix becomes the lower viscosity component and may begin to control the blend flow. Thus, the η/η_0 ratio will be less affected by δ. Our investigation was performed just near the turning range of δ.

Equation (7) depicts the viscosity decrease independent of the polymer pair studied by our own experiment. Also, for fixed τ, Figures 8 and 9 demonstrate a further example of a polyamide/TLCP blend with different weight ratios. The rheological data in Figure 8 were taken from Ref. 1. It is obvious that the lowest blend viscosity is obtained at a TLCP loading only of 5%. With increase of the TLCP added, the blend viscosity increased again. This result is somewhat different to the PES/TLCP blend reported above. However, the weight fraction dependence of the blend viscosity also obeyed eq. (7) quite well (see Fig. 9).
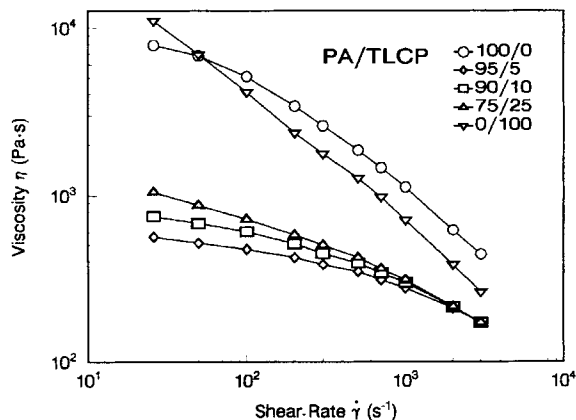
The parameters were also evaluated by fitting the rheological data to eq. (7) and are listed in Table II. It appears to be natural that both the ϵ and δ values were significantly lower than those of the PES/TLCP blend discussed previously.

It is interesting to note that our derivation of the viscosity function (7) was not restricted to TP/TLCP systems. The negative deviation flow behavior from the log-additivity rule has been also widely observed on different blends, e.g., polycarbonate/polyolefin blends reported by Huang et al.[14] They found that, in both PC/HDPE and PC/PP systems, the addition of 5% polyolefins to 95% PC reduced the viscosity of the two-phase system considerably to a value lower than that of both parent polymers. Utraki and Sammut[15] examined the morphology of an LLDPE blend containing 25% PC and reported that the low viscosity component migrated to the capillary wall and controlled the flow behavior. As a result, they also observed the viscosity reduction. In any case, an interfacial lubrication or an interfacial slippage of these incompatible systems is often a reasonable concept for understanding the viscosity reduction. It is hoped that function (7) can serve as

Figure 8   Experimental viscosity curves of PA, TLCP, and their blends of different blending ratios.[1]

Table II   Parameters Provided by Fitting the Experimental Data to Eq. (7) for PA/TLCP Blends

τ (kPa)	$K(1-\lambda)$	ϵ	δ
300	29.00	0.03	1.384
340	32.90	0.06	1.100
387	38.39	0.10	0.814
440	43.73	0.14	0.391
500	47.14	0.15	0.391

a possible basic tool to deal with the viscosity reduction of two-phase systems.

CONCLUSION

A generalized function was derived to evaluate the relationship between the blend viscosity reduction and TLCP weight fraction according to the following model: In the case of a steady-state flow of an incompatible TP/TLCP binary system through a capillary, the dispersed lower viscous TLCP domains are shear-induced to form a fibrillar structure. The fibrils migrate to the capillary wall under certain shear conditions and form there a TLCP-rich concentric interlayer or a thin skin layer. Interfacial slippage of this layer or skin layer is the mechanistic explanation of the observed negative deviation effect.

Computer fitting and calculation of the experimental data could give property-related parameters such as K, ϵ, and δ. These parameters could characterize the change manner of the blend viscosity with the TLCP weight fraction. Comparison of the theoretical curves with the experimental data from own measurement or from literature gave satisfactory results.

Therefore, this function has been proved to be a useful tool to deal with the viscosity reduction behavior. Its applicability has been found to be independent of the special polymer pairs, e.g., TLCP/TP blends, studied by our own experiments.

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