

Energy Model of the Interfacial Slip of Polymer Blends Under Steady Shear

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ABSTRACT: Interfacial slip at high-density polyethylene (HDPE)/polystyrene (PS) and high-impact polystyrene (HIPS)/PS interfaces under steady shear was studied. The multilayer structure and energy model for steady shear proposed by Lam and colleagues was employed. Results indicated that there was no interfacial slip at the HIPS/PS interface. However, interfacial slip was detected for HDPE/PS

under steady shear. Small interfacial thickness and weak interactions between HDPE and PS was proposed as the reason for interfacial slip at the HDPE/PS interface. Chain orientation under shear was believed to promote chain disentanglement in the interfacial layer and therefore increase interfacial slip. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1464–1470, 2003

INTRODUCTION

A polymer blend can combine the advantageous properties of the component polymers if the right components and appropriate blending methods are employed. Compared to synthesizing a new polymer, a polymer blend with similar properties can be developed with relatively short development time and low development costs. This makes polymer blending a continuously active and fruitful research area.

Rheology in the polymer blending process is critical because it controls the morphology of the blend products. The relationship between the viscosity of a polymer blend and that of its components varies and depends on the specific blends. Experimental and empirical rules of mixture were generalized from viscosity data by some researchers. These rules adopt different forms (logarithmic, reciprocal, and linear) in dealing with different blend systems.^{1–4}

Negative deviation from the rule of mixture for some blend systems was reported by some researchers.^{5–8} Slip at the interface of the component polymers and/or at the wall surface has been proposed to be the main reason for this phenomenon. Immiscible polymers have low entanglement densities and weak interactions at the interface and therefore cannot sustain high stress transferred from one component to the others when they are under shear. Interfacial slip is believed to occur under this situation.^{9,10}

Zhao and Macosko¹¹ investigated interfacial slip by extrusion of multi-alternating polypropylene (PP)/polystyrene (PS) layers. The viscosity measured by both in-line slit rheometer and rotary rheometer with parallel plates decreased with the number of the layers. The slip velocity was also calculated from viscosity measurements. Interfacial slip was detected in multilayer extrusion and steady shear in a rotary rheometer, but not in dynamic shear because of low shear stress. The detected interfacial slip was small and manifested only when there was a significant number of interfaces.

In parallel with Zhao and Macosko¹¹ and independently, Lam et al.¹² simplified the morphology of a polymer blend into a multilayer structure and, on the basis of this structure, proposed an energy model to quantify interfacial slip at high-impact polystyrene (HIPS)/PS and liquid crystalline polymer (LCP)/polycarbonate (PC) interfaces. A temperature ramp test under dynamic shear was employed in their experiments. Significant interfacial slip was discovered at the LCP/PC interface, but no interfacial slip for the HIPS/PS interface. Because of the complex nature and thermal history effects of LCPs, the study of interfacial slip at the LCP/PC interface was complicated.

As such, the existence of significant interfacial slip for other polymer pairs, which are well behaved rheologically without the complication of thermal history effects, remains to be investigated. Thus, in this study, interfacial slip at high-density polyethylene (HDPE)/PS and HIPS/PS interfaces under steady shear were studied on the basis of the energy model. All polymers are well-behaved thermoplastics that

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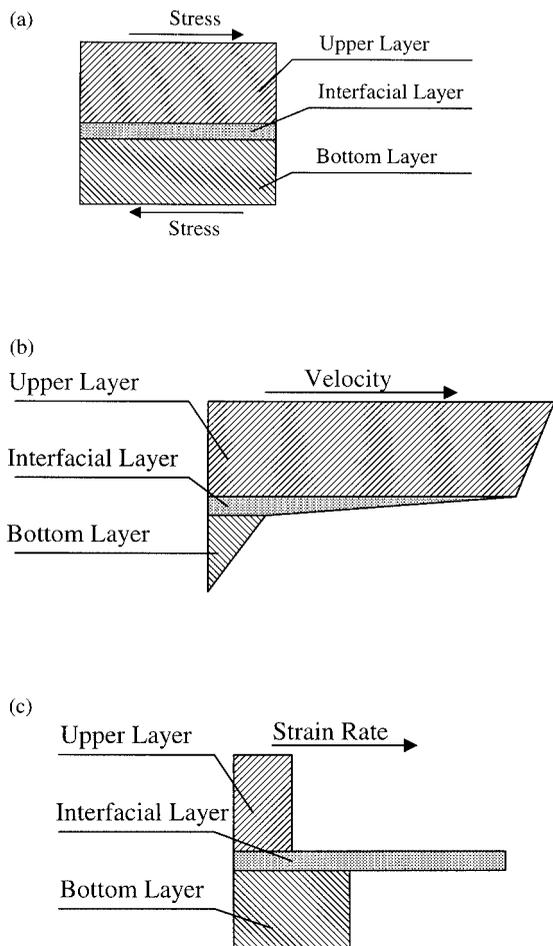


Figure 1 Multilayer structure of the energy model: (a) layer structure of the model; (b) velocity distribution of each layer; (c) strain rate of each layer.

have stable rheological properties. It is also easier to apply the energy model in steady shear than in dynamic shear. Energy factors were calculated to quantify their interfacial slip. Formulas for interfacial slip velocity were also derived on the basis of the energy model. Reasons are given for the different interfacial slip behavior between HIPS/PS and HDPE/PS on the basis of polymer thermodynamics.

THEORETICAL MODEL

A polymer blend consists of a matrix phase, one or more dispersive phases, and interfaces between them formed by chain interdiffusion. Its morphology under shear can be simplified into a multilayer structure, as shown in Figure 1(a).¹² This structure consists of three layers: the upper, interfacial, and bottom layers. They correspond to the matrix phase, interface, and dispersive phase in the polymer blend. By applying a uniform shear stress at the top surface with the bottom surface fixed, and assuming uniform viscosity within each layer, the velocity distribution and shear strain

rate for the three layers may be represented schematically [see Fig. 1(b) and (c), respectively]. From these figures, one may see that the shear rates and shear strains in the three layers are different because of the different viscosities of the three layers. Although this uniform layered configuration is not geometrically representative of the actual blend, it allows special experimental procedure and setup, which conform to the assumptions of the model, to be established for the verification of the hypothesis if interfacial slip occurs between two polymer components.

The essence of the energy model was to calculate the energy consumption in each layer of the three-layer structure when the structure undergoes shear deformation. An energy factor was defined to indicate the energy fraction of the interfacial layer. A high energy consumption in the interfacial layer means a large strain in this layer. Because the interfacial layer is very thin (several nanometers for immiscible polymers), this large strain may manifest macroscopically as interfacial slip between the upper and bottom layers.

Calculation of the energy factor for steady shear was detailed by Lam et al.¹² The power consumptions per unit volume on the upper layer (E_U), interfacial layer (E_I), bottom layer (E_B), and the total multilayer structure (E_T) are written as follows:

$$\begin{aligned} E_U &= \tau \dot{\gamma}_U \\ E_I &= \tau \dot{\gamma}_I \\ E_B &= \tau \dot{\gamma}_B \\ E_T &= \tau \dot{\gamma}_T \end{aligned} \tag{1}$$

where τ and $\dot{\gamma}$ denote shear stress and shear rate, respectively. The energy factor ϕ was defined as

$$\begin{aligned} \phi &= \frac{E_I C_I}{E_T} = \frac{E_T - E_U C_U - E_B C_B}{E_T} \\ &= 1 - \frac{\dot{\gamma}_U C_U + \dot{\gamma}_B C_B}{\dot{\gamma}_T} \end{aligned} \tag{2}$$

The shear rates for the various layers and the total structure can be expressed as

$$\begin{aligned} \dot{\gamma}_U &= \frac{\tau}{\eta_U}; & \dot{\gamma}_B &= \frac{\tau}{\eta_B} \\ \dot{\gamma}_I &= \frac{\tau}{\eta_I}; & \dot{\gamma}_T &= \frac{\tau}{\eta_T} \end{aligned} \tag{3}$$

where η_U , η_B , and η_T denote the viscosity of the upper and bottom layers and the total structure. Combining eqs. (2) and (3) gives

$$\phi = 1 - \frac{\eta_T(C_B \eta_U + C_U \eta_B)}{\eta_B \eta_U} \tag{4}$$

This is the energy factor for steady shear. All the parameters on the right side of the equation can be obtained experimentally. Equation (4) can also be rearranged to predict the viscosity of the blend:

$$\eta_T = \frac{(1 - \varphi)\eta_B\eta_U}{C_B\eta_U + C_U\eta_B} \quad (5)$$

When there is no interfacial slip ($\varphi = 0$), eq. (5) reduces to the reciprocal rule of mixture, expressed as

$$\frac{1}{\eta_T} = \frac{C_U}{\eta_U} + \frac{C_B}{\eta_B} \quad (6)$$

It must be highlighted that, although the reciprocal rule is empirical, eqs. (5) and (6) are derived from the first principle based on the energy concept for the parallel layered configuration. From Figure 1(b), $\dot{\gamma}_T$ can be obtained as

$$\begin{aligned} \dot{\gamma}_T &= \frac{\Delta V_T}{H_T} = \frac{\Delta V_U + \Delta V_I + \Delta V_B}{H_T} \\ &= \frac{\dot{\gamma}_U H_U + \Delta V_I + \dot{\gamma}_B H_B}{H_T} = \dot{\gamma}_U C_U + \frac{\Delta V_I}{H_T} + \dot{\gamma}_B C_B \end{aligned} \quad (7)$$

where V and H denote velocity and thickness, respectively. Hence, slip velocity ΔV_I can be obtained by arranging eq. (7), as follows:

$$\Delta V_I = H_T(\dot{\gamma}_T - \dot{\gamma}_U C_U - \dot{\gamma}_B C_B) \quad (8)$$

Combining eq. (4) with eq. (8) gives the relationship between the energy factor and the slip velocity:

$$\Delta V_I = H_T \dot{\gamma}_T \varphi \quad (9)$$

Equation (9) shows that at the same shear rate, the slip velocity increases linearly with the energy factor.

In eq. (4), several important variables have to be determined before the energy factor φ can be calculated. Among these variables, C_U and C_B can be obtained by measuring the thicknesses of the upper and bottom layers because they have the same cross-sectional area. The viscosity of the total structure η_T can be measured directly by the rheometer. However, we cannot determine either the shear rate or the viscosity of individual components (η_U and η_B) directly, given that all layers experience the same shear stress rather than the same shear rate. However, the required viscosity of an individual component can be obtained by performing separate, independent experiments consisting only of the component. Subsequently, the corresponding shear rates and viscosities in the individual layers of the multilayer structure can be determined from these experiments.¹²

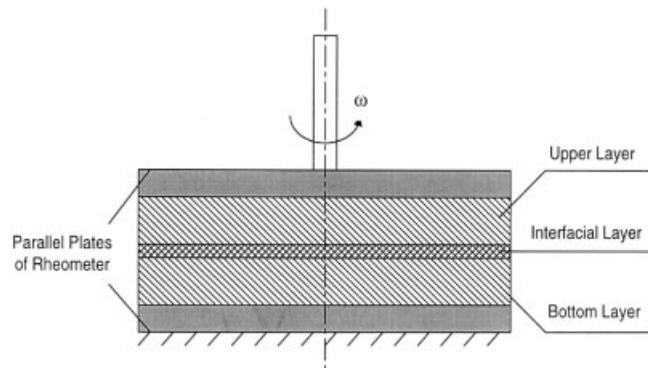


Figure 2 Multilayer structure between parallel plates of the rheometer.

EXPERIMENTAL

Polymer pairs HIPS/PS and HDPE/PS were employed to study their interfacial slip behavior by use of the energy model. HIPS (Dow 498) and PS (Dow 666H) were obtained from Dow Chemical (Midland, MI). HIPS is a blend of PS and styrene-*graft*-butadiene copolymer. The butadiene content was about 5%. Because butadiene is not compatible with styrene, butadiene exists in discrete droplets of about 10 μm . HDPE was from ExxonMobil (Model Mobil H-UP921, Al-Jubail, Saudi Arabia). All polymers were injection molded into disks (diameter, 30 mm; thickness, 1 mm) for rheological tests.

The Advanced Rheometric Expansion System (ARES) (Rheometric Scientific, Inc., Piscataway, NJ) with parallel-plate geometry was employed with testing and boundary conditions conforming to the requirements of the model (see Fig. 2). Two polymer disks (upper layer and bottom layer) were superimposed between the two parallel plates and compressed to form the multilayer structure. The diameter of the parallel plates was 25 mm. Steady shear viscosities were obtained over the range of shear rates of 0.1–1 s^{-1} , given that higher shear rates might have caused edge failure and would have jeopardized the reliability of the data. Two types of sample loadings were used for the steady test. First, single disc loadings were used to obtain the steady viscosities of all individual polymer types in a multilayer structure. Then multidisk loading was employed to obtain the viscosity of the multilayer structure at the same testing condition. Based on the values for both single and multilayer samples, the constant stress line could be constructed and the energy factor could be calculated, as documented by Lam et al.¹²

RESULTS AND DISCUSSION

Results of steady shear tests for single-layer HDPE, HIPS, and PS are shown in Figure 3. From this figure, shear thinning can be observed for PS and HIPS, but it

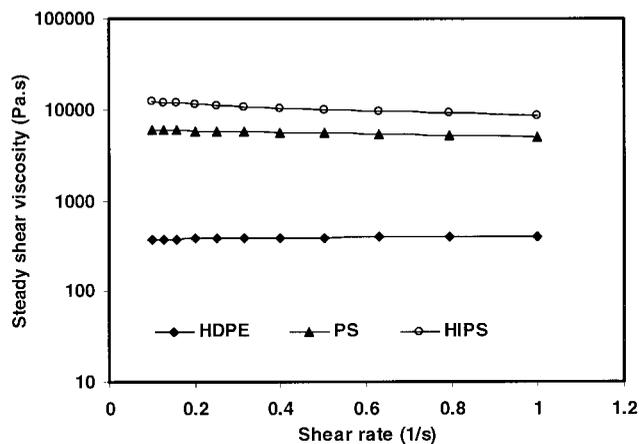


Figure 3 Steady shear viscosity as a function of shear rate for various polymers at 200°C.

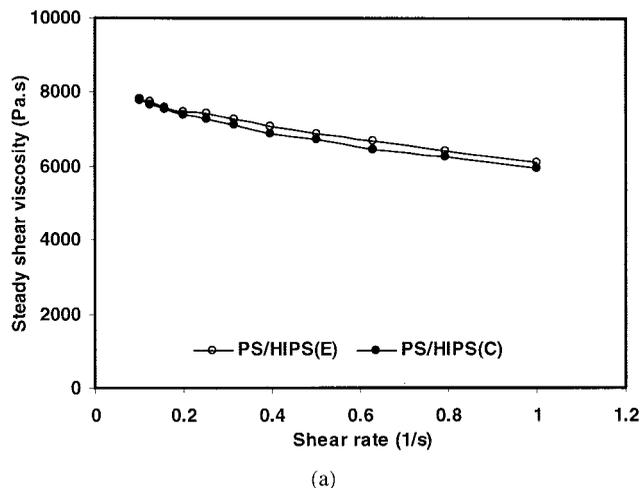
is not obvious for HDPE within this narrow range of shear rates. All the curves are the average values of three runs for each material. Steady shear results for multilayer HDPE/PS and HIPS/PS are shown in Figure 4. After the η versus $\dot{\gamma}$ plots for individual layers and multilayer structures have been obtained, the viscosities of the individual layers and the multilayer structures at the same shear stress can be obtained using the constant stress line.¹²

The energy model gives the viscosity of the multilayer structure by eq. (6), which is the same as the reciprocal rule of mixtures, when there is no interfacial slip ($\varphi = 0$). The viscosities of HDPE/PS and HIPS/PS multilayer structures were calculated by use of this equation and compared with the experimental values in Figure 4. If interfacial slip does not exist for a certain polymer pair, the experimental curves should be close to the corresponding theoretical curves. From this figure, one can see that for HIPS/PS, the experimental and calculated values are in substantial agreement [Fig. 4(a)]. The maximum percentage deviations are 3.1% (see Fig. 5). In contrast, HDPE/PS reveals a greater difference between the measured and calculated values [Fig. 4(b)], which amounts to 11% (Fig. 5). The experimental value is consistently below the value calculated by the model. According to the model, this negative deviation from eq. (6) implies that there was slip at the HDPE/PS interface. The corresponding energy factors for HIPS/PS and HDPE/PS were calculated accordingly, by use of eq. (4), and are given in Figure 6.

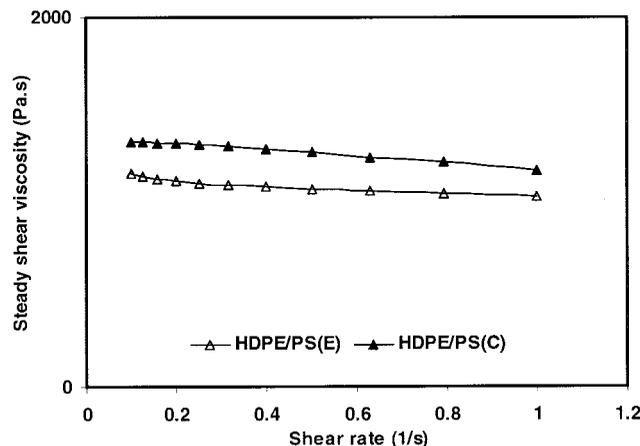
The energy factor of HDPE/PS is well above that of HIPS/PS in Figure 6. Energy factors reported in Figure 6 were calculated by use of the mean values of various parameters on the right side of eq. (4). To ensure that the obtained energy factor indicating slip was not the result of experimental scatter, an error analysis can be performed. The error of these energy factors can be obtained provided that the errors of the

parameters are known.¹³ The fractional errors of the viscosities for pure polymers (η_U and η_B) can be controlled within 2–3%. The fractional error of the viscosity for multilayer structures (η_T) is greater (<5%) because of the addition of interfaces. Volume ratios (C_U and C_B) are slightly different in each test, with an error of <5%. Assuming a fractional error of 3% for η_U and η_B , and 5% for C_U , C_B , and η_T , then the fractional errors for the energy factors of HDPE/PS and HIPS/PS are 55 and 218%, respectively. (See the Appendix for details of the calculation.)

To account for slip, the proposed energy model predicts an energy factor between 0 and 1, where 0 = the nonslip condition and 1 = 100% slip at the interface. Thus, the slightly negative value for the energy factor for HIPS/PS, as shown in Figure 6, could not be predicted by the energy model. However, error analysis indicated that the error for the energy



(a)



(b)

Figure 4 Steady shear viscosity as a function of shear rates for HDPE/PS and HIPS/PS. “E” and “C” denote experimental and calculated, respectively. All values in this plot are average values of three runs.

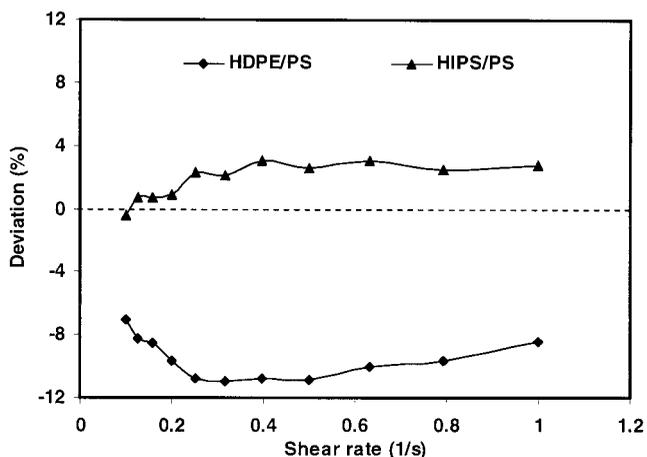


Figure 5 Deviation of experimental viscosities from the rule-of-mixture predicted values for HDPE/PS and HIPS/PS at 200°C.

factor was 218%. An error greater than 100% indicates that no conclusion can be reached on the slip phenomenon, given that the nonzero value of the energy is within experimental scatter. Thus, the existence of interfacial slip at the HIPS/PS interface is not apparent. This confirms the results of Lam et al.,¹² who reached the same conclusion for tests conducted under dynamic shear and thermal cycling.

For the HDPE/PS interface, Figure 6 shows that the energy factor is positive. The error for the energy factor of 55% is substantial; however, even taking the lower limit of the energy factor (~ 0.06), it remains positive, indicating the existence of slip.

The energy factor of HDPE/PS increases with shear rate and reaches a maximum at around 0.3 s^{-1} , after which it slowly decreases. Figure 3 shows that PS has a more severe shear thinning behavior than that of HDPE. Therefore the energy proportion consumed in PS increases as the shear rate increases. This change of

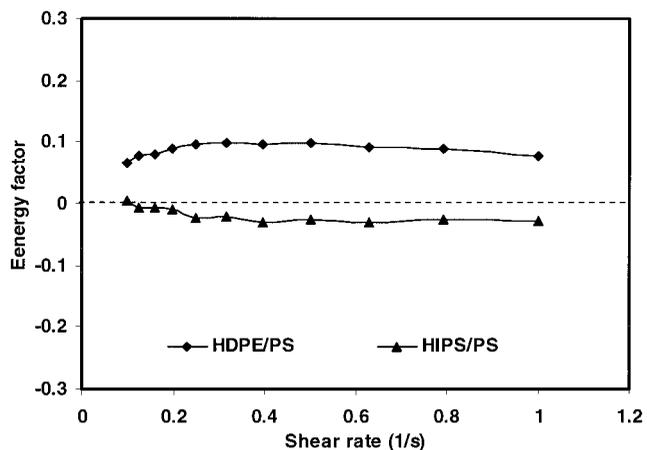


Figure 6 The energy factor as a function of shear rate for HDPE/PS and HIPS/PS at 200°C.

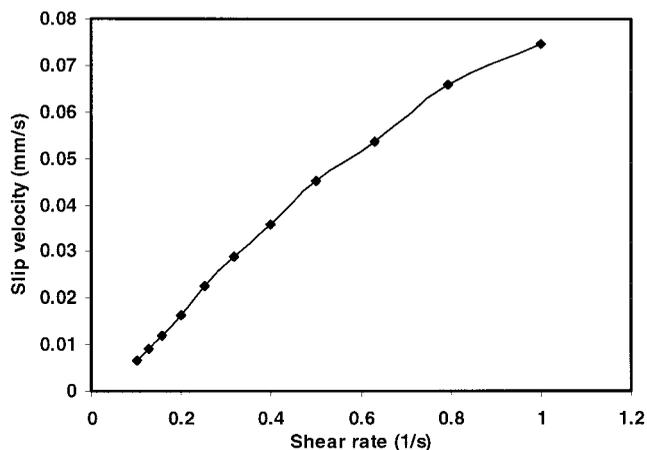


Figure 7 Slip velocity versus shear rate for HDPE/PS at 200°C.

energy distribution may lower the energy proportion consumed in the interfacial layer and thus decrease the energy factor as the shear rate is increased. The increase of the energy factor at the beginning is attributed to the mounting shear stress.

If shear rates of a multilayer structure and the corresponding upper and bottom layers are known, slip velocities can be calculated by use of eq. (9). Substituting H_T (0.8 mm), shear rates, and energy factors into eq. (9) produces slip velocities at the HDPE/PS interface at various shear rates (see Fig. 7). Figure 7 shows that slip velocity is proportional to the shear rate. This is reasonable because a higher shear rate (shear stress) promotes chain disentanglement in the interfacial layer.

Slip may occur at interface when the interfacial strength is too low to sustain the shear stress applied on it. Two basic steps are required for achieving a fully developed interfacial layer (maximum interfacial strength). The first step is the wetting process between the two polymers. Without wetting, an intimate contact between the two surfaces cannot be achieved and the second step (i.e., chain interdiffusion at the interface) cannot start. As a result, the interfacial strength would be low.

In the case of liquid B spreading on liquid A, the condition for spontaneous spreading is¹⁴

$$\gamma_A - \gamma_B > \gamma_{AB} \quad (10)$$

where γ denotes either surface tension or interfacial tension. If this requirement is met by the polymer pairs, intimate contact between them can be achieved and the interfacial strength will depend greatly on the degree of interdiffusion (interfacial thickness) and mutual entanglements at the interface. Interaction thickness d_∞ can be related to the Flory interaction parameter¹⁵ through

$$d_{\infty} = 2\beta / (6\chi_{AB})^{1/2} \quad (11)$$

where β is the statistical segment length.

Surface tension and interfacial tension at certain temperatures for some polymers can be obtained from the *Polymer Handbook*.¹⁶ Surface tensions of HDPE and PS and their interfacial tension at 200°C are 25.4, 27.7, and 4.7 dyn/cm, respectively. HDPE and PS cannot wet each other at 200°C because $\gamma_{PS} - \gamma_{HDPE} < \gamma_{PS/HDPE}$. Therefore, intimate contact between them is difficult to obtain. Even if interdiffusion starts at the interface, their equilibrium interfacial thickness is intrinsically small, given that HDPE and PS are immiscible polymers (high Flory interaction parameter). In eq. (11), the statistical segment lengths (β) of HDPE and PS are 5.64 and 6.89 Å, respectively.¹⁷ The Flory interaction parameter χ_{AB} can be calculated from the following formula:

$$\chi_{AB} = \frac{BV_{\text{ref}}}{RT} = \frac{V_{\text{ref}}}{RT} (\delta_A - \delta_B)^2 \quad (12)$$

where the solubility parameter δ of HDPE and PS can be obtained from the *Polymer Handbook*.¹⁶ V_{ref} is the reference volume and is usually taken as the molar volume of HDPE or PS (here the average value of HDPE and PS was used), R is the gas constant, and T is the temperature. Through the use of this equation, χ_{AB} was calculated to be 0.056 for HDPE/PS. Thus, with the values of β and χ_{AB} , eq. (11) gives 21.5 Å for the interfacial thickness of the HDPE/PS interface. This value is very small compared to a typical molecular radius of gyration R_g , which is in the order of 10^2 Å. Therefore full entanglement between HDPE and PS is not achieved in the interfacial layer and thus the interfacial strength is low.

In contrast, because HIPS contains a 95% matrix of PS, and butadiene exists as dispersive droplets, the existence of butadiene has little influence on the wettability and miscibility of the PS matrix to other materials. Therefore, HIPS and PS can be considered to be completely wettable and miscible polymers. They can establish intimate contact and the interface between them disappears after a period of diffusion time. Hence, the "interfacial" strength equals the matrix strength for HIPS/PS.

Wetting and interdiffusion, two critical steps of establishing an equilibrium interface, have been discussed. From the calculations, it is found that in both steps, the HDPE/PS encountered great resistance to form a strong interface; thus, its resistance to the applied shear stress in the rheological tests is weak compared to that of HIPS/PS. Moreover, molecular chains tend to orient in the shear direction under steady shear. This orientation may considerably facilitate the disentanglement in the interfacial layer of HDPE/PS.

Therefore the entanglement density in the interfacial layer under shear is even lower than that in the quiescent state. Hence, the strength of the interfacial layer of HDPE/PS, which is already very low compared to that of HIPS/PS, will decrease further under shear. These explanations provide the reasons for the experimental observation that HDPE/PS manifested an observable interfacial slip.

One may argue that the negative viscosity deviation from the rule of mixtures is attributable to the wall slip at the parallel-plate surfaces rather than the interfacial slip at the polymer interfaces. The parallel plates are made of metal and have very high surface tension. The adsorption of polymer chains to the metal surface is very strong. Desorption and disentanglement are unlikely to occur at low shear stress. As documented by other researchers,^{18–20} wall slip occurs at a shear stress ranging from 0.1 to 1 MPa, depending on the surface conditions. In our work, the maximum shear stress was experienced by PS, which is less than 5000 Pa. Therefore, the negative deviation observed in our work cannot be attributed to wall slip.

CONCLUSIONS

The energy model, in conjunction with the parallel-plate testing configuration, was found to be suitable for studying interfacial slip in polymer blends. Through the calculation of the energy factor, it was found that HDPE/PS under steady shear has interfacial slip, which could be detected by a parallel-plate rheometer. The reasons proposed were its small interfacial thickness and weak interfacial strength. Full mutual entanglements at the interface are achieved only with some difficulty when the interfacial thickness is small. HIPS and PS are miscible and their interfacial layer has the same interfacial strength as that of their matrix and thus no interfacial slip was detected.

APPENDIX

Error analysis for steady shear

The equation used to calculate the energy factor under steady shear is

$$\varphi = 1 - \eta_T \left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U} \right) \quad (A.1)$$

Assuming the fractional error of 3% for η_U and η_B , and 5% for C_U , C_B , and η_T , then the fractional error of $\frac{C_B}{\eta_B}$ in eq. (A.1) is

$$\begin{aligned} \frac{\Delta(C_B/\eta_B)}{|C_B/\eta_B|} &= \sqrt{\left(\frac{\Delta C_B}{|C_B|} \right)^2 + \left(\frac{\Delta \eta_B}{|\eta_B|} \right)^2} \\ &= \sqrt{(5\%)^2 + (3\%)^2} = 5.8\% \quad (A.2) \end{aligned}$$

and the fractional error of $\frac{C_U}{\eta_U}$ is

$$\frac{\Delta(C_U/\eta_U)}{|C_U/\eta_U|} = \sqrt{\left(\frac{\Delta C_U}{|C_U|}\right)^2 + \left(\frac{\Delta \eta_U}{|\eta_U|}\right)^2} = \sqrt{(5\%)^2 + (3\%)^2} = 5.8\% \quad (\text{A.3})$$

Therefore the fractional error of $\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)$ can be given by

$$\begin{aligned} \frac{\Delta\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)}{\left|\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right|} &= \frac{\sqrt{\left(\Delta\left(\frac{C_B}{\eta_B}\right)\right)^2 + \left(\Delta\left(\frac{C_U}{\eta_U}\right)\right)^2}}{\left|\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right|} \\ &= \frac{\sqrt{\left(5.8\% \times \left|\frac{C_B}{\eta_B}\right|\right)^2 + \left(5.8\% \times \left|\frac{C_U}{\eta_U}\right|\right)^2}}{\left|\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right|} \end{aligned} \quad (\text{A.4})$$

Substituting the mean values of C_U , C_B , η_U , and η_B for HDPE/PS and HIPS/PS into eq. (A.4) gives

$$\begin{aligned} \frac{\Delta\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)}{\left|\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right|} &= \frac{\sqrt{\left(5.8\% \times \left|\frac{C_B}{\eta_B}\right|\right)^2 + \left(5.8\% \times \left|\frac{C_U}{\eta_U}\right|\right)^2}}{\left|\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right|} \\ &= \begin{cases} 5.0\% \text{ HDPE/PS} \\ 4.3\% \text{ HIPS/PS} \end{cases} \end{aligned} \quad (\text{A.5})$$

Hence the fractional error of $\eta_T\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)$ can be obtained as

$$\begin{aligned} \frac{\Delta\left(\eta_T\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)\right)}{\left|\eta_T\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)\right|} &= \sqrt{\left(\frac{\Delta \eta_T}{|\eta_T|}\right)^2 + \left(\frac{\Delta\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)}{\left|\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right|}\right)^2} \\ &= \begin{cases} 7.1\% \text{ HDPE/PS} \\ 6.6\% \text{ HIPS/PS} \end{cases} \end{aligned} \quad (\text{A.6})$$

From eq. (A.1) the absolute error of the energy factor is given by

$$\Delta \varphi = \Delta\left(1 - \eta_T\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)\right) = \Delta\left(\eta_T\left(\frac{C_B}{\eta_B} + \frac{C_U}{\eta_U}\right)\right) \quad (\text{A.7})$$

Combining eqs. (A.6) and (A.7) and substituting mean values of η_T , η_B , η_U , C_B , and C_U can give the absolute and fractional error of the energy factor, as follows:

$$\Delta \varphi = \begin{cases} 0.063 \text{ HDPE/PS} \\ 0.068 \text{ HIPS/PS} \end{cases} \quad (\text{A.8})$$

$$\frac{\Delta \varphi}{|\varphi|} = \begin{cases} 55.4\% & \max|\varphi| = 0.114 \text{ HDPE/PS} \\ 218.5\% & \max|\varphi| = 0.031 \text{ HIPS/PS} \end{cases} \quad (\text{A.9})$$

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