Interfacial Properties of Polycarbonate/Liquid-Crystal Polymer and Polystyrene/High-Impact Polystyrene Polymer Pairs under Shear Deformation

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ABSTRACT: We developed an energy model derived from the first principle for multilayer configurations to enhance our understanding of the interfacial property between two polymers under shear deformation. We carried out specific experiments satisfying the boundary and loading conditions of the model to obtain the energy dissipation factor (β), which characterized and quantified the interfacial property. Two polymer pairs, the miscible system polystyrene (PS)/high-impact polystyrene (HIPS) and the immiscible system polycarbonate (PC)/liquid-crystal polymer (LCP), were investigated. As expected, β was zero for PS/HIPS, reflecting the strong interaction at the PS/HIPS interface. For PC/LCP, the value of β could be significant, and its behavior was complex; it reflected the thermal sensitivity and thermal history effect of the PC/LCP interface. A positive value of β also indicated the possibility of slip at the interface and provided an explanation for the negative deviation from the rule of mixture. This complex behavior of the interface was attributed to the changes in the phases and microstructure of LCPs and, therefore, the LCP/PC interface as thermal cycling was carried out in the melting/nematic range of LCPs. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 258–269, 2003

Key words: liquid-crystalline polymers (LCP); viscosity; interfaces

INTRODUCTION

Liquid-crystal polymers (LCPs) represent a new class of materials with unique chemical and physical properties. Exceptional strength and stiffness, a low coefficient of thermal expansion, chemical resistance, and excellent electrical and optical properties are some of the features of LCPs. Although many macroscopic properties of LCPs are extremely advantageous, blends containing LCPs have also been studied extensively for their potential as processing aids and reinforcements for thermoplastic polymers. It has been shown[1–8] that small amounts of LCPs may significantly lower the melt viscosity of many polymers and, therefore, enhance their processability. LCPs can be blended with many common thermoplastics, without the processing techniques normally used for them being changed. In situ LCP fiber composites may be obtained as long as the type of flow promotes the elongation of the LCP particles into fibrils. The flow properties of LCP blends have been observed to deviate from the normal rule of mixture. Many researchers have studied LCP fiber formation and the viscosity deviation of LCP blends. They have used different approaches and reached conclusions on the effects of various parameters on these two phenomena. The parameters investigated include the viscosity ratio, interfacial tension, LCP migration, and interfacial slippage and nematic temperature of LCPs. Many contradictory results have been reported by different researchers. Because of our limited knowledge of LCPs (blends) and the complexity of the phenomena, including the sensitivity of LCP blends to thermal history, a widely accepted mechanism and the associated governing parameters of such phenomena have not been obtained. However, the understanding and prediction of the rheological behavior of LCP blends under various conditions are important for the processing of LCP blends.

One of the key aspects significant in determining the rheological behavior of LCP blends and, indeed, any immiscible polymer blends is the behavior of the interface between the polymers subjected to shear stress or strain. This article focuses on the development of a model based on the energy concept and the associated experimental procedure for a quantitative description and understanding of this interfacial behavior between two polymers, particularly between LCPs and polycarbonate (PC). The interfacial property was studied through theoretical development and experimen-

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tal investigations of the energy dissipation factor, which characterizes the energy dissipation in the interface.

Although this investigation focuses on the LCP/PC interface, the model developed is general and can be applied to the study of the interface between any two polymers. Indeed, the model was first validated with a polystyrene (PS)/high-impact polystyrene (HIPS) interface, a miscible polymer system.

The model has been developed on the basis of a multilayer structure and, therefore, on a planar interface between two polymers; as a result, it does not represent the morphology of any actual polymer blend systems. However, by shedding light on the behavior of the interface between two polymers, we hope that some understanding of the behavior of the polymer blends can be obtained. In particular, some useful insight into the role of the interface might be provided concerning the negative deviation from the rule of mixture for LCP blends.

THEORETICAL DEVELOPMENT OF THE ENERGY MODEL

In this study, the multiple-layer model of Lyngaae et al.[9] is used. However, instead of using the model for empirical correlation, we analyze the behavior of the multilayer system from the first principle based on the energy concept. A single parameter is obtained to provide a quantitative measure of the proportion of energy consumed by the individual components and the interface under shear stress/strain. By focusing on the changes in this parameter, we can assess the effect of various testing conditions on the interface. This approach has the advantage that the effect of the viscosity ratio, the relative concentration of the components, and the total energy input can be related through the model. By knowing the proportion of the energy consumed by LCP, we hope that conditions favorable to fiber formation can be determined for future investigations.

Layer concept of the model

It is not entirely obvious what the most appropriate way is to model the interface. It could be assumed that the interface between an LCP and PC exists as an interfacial layer, having, therefore, a finite thickness. Alternatively, it could be assumed that there is a distinct interface between an LCP and PC with no interfacial layer or an interfacial layer with zero thickness. However, even if the interface has a finite thickness, it can be safely assumed that the interfacial layer is thin. Therefore, in the development of the model, we have adopted the approach that the interaction between the components could be represented by an interfacial layer through a multilayer model. Subsequently, by

assuming that the thickness of the interfacial layer approaches zero, we can use the model to describe either a thin interfacial layer or a distinct interface with zero thickness.

To bring out the essential features of the layer concept, we have considered a multilayer model, as shown in Figure 1(a), for the investigation into the interfacial properties between LCP and PC under shear stress/strain. This structure consists of three layers: LCP, PC, and the interfacial layer. By applying a uniform shear stress at the top surface with the bottom surface fixed and assuming uniform viscosity within each layer, we can represent the velocity distribution and shear strain rate for the three layers schematically, as shown in Figure 1(b,c), respectively. Although this layered configuration does not represent geometrically a polymer blend, it provides a means to characterize the interface between a pair of polymers, the major objective of this investigation. A special experimental procedure and setup, conforming to the assumptions of the model, could be established to obtain the constant in the model and, therefore, quantified the behavior of the interface.

Derivations of the governing equations

As the motivation for using an interfacial layer concept is to lump together the effects of all the unknown interaction factors, it is convenient to conduct the analysis on the basis of energy or power dissipation. For an applied stress by parallel plates, as shown in Figure 1(a), the equilibrium requirement dictates that the shear stress experienced by each individual layer must be the same.

In addition, because the interfacial layer is thin or small, there will be negligible elastic energy stored within the layer. The effect of the interfacial layer will be reflected predominantly by the dissipative energy component. Therefore, for this analysis, the elastic energy component is ignored, and our attention is focused on the dissipative energy component.

Considering the structure in Figure 1(a) and ignoring the elastic component, we can assume that the power consumed by the LCP layer, the PC layer, and the interfacial layer per unit volume of the structure is as follows:

$$P_{LCP} = \tau \dot{\gamma}_{LCP} c_{LCP} \tag{1}$$

$$P_{PC} = \tau \dot{\gamma}_{PC} c_{PC} \tag{2}$$

$$P_{IL} = \tau \dot{\gamma}_{IL} c_{IL} \tag{3}$$

The total input power is equal to the total power consumed:
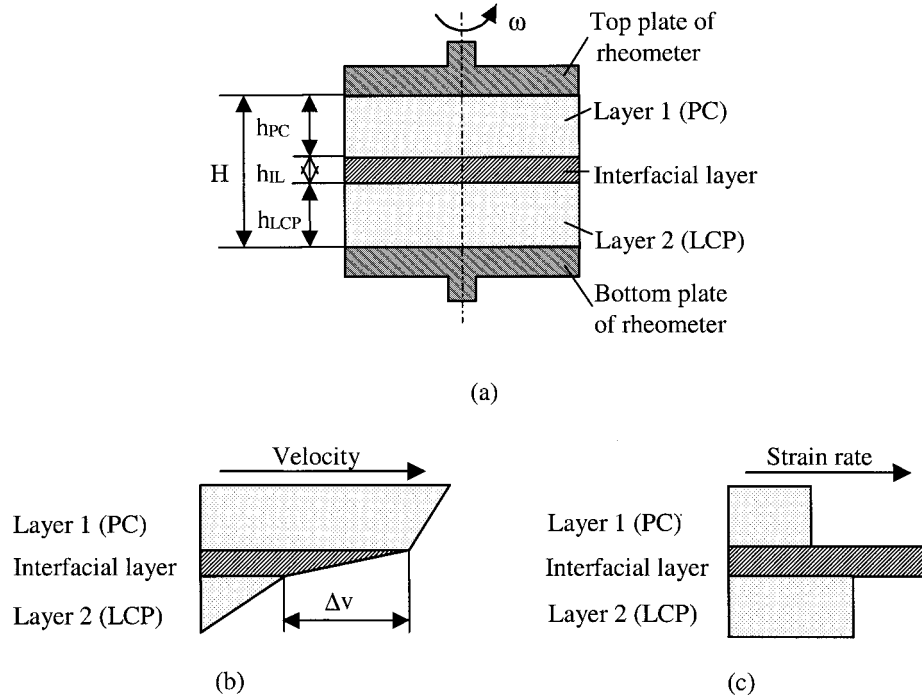
Figure 1 Model with a layer structure: (a) the layer structure, (b) the velocity distribution of each layer, and (c) the strain rate of each layer.

$$\tau\dot{\gamma}_{\text{ave}} = P_{\text{PC}} + P_{\text{LCP}} + P_{\text{IL}} \qquad (4)$$

Substituting eqs. (1)–(3) into eq. (4), we have

$$\tau\dot{\gamma}_{\text{ave}} = \tau\dot{\gamma}_{\text{PC}}c_{\text{PC}} + \tau\dot{\gamma}_{\text{LCP}}c_{\text{LCP}} + \tau\dot{\gamma}_{\text{IL}}c_{\text{IL}} \qquad (5)$$

where τ is the applied shear stress and c_{PC}, c_{LCP}, and c_{IL} are the volume fractions of the PC layer, LCP layer, and interfacial layer, respectively.

A description of eq. (5) is given in Figure 1, which reveals the velocity and strain rate profiles for the PC, LCP, and interfacial layers. H represents the total thickness of the multilayer structure. The terms h_{LCP}, h_{PC}, and h_{IL} represent the thicknesses of the LCP layer, PC layer, and interfacial layer, respectively. v denotes the total velocity; Δv denotes the velocity discontinuity across the interfaces between PC and LCP layers. Therefore,

$$\Delta v = h_{\text{IL}} \times \dot{\gamma}_{\text{IL}} = c_{\text{IL}} \times \dot{\gamma}_{\text{IL}} \times H \qquad (6)$$

$$v = H \times \dot{\gamma}_{\text{ave}} \qquad (7)$$

Defining the strain rate ratio, we obtain

$$\phi = \frac{\dot{\gamma}_{\text{IL}}}{\dot{\gamma}_{\text{ave}}} \qquad (8)$$

Then, from eqs. (6)–(8), we have

$$c_{\text{IL}}\phi = \frac{c_{\text{IL}}\dot{\gamma}_{\text{IL}}}{\dot{\gamma}_{\text{ave}}} = \frac{\Delta v}{v} \qquad (9)$$

From the definition of viscosity

$$\dot{\gamma}_{\text{LCP}} = \frac{\tau}{\eta_{\text{LCP}}}$$

$$\dot{\gamma}_{\text{PC}} = \frac{\tau}{\eta_{\text{PC}}}$$

$$\dot{\gamma}_{\text{IL}} = \frac{\tau}{\eta_{\text{IL}}}$$

$$\dot{\gamma}_{\text{ave}} = \frac{\tau}{\eta_{\text{ave}}} \qquad (10)$$

and eqs. (5) and (9), we obtain

$$\eta_{\text{ave}} = \frac{(1 - c_{\text{IL}}\phi)\eta_{\text{PC}}\eta_{\text{LCP}}}{c_{\text{PC}}\eta_{\text{LCP}} + c_{\text{LCP}}\eta_{\text{PC}}} \qquad (11)$$

In addition, it should be noted that the interfacial layer is thin or zero:

$$c_{\text{PC}} + c_{\text{LCP}} + c_{\text{IL}} = 1$$

$$c_{\text{IL}} \ll c_{\text{PC}}, c_{\text{LCP}}$$

$$c_{PC} + c_{LCP} \approx 1 \qquad (12)$$

Equation (9) indicates that if there is no velocity discontinuity across the interface between PC and LCP, that is, no slip, then $\Delta v = 0$ and $c_{IL}\phi = 0$. However, as long as there is velocity discontinuity (slip or intense shear deformation) across the interface or interfacial layer, $\Delta v > 0$. This indicates that even for an interfacial layer that is thin or close to zero thickness, that is, when c_{IL} is close to zero, the product $c_{IL}\phi$ is finite. Further analysis indicates that

$$c_{IL}\phi = c_{IL}\frac{\dot{\gamma}_{IL}}{\dot{\gamma}_{ave}} = \frac{c_{IL}\tau\dot{\gamma}_{IL}}{\tau\dot{\gamma}_{ave}} = \frac{\text{Interfacial energy dissipated}}{\text{Total input energy dissipated}} \qquad (13)$$

Equation (13) shows that $c_{IL}\phi$ represents the proportion of the total input energy consumed by the interface. Now, we define an overall energy dissipation factor (β) for the interfacial layer as follows:

$$\beta = c_{IL}\phi = \frac{c_{IL}\tau\dot{\gamma}_{IL}}{\tau\dot{\gamma}_{ave}} = \left(\frac{\Delta v}{v}\right) \qquad (14)$$

According to eq. (14), β can also be interpreted as the velocity slip factor between LCP and PC. Equation (11) can now be written as

$$\eta_{ave} = \frac{(1 - \beta)\eta_{PC}\eta_{LCP}}{c_{PC}\eta_{LCP} + c_{LCP}\eta_{PC}} \qquad (15)$$

If the interfacial layer does not exist, or is perfectly rigid, the interfacial shear strain rate is zero ($\dot{\gamma}_{IL} = 0$). According to eq. (14), $\beta = 0$. In this case, from eq. (15), we will obtain the rule of mixture ($1/\eta_{ave} = c_{LCP}/\eta_{LCP} + c_{PC}/\eta_{PC}$). This model predicts that a negative deviation from the rule of mixture, at least for the multilayer configuration, is caused by the existence of a slip or velocity jump across the interface, with a nonzero β as the governing parameter. Although a PC/LCP blend cannot be directly compared with the multilayered configuration, it is interesting to note that the viscosity value of the blend is lower than that predicted by the rule of mixture. Therefore, the model provides a possible explanation for the negative deviation from the rule of mixture for a polymer blend, namely, slip at the interface.

Determination of β

Rotational rheometer with parallel-plate geometry

The Advanced Rheometric Expansion System (ARES) from Rheometric Scientific, Inc. (Piscataway, NJ), was used to measure the viscosity. For this investigation, the parallel-plate geometry was employed. This geom-

etry was chosen because it satisfies the assumptions and boundary conditions used in the development of the multilayer model.

For the measurement of the dynamic viscosity, by assuming that the Cox–Merz rule holds, we can define the relationship between the frequency ω and shear rate $\dot{\gamma}$ as follows:

$$\dot{\gamma} = \omega\gamma \qquad (16)$$

Calculation of β

To determine β, we have to calculate the energy consumed by each individual layer first. For a multiple-layer model, all layers experience the same shear stress rather than the same shear rate. When we obtain experimentally the viscosity [point A in Fig. 2(a)] of a PC/LCP blend multilayered structure, we cannot determine the shear rate or viscosity of individual components directly. However, because all the components experience the same stress, a constant stress line (log η + log $\dot{\gamma}$ = log τ = constant) passing through point A can be drawn, as shown in Figure 2(a). The solutions for the individual components will be on this constant stress line.

If the viscosity versus the shear rate for a pure component is known, the viscosity and shear rate for the individual component under testing condition A can be calculated. As shown in Figure 2(b), point B, the intercept between the constant stress line and the line of viscosity versus the shear rate for PC, gives the viscosity and shear rate for the PC component under testing condition A for the overall structure. Similarly, point C, which represents the viscosity and shear rate for the LCP component under testing condition A for the overall structure, can be calculated.

In eq. (15), the values of η_{ave}, η_{PC}, and η_{LCP} are given by the values of the viscosity at points A, B, and C, respectively. The terms c_{PC} and c_{LCP} can be obtained by the thicknesses of the PC and LCP layers being measured as a proportion of the total thickness of the sample. As β is now the only unknown in eq. (15), it can be solved with the following expression:

$$\beta = 1 - \frac{\eta_{ave}(c_{PC}\eta_{LCP} + c_{LCP}\eta_{PC})}{\eta_{PC}\eta_{LCP}} \qquad (17)$$

Viscosity versus the shear rate for pure PC and LCP

To obtain the interfacial properties, we first had to determine the rheological response of pure LCP and PC as the reference data. One of the aims of this work was to investigate the effect of temperature on the interfacial properties. However, obtaining the reference data of the viscosity versus the shear rate for pure LCP is not straightforward because it is sensitive to
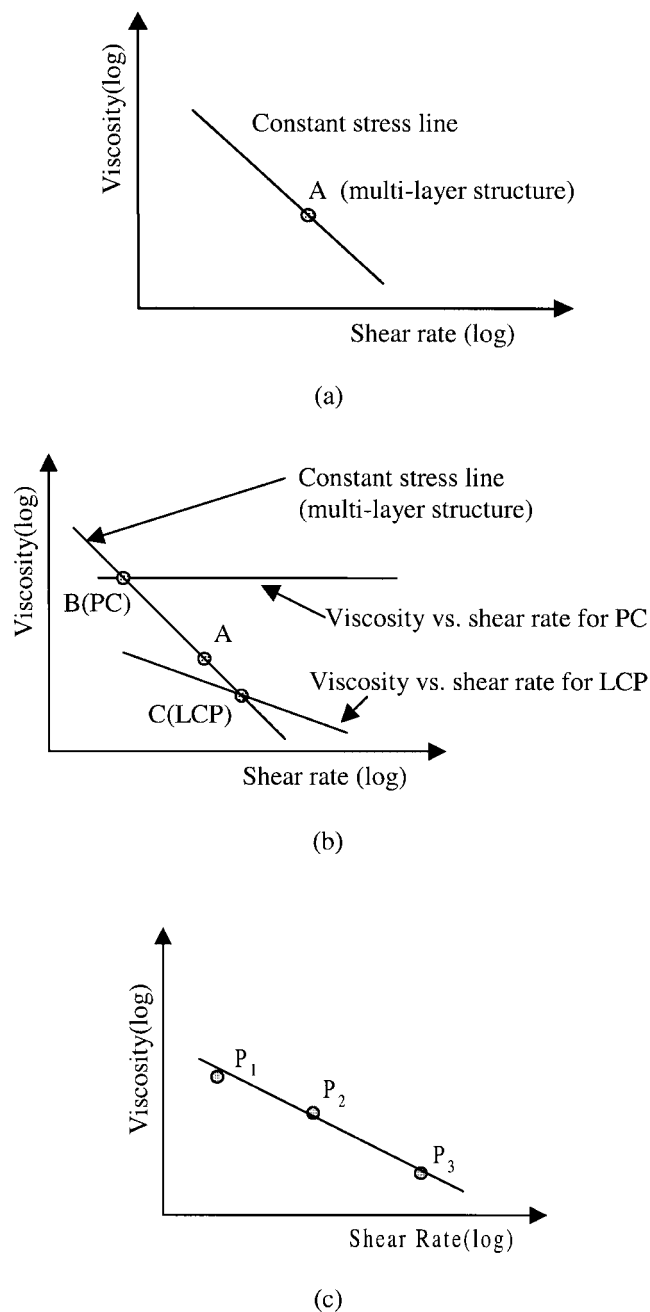
Figure 2 Determination of the viscosities of the individual components for β: (a) the constant stress line for a multilayer structure, (b) the viscosity/shear rate relationship for the individual components under constant stress, and (c) the power-law curve fit for LCP.

both the thermal history and shear rate. To ensure the repeatability of the test, we decided that for all tests with LCP, LCP would first be conditioned at a common elevated temperature for approximately 5 min. To minimize the effect of the thermal history, we obtained the viscosity under thermal cycling. There were two reasons for conducting the tests under thermal cycling: (1) with thermal cycling, LCP would be thermally conditioned, so any variation due to a ther-

mal history effect would be minimized, and (2) any variation caused by any thermal history effect could be observed from the changes in the properties of LCP (or an LCP/PC layered arrangement) from cycle to cycle.

However, each thermal cycling test can only provide a single test point of log η versus log $\dot{\gamma}$ under the particular thermal cycle of interest. To obtain other values of log η versus log $\dot{\gamma}$, we have to repeat the tests under different $\dot{\gamma}$ values or at different frequencies. Figure 2(c) shows schematically three values, P_1, P_2, and P_3, obtained with the aforementioned procedure.

The viscosity versus the shear rate for a range of shear rates for LCP may now be obtained by a curve being fit over all these data points. To achieve this, we assume that LCP obeys the power-law relationship with

$$\eta = m\dot{\gamma}^{n-1} \tag{18}$$

where m and n are material constants. Equation (18) can be rewritten as follows:

$$\log \eta = (n-1)\log \dot{\gamma} + \log m \tag{19}$$

To obtain the coefficients m and n, we can fit a least-squares curve to the data points, as shown in Figure 2(c).

The adoption of the power law is justified on the following basis: (1) data obtained by Denn et al.[10] showed shear thinning behavior over 8 decades of the shear rate; (2) our experimental data showed similar behavior; and (3) the behavior could be described by eq. (19) with little error, especially if the data points for curve fitting were obtained close to the point of interest.

Pure PC is not very sensitive to the shear rate. Therefore, the viscosity value over a wide range of shear rates under different temperatures can be obtained directly with the dynamic temperature ramp test.

So far, a complete mathematical model has been developed with the potential to characterize the viscosity behavior of the interface of two polymers under shear deformation. In this model, the multilayer structure has been established, and the energy consumption in each layer has been calculated, including that of the interface. The numerical procedure for the determination of the various parameters from a parallel-plate test has also been described. The outcomes of the experimental investigations and the validation of the model are now presented.

EXPERIMENTAL

For the validation of the energy model, a multiple-layer experiment was designed and carried out on the

rotational rheometer. Although the main thrust of this investigation was the PC/LCP system, an immiscible polymer pair, a miscible polymer pair, PS/HIPS, was also investigated for the calibration or validation of the model.

Because LCP in the PC/LCP system has a nematic temperature, tests were carried out at temperature ranges both at and below the nematic temperature range of LCP. As the nematic temperature is also close to the melting point of LCP, this meant that the tests were carried out both above and below the melting temperature of LCP. With a significant difference in the structure and state of LCP above and below the nematic (melting) temperature, it was expected that there could be a significant difference in the interfacial properties above and below the nematic temperature. With tests conducted under thermal cycling, the changes in the interfacial properties with temperature changes could be observed easily.

For the purpose of validation, a miscible polymer pair, the PS/HIPS system, was also tested for one temperature range. It was expected that the interaction between a miscible polymer pair at the interface would be strong, and any significant slip or velocity discontinuity at the interface would be unlikely.

Materials

Four kinds of materials, PS, HIPS, PC3200, and LCP5000, were used to conduct the experiments. The PS (Styron 666H) was general-purpose. HIPS (Styron 470) was high-impact. Dow Chemical Co. (Midland, MI) provided the PS and HIPS. The LCP (Rodrun LC 5000), provided by Unitika (Osaka, Japan), was a *p*-hydroxybenzoic acid (HBA)/polyethylene terephthalate (PET) (80/20) copolymer. The PC (PC3200) was provided by Bayer (Pittsburgh, PA).

Testing

Differential scanning calorimetry(DSC) measurements

DSC was used to characterize the polymer blends and investigate the effects of the thermal history. The aim of this experiment was to measure the nematic temperature of LCP so that the appropriate temperature ranges of the multiple-layer experiments and rheological tests could be determined. The experiments were carried out on a DSC 7 (PerkinElmer, Shelton, CT) at a heating rate of 10°C/min.

Thermogravimetric analysis (TGA)

TGA was used to study the thermal decomposition behavior of LCP, so the temperatures employed in the subsequent experiments were lower than the degra-

TABLE I
Molding Conditions of Discs

	PS and HIPS discs	PC and LCP discs
Hopper section temperature (°C)	180	270
Barrel section temperature (°C)	200	280
Nozzle section temperature (°C)	200	280
Injection speed (rpm)	140	140

dation temperature of LCP. The sample was heated from 25 to 500°C under a nitrogen atmosphere. The heating was controlled at a rate of 10°C/min.

Injection molding

Pellets of pure PS, pure HIPS, pure PC, and pure LCP were injection-molded by a Manumold (Aylesbury, UK) 77/30 injection-molding machine to produce the discs for rheological testing. The discs were 25 mm in diameter and 1 mm thick. For the removal of the absorbed moisture, PC and LCP pellets were dried at 120°C in vacuo for at least 12 h before injection molding. Drying was not necessary for PS and HIPS. Table I shows the molding conditions of these discs.

Rheological tests

An ARES from Rheometric Scientific with parallel-plate geometry was used. The diameter of the parallel plate was 25 mm. To reveal the effect of the thermal history on the rheological behavior of the blend, we carried out dynamic frequency ramp tests. The discs of PC and LCP were separately tested to determine their rheological behavior.

Multilayer experiments

To investigate the effect of the interface, experiments that satisfied the loading and boundary conditions of the multilayer model were designed and conducted for the measurement of the viscosity. The dynamic temperature ramp tests were performed on the ARES rheometer with parallel-plate geometry, as shown in Figure 1(a). A similar configuration was used to examine both the LCP/PC and PS/HIPS systems. The details of the experiments are presented later.

For the PS/HIPS system, the experiments were carried out on PS discs, HIPS discs, and the PS/HIPS configurations. In the dynamic temperature ramp tests, a temperature range of 170–210°C was employed.

Similarly, for the PC/LCP system, the tests were conducted on PC discs, LCP discs, and PC/LCP sandwich lay-ups. For this particular LCP, the nematic temperature and melting temperature were similar. Because the effects of the nematic and melting tem-

peratures were significant for the LCP system, tests both above and below the nematic and melting temperatures of LCP were employed for the PC/LCP system. All tests involving LCP began with the temperature held at 180°C for approximately 5 min before the rheological tests were conducted.

A strain sweep was conducted initially to determine the strain of the linear viscoelastic region of the materials. The strain within the linear viscoelastic region (1% in our experiments) was used for the subsequent dynamic temperature ramp tests. A frequency of 15 rad/s was employed. The heating or cooling rate of the dynamic temperature ramps was 2°C/min.

At the end of each experiment, the thickness of each layer was measured after the sample was removed from the rheometer. For sandwich configurations, the ratio of the respective thicknesses was used to obtain the volume fraction of each layer, as required for the energy model.

It is known that LCP does not always follow the Cox–Merz rule, and a possible contributing factor to this departure from the Cox–Merz rule is the fibrillation of LCP under deformation. With a parallel-plate configuration, there will be no extensional flow, which promotes fibrillation. In addition, with a small strain (1%), fibrillation would not be expected, and it did not occur in our experimental investigation. In addition, if there was any departure from the Cox–Merz rule, the effect would be felt by LCP in both the pure LCP and LCP/PC configurations. As β for the quantification of the interfacial properties was obtained by the effect of LCP and PC being deducted from the LCP/PC configuration, the departure from the Cox–Merz rule due to the behavior of LCP, if any, for the existing setup would be accounted for in the calculation of β. However, caution should be exercised if the results are to be extended to other situations, especially if there is fibrillation.

RESULTS AND DISCUSSION

Thermal analysis

From Figure 3, the thermal properties of PC, LCP, and their blends can be obtained. As there was only one peak for LCP, it indicated that the nematic and melting ranges were similar. The nematic and melting temperatures of LCP were between 290 and 310°C, with the peak at 296°C. The glass-transition temperature of PC was 148°C. The glass-transition temperature was almost the same for the PC and PC/LCP blends, indicated that LCP and PC were immiscible. The degradation temperature of LCP was approximately 400°C. For PC, the processing temperature suggested by the manufacturer was about 316°C. Therefore, degradation would not occur as the temperatures for all subsequent experiments did not exceed 310°C.
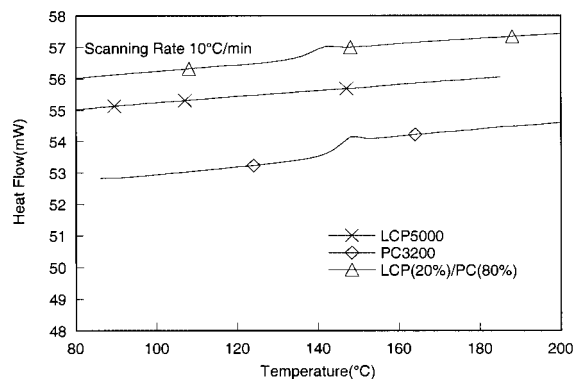
(a)
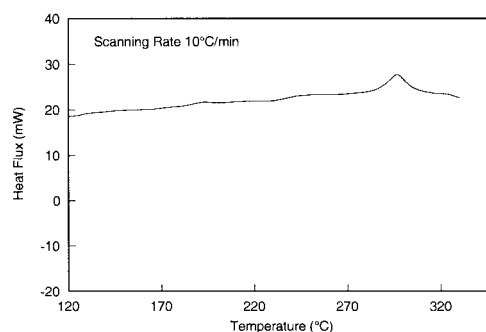
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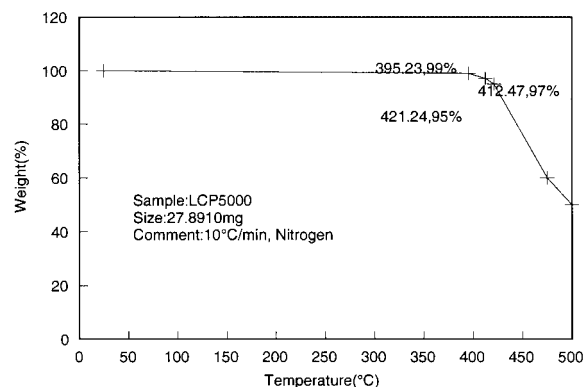
(c)

Figure 3 Thermal analysis results for PC, LCP, and their blend: (a) DSC heating traces for PC, LCP, and their blend; (b) DSC heating trace for LCP over a wide temperature range; and (c) TGA curve for LCP.

Dynamic temperature ramp tests

The experimental results for the viscosity measurements for various systems are presented in Figures 4–6. The calculated values of β based on these results for various sandwiched configurations are contained in Figures 7–9.
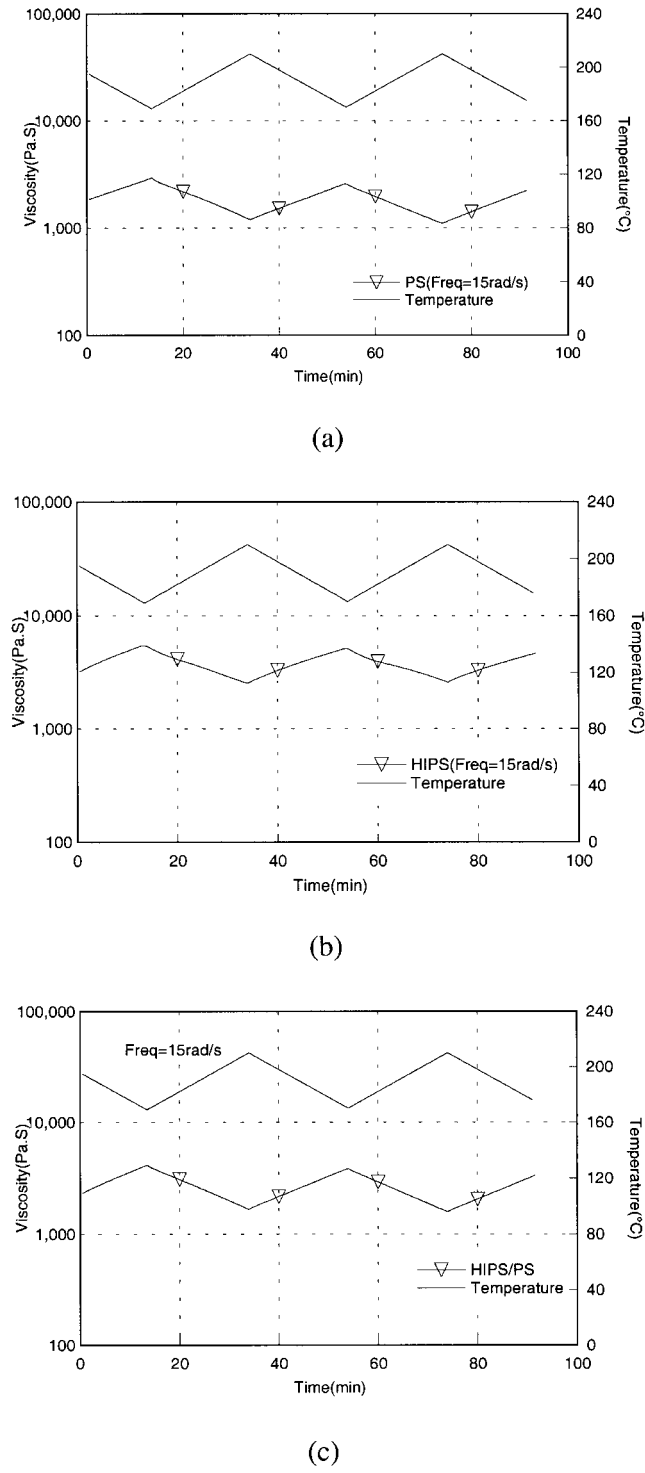
(a)

(b)

(c)

Figure 4 Viscosity plots of PS, HIPS, and their blend: (a) pure PS, (b) pure HIPS, and (c) PS/HIPS layer configuration.

PS/HIPS system

As shown in Figure 4, the behavior of the PS, HIPS, and PS/HIPS system was as expected, with a 180° phase lag between the temperature stimuli and the viscosity responses.

β was calculated with eq. (17) (see Fig. 7). Within a tolerance of ± 0.15, β was close to zero for the HIPS/PS system.

The small value of β indicated that the interaction at the interface was strong, as expected for a miscible polymer pair. There was negligible, if any, interfacial slip or velocity discontinuity across the PS and HIPS interface. As discussed earlier in eq. (15), when $\beta = 0$, the viscosity of the sandwich configuration followed the rule of mixture for the multilayer system. This also provided a strong indication that the PS/HIPS polymer blend system would observe the rule of mixture as expected.
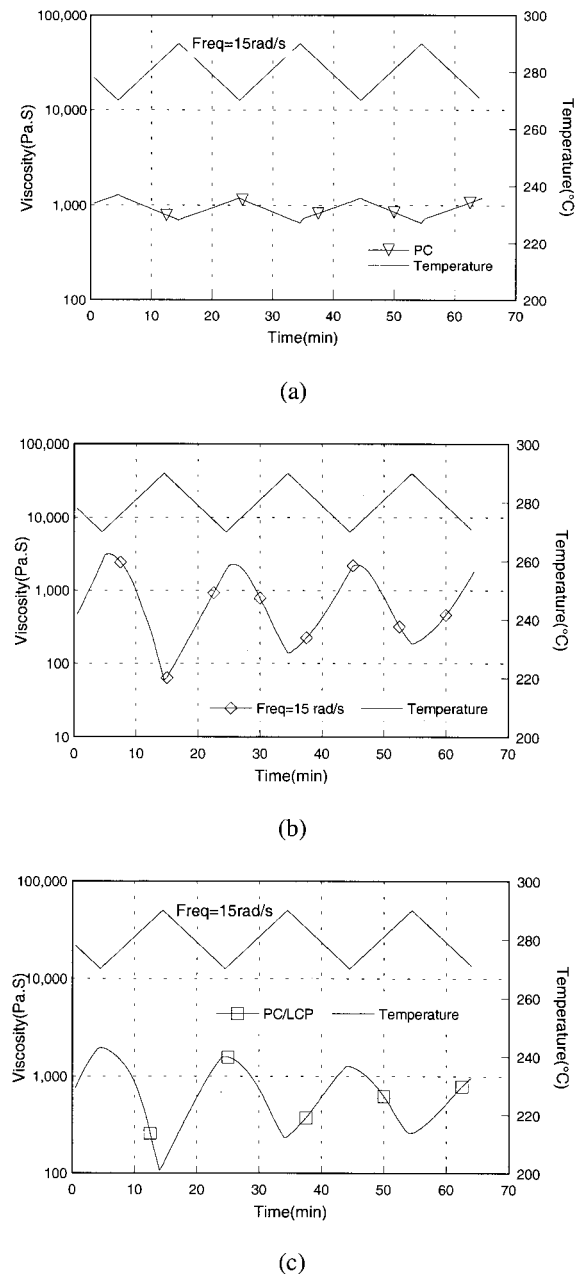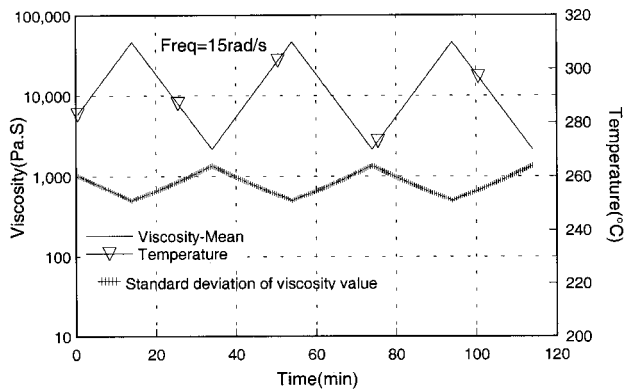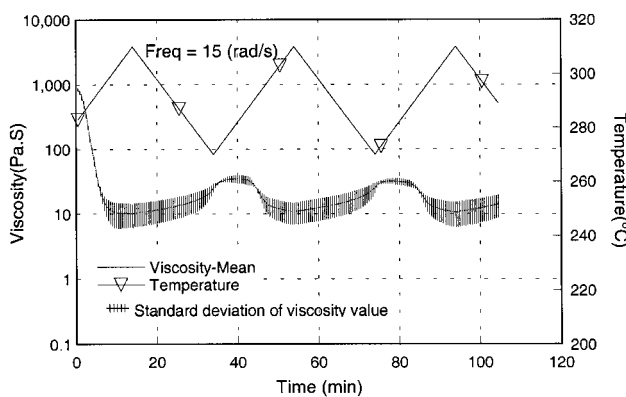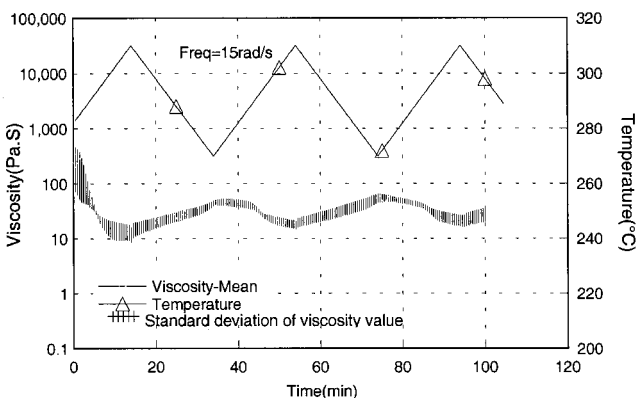

(a)

(b)

(c)

Figure 5 Viscosity plots of PC, LCP, and their blend at test temperatures below the nematic temperature of LCP: (a) pure PC, (b) pure LCP, and (c) PC/LCP configuration.

(a)

(b)

(c)

Figure 6 Viscosity plots of PC, LCP, and their blend at test temperatures at the nematic temperature of LCP: (a) pure PC, (b) pure LCP, and (c) PC/LCP configuration.

PC/LCP system with the temperature range below the melting/nematic temperature

Dynamic temperature ramp results are shown in Figure 5. The test temperatures ranged from 270 to 290°C, that is, below the nematic temperature of LCP.

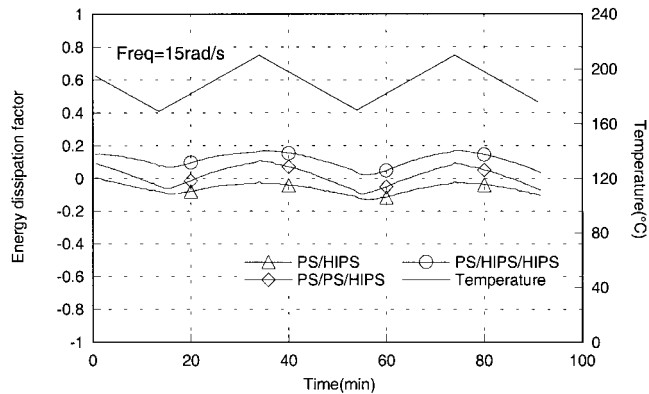The viscosity of the sandwiched configuration [Fig. 5(c)] was between those of pure PC [Fig. 5(a)] and

Figure 7 Variations of β as a function of time for various PS/HIPS configurations.

pure LCP [Fig. 5(b)]. Within a tolerance of ± 0.15, Figure 8 shows that the computed β values were close to zero. Therefore, conclusions were reached similar to those for the aforementioned PS/HIPS system.

From Figure 5(b,c), it can be observed that the responses of LCP and LCP/PC configuration were cyclically stable after the first cycle. Therefore, any variation of results caused by thermal history effect would be small.

PC/LCP system with the temperature range at the melting/nematic temperature

For this set of experiments, the test temperature was varied from 270 to 310°C so that part of the thermal cycle was in the melting/nematic temperature range.

The viscosity results for pure PC, pure LCP, and the PC/LCP configuration are shown in Figure 6(a–c), respectively. Five samples were tested for each experiment. At the beginning of the multiple-layer experiments, the standard deviations of the viscosity values of PC/LCP were significant. However, the standard deviations of the viscosity values of pure PC and LCP were less. This indicated that there were interactions
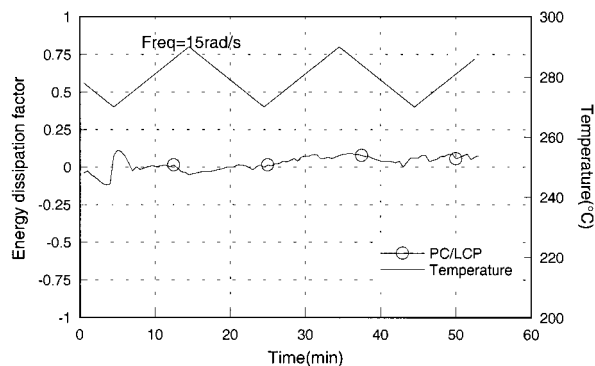

Figure 8 Variations of β as a function of time for PC/LCP configurations at test temperatures below the nematic temperature of LCP.
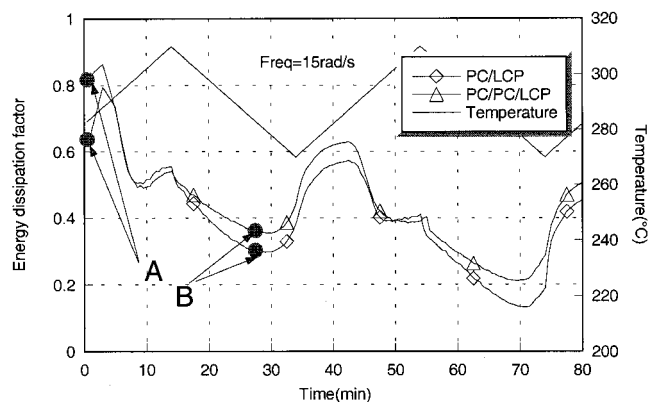
Figure 9 Variations of β as a function of time for PC/LCP configurations at test temperatures at the nematic temperature of LCP.

between PC and LCP at the interface at the beginning of the experiments. This instability was also described by Lyngaae et al.[9]

Figure 6(b,c) indicates that the cyclic responses of LCP and LCP/PC were stable after the initial one-half of a thermal cycle. Therefore, the thermal history would not have a significant effect after the first half-cycle.

Figure 9 shows the variation of β with the thermal cycle. β not only changed with temperature, but it was also a function of the direction of the temperature change, that is, heating or cooling.

Point A (time $\approx$ 0) in Figure 9 represents the beginning of the multiple-layer tests, the temperature of which was about 283°C. At the beginning of the measurements (i.e., point A), the viscosity of the PC/LCP configuration [Fig. 6(c)] was less than those of the individual components [Fig. 6(a,b)]. In addition, at point A, β was about 0.72, which indicated that a significant proportion of the energy (72% of the total) was dissipated at the interface, implying that there was significant slip between LCP and PC. This resulted in a significant negative deviation from the rule of mixture for the test configuration.

The material at point B (time $\approx$ 27 min) had the same temperature as point A. However, the material at point B had experienced a thermal cycle in which the temperature was increased to 310°C before being decreased to 283°C. From point A to point B, the viscosity of PC only changed relatively slightly, as indicated in Figure 6(a). However, for LCP and the PC/LCP configuration, a significant reduction in the viscosity was observed, as shown in Figure 6(b,c), respectively. Although a negative deviation still existed at point B in Figure 9, it was much less than that at point A. In addition, at point B, β for the sandwiched configuration was about 0.33 (it was about 0.6–0.8 at point A). This indicated that although there remained significant energy dissipation at the interface, it was much lower at point B than at point A.

Using a similar multilayer configuration and focusing on the changes in bulk rheological responses, investigations have been made into the effects of interfacial diffusion for the PS/PS interface.[11,12] For this investigation, although the interface was between two different polymers, diffusion at the interfacial layer could be a possible explanation for the changes in the interface properties, as represented by the changes in the β value.

However, the tests discussed in a previous section (PC/LCP system with the Temperature Range below the Melting/Nematic Temperature) indicated that below the melting/nematic temperatures, there was no slip, and the β value was close to zero. Therefore, the melting/nematic temperature was a significant parameter affecting the interfacial properties of LCP/PC. Therefore, a more likely and dominant possibility was the change in the microstructure and state of LCP as a function of temperature, which led to the changes in the interfacial properties between LCP and PC.

Thermal history and temperature effect of LCP

The sensitivity of LCP to the thermal history effect is well known and accepted. Therefore, a possible point of contention was that the interfacial slip or velocity discontinuity observed for PC/LCP, as reflected in the positive value of β in Figure 9, could be due to the thermal sensitivity of LCP. However, as discussed in previous sections (PC/LCP System with the Temperature Range below the Melting/Nematic Temperature and PC/LCP System with the Temperature Range at the Melting/Nematic Temperature), this was unlikely because dynamic thermal stability had largely been achieved after the first half of the cycle. In addition, the value of β shown in Figure 9 varies between 0.2 and 0.6, indicating that 20–60% of the total dissipative energy was consumed at the interface. With a large magnitude of β, it was also unlikely that the value of β was a result of spurious experimental readings due to variations caused by a thermal history effect or thermal sensitivity of LCP.

Indeed, this investigation provided strong evidence that the interface between PC and LCP was a function of temperature and thermal history. Figure 9 indicates clearly that for the same temperature, the value of β was different, depending on whether the temperature was increasing or decreasing. For example, at 280°C, when the temperature was decreasing, β was about 0.2–0.3, but with the temperature increasing, β was about 0.5–0.6. An explanation for this observation was that for the temperature range investigated, LCP was undergoing both phase changes (melting and solidification) and changes in microstructure (crossing the nematic temperature). With changes in both the phase and microstructure, one would expect the interface property between LCP and PC to change. In addition,

both phase and microstructure changes are time-dependent and not an instantaneous function of temperature, so there would be a time lag. This would explain the different in the behavior of the interface (as reflected by β) depending on the temperature increasing or decreasing.

It is an accepted fact that LCP itself is sensitive to temperature and thermal history. However, this investigation provided evidence that the sensitivity of LCP blends to temperature and thermal history could be exasperated by the sensitivity of the interface to temperature and thermal history. Until now, those studying the sensitivity of LCP blends, as reported in the literature, had not considered the sensitivity of the interface separately.

Negative deviation of the PC/LCP blend viscosity

Some researchers[13] attributed the lowering of the viscosity of LCP blends below those of its individual components to the migration of LCP to the die wall, which was presumed to promote slipping between the die wall and LCP. However, contradictory results on this have been reported by different researchers. Some researchers[14–18] observed a negative deviation of the LCP blends in their studies, but others[19] did not observe the negative deviation of the LCP blends. The results of our multiple-layer experiments, as shown in Figure 9, although they might not be translated directly to a blend, also showed that the negative deviation at point B (the lower value of β) was not as significant as that of point A (the higher value of β) for a test range above the nematic and melting temperatures. As shown in Figure 8, no negative deviation was observed for temperatures below the nematic and melting temperatures (the value of β was close to zero). These researchers might employ different methods at different temperature ranges to study the viscosity behavior of LCP blends. Therefore, different thermal histories might be induced in each study. As discussed in the previous section, the interfacial property was sensitive to the thermal history, and this could be an explanation for some of the contradictory results for the viscosity values of LCP blends.

With the parallel-plate rheometer, there was no shear gradient in the through-thickness direction. In addition, the multiple-layer configurations ensured that the migration of LCP to the die wall was not an issue. Therefore, the migration of LCP to the die wall could not be used to explain the negative deviation from the rule of mixture in the multiple-layer experiments.

As the thermal history played an important role in the viscosity of pure LCP, it was tempting to postulate that the negative deviation of LCP blends from the rule of mixture was caused by the effect of the thermal history on the viscosity behavior of LCP. However, β

was computed by the deduction from the total dissipative energy the components of the dissipative energy of LCP and PC. By ensuring that LCP had a similar thermal history, we included the change in the viscosity of LCP due to the thermal history effect. Therefore, the changes in the viscosity behavior of LCP due to the thermal history could not explain the changes in β and the negative deviation from the rule of mixture. Therefore, the only remaining possibility for explaining this negative deviation was the energy dissipation in the interfacial layer, which was directly related to slip and/or another energy dissipation mechanism between PC and LCP.

CONCLUSIONS

An energy model and a specific experimental procedure were proposed for the development of an understanding of the interfacial behavior of polymer pairs under shear deformation. As shear deformation is the dominant deformation mode for the characterization of the viscosity behavior of polymer blends, this investigation could contribute to a better understanding of the rheological behavior of polymer blends. A new physical parameter, β, was proposed for the characterization of the property of the interface under shear deformation.

For the PS/HIPS polymer pairs, β was close to zero. This indicated that there was strong interfacial interaction with negligible slip at the interface. This was expected for a miscible polymer pair such as PS/HIPS.

Below the melting/nematic temperature of LCP, β was close to zero for the thermal cycling of PC/LCP. This indicated negligible slip and little energy dissipation in the interface of PC/LCP. In the melting/nematic temperature range of LCP, the large and positive value of β for the thermal cycling of PC/LCP indicated slip and/or energy dissipation in the interface. It provided a possible explanation for the negative deviation from the rule of mixture in LCP blends.

The changes in the interfacial properties for PC/LCP at the melting/nematic temperature range of LCP were likely caused by the changes in the phase and microstructure of LCP.

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