Slip at polymer–polymer interfaces: Rheological measurements on coextruded multilayers

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Synopsis

Polypropylene (PP) and polystyrene (PS), with closely matched viscosity, were coextruded into 8, 32, and 64 alternating layers. The apparent steady shear viscosity of these multilayer samples was measured with an in-line slit rheometer and with a parallel-plate rheometer. In both cases the apparent viscosity decreased with the number of layers providing strong evidence for interfacial slip. The velocity difference across the interface (interfacial slip velocity) versus shear stress, $\Delta V_I(\tau)$, was calculated from the apparent viscosity measurements. $\Delta V_I(\tau)$ showed sigmoidal behavior: a region of very low slip ($< 10^{-3}$ m) at low shear stress, a strongly increasing region at $\tau > 10^3$ Pa followed by a linear region $\Delta V_I = \tau/\beta_I$. These data could be fit with a modified Ellis model. The same function fit the different number of layers and both slit and parallel-plate data indicating $\Delta V_I(\tau)$ is a material property of the PP/PS pair. Slip was also observed in PS/PMMA (polymethyl methacrylate) and PP/aPA (amorphous nylon) pairs. Addition of a premade P(S-b-EE) diblock copolymer to the PP/PS pair was able to suppress the interfacial slip but only after enough time for sufficient block copolymers to diffuse to the interfaces. The in situ formed graft copolymer of maleated PP with aPA at the interface of the PP/aPA pair directly suppressed the slip. Our results are in qualitative agreement with the theory of Furukawa (1989) and de Gennes (1992), which predicts fewer chain entanglements near the interface between two immiscible polymers, and thus a narrow region ($\sim$ interfacial width) with lower viscosity. This lower viscosity is the cause of apparent interfacial slip. Goveas and Fredrickson (1998) extended these ideas to calculate the slip in a symmetric bilayer where both bulk and interface are Newtonian. Their results are in qualitative agreement with our observation but predict a stronger slip. Our results also indicate that the anomalously low viscosity reported by a number of researchers for immiscible polymer blends is due to interfacial slip. Blends of PP and PS show similar negative viscosity deviations to those reported but only at $\tau > 2000$ Pa. No negative deviations were found for linear viscoelastic (low-stress) measurements. © 2002 The Society of Rheology.

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I. INTRODUCTION

Since the 1970s, there have been reports of anomalously low viscosity of immiscible polymer blends. In some systems, they are even lower than either of the components. Most of these studies have been with capillary rheometers at higher shear rates and have often been reported as part of blend processing studies in technological journals. No fundamental investigation of this anomaly appears available. Here, we report rheological

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studies on well-characterized blends and layered composites of the same polymers. Our results show that the anomalously low viscosity of blends is likely due to interfacial slip. Utracki (1982, 1983) has reviewed blends which showed anomalously low viscosity. As summarized in Table I, a negative viscosity deviation has been observed in a wide range of immiscible blends. The deviation is calculated as

\[
\text{dev.} = \frac{\eta_{av} - \eta_{ex}}{\eta_{ex}},
\]

where \(\eta_{ex}\) is the measured blend viscosity, and \(\eta_{av}\) is the calculated blend viscosity using the log-additive mixing rule

\[
\log \eta_{av} = \phi_1 \log \eta_1 + \phi_2 \log \eta_2,
\]

where \(\phi_i\) and \(\eta_i\) are the volume fraction and viscosity of the components. The deviation listed in Table I is the maximum value. It varies from 20% to 2000%. The Flory–Huggins interaction parameter \(\chi\) is calculated using either interfacial tension measurements or solubility parameters [Wu (1982); Grulke (1989)], and is also listed in Table I. In general, it appears that systems which are more incompatible (having large \(\chi\)) show larger viscosity deviation.

Emulsion models predict a higher viscosity of the blends than that of the matrix, and the available semiempirical mixing rules predict some average blend viscosity like Eq. (2). To account for the anomalously lower viscosity of blends, Lin (1979) proposed interfacial slip. He derived an equation to calculate blend viscosity from viscosities of the components. It is similar in form to that of Heitmiller (1964) with an addition interfacial slip parameter. Lin used his equation to fit the viscosity of polypropylene–polystyrene (PP/PS) melt blend measured by Han and Yu (1972). Although the fit was good, the mechanism for interfacial slip was not clear, and the slip parameter was simply a fitting constant. Despite this, Lin’s equation has been used by many researchers [Lyngaae-Jorgensen et al. (1988); Cohen and Schroeder (1990); Zhao et al. (1997); Bousmina et al. (1999)].

In recent experiments by Chan and Feng (1997), HDPE blended with fluoroelastomer was extruded through a slit die. They measured fluorine on the die wall but almost no fluorine on the surface of the extrudates. This indicates slip between bulk HDPE and a thin fluoroelastomer layer on the die wall. Using depth-resolved light microscopy, Migler et al. (2001) directly observed the slippage of LLDPE on a thin layer of fluoropolymer on

<table>
<thead>
<tr>
<th>Blends</th>
<th>(T (\degree\text{C}))</th>
<th>dev. (%)</th>
<th>(\chi^2)</th>
<th>(l_e (\mu\text{m}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE/PS</td>
<td>200</td>
<td>20</td>
<td>0.056</td>
<td>10</td>
<td>[Han and Yu (1971)]</td>
</tr>
<tr>
<td>PMMA/PS</td>
<td>220</td>
<td>58</td>
<td>0.032</td>
<td>21</td>
<td>[Utracki and Kamal (1982)]</td>
</tr>
<tr>
<td>HDPE/PP</td>
<td>200</td>
<td>70</td>
<td>0.022</td>
<td>9</td>
<td>[Alle and Lyngaae-Jorgensen (1980)]</td>
</tr>
<tr>
<td>EPDM/PE</td>
<td>190</td>
<td>85</td>
<td>0.048</td>
<td>20</td>
<td>[Kapuscinski and Schreiber (1979)]</td>
</tr>
<tr>
<td>PP/PS</td>
<td>200</td>
<td>150</td>
<td>0.042</td>
<td>10</td>
<td>[Han and Yu (1972)]</td>
</tr>
<tr>
<td>EPDM/Viton(^b)</td>
<td>160</td>
<td>340</td>
<td>0.103</td>
<td>28</td>
<td>[Shih (1976)]</td>
</tr>
<tr>
<td>EP rubber/PP</td>
<td>200</td>
<td>700</td>
<td>0.054</td>
<td>40</td>
<td>[Danesi and Porter (1978)]</td>
</tr>
<tr>
<td>PC/PS</td>
<td>180</td>
<td>1890</td>
<td>0.165</td>
<td>30</td>
<td>[Lipatov et al. (1981)]</td>
</tr>
<tr>
<td>PMMA/PA-12</td>
<td>210</td>
<td>1900</td>
<td>0.577</td>
<td>45</td>
<td>[Utracki and Kamal (1982)]</td>
</tr>
</tbody>
</table>

\(^a\)\(\chi\), Flory–Huggins interaction parameter, calculated from solubility parameters or scaled from interfacial tension.

\(^b\)Fluoroelastomer made by Dupont.
the die wall. Levitt and Macosko (1999) studied the deformation of PP drops in a PS matrix with and without adding block copolymers. Drop deformation with block copolymers was found to be greatly enhanced which could not be explained by simply a reduction of interfacial tension. They proposed that significant slip occurred between the bare PP/PS interfaces, and that block copolymers suppressed this slip.

A mechanism to explain the apparent slip at polymer–polymer melt interfaces based on polymer chain dynamics was proposed by Furukawa (1989), Brochard-Wyart et al. (1990), and de Gennes (1992). They assume polymers A and B are symmetric, i.e., identical friction coefficient $\zeta$, statistic segment length $b$ and chain length $N$, and weakly incompatible, i.e., $1/N \ll \chi < 1$. Then, there exists an interfacial region consisting mainly of interpenetrating loops of chains A and B. The average length of the loops, $m$, scales as $m \sim 1/\chi$, and the interfacial width $a_I$ scales as $a_I \sim b/\sqrt{6N}$. Then, the number of chain entanglements in the interfacial region $a_I/N_e$ is less than the entanglement density in the bulk phase $R_g/N_e$, where $N_e$ is the length of one entanglement. Thus, there is a lower viscosity region near the interface. This low-viscosity region does not lead to a true interfacial slip, i.e., a velocity discontinuity, as observed at the interface between a polymer melt and a solid wall above a critical stress [Wang (1999)]. Rather, as shown in Fig. 1, when a shear stress is applied parallel to the interface, the shear rate is discontinuous across the interfacial region. This lower viscosity of the interfacial region reduces the apparent blend viscosity.

de Gennes introduced an extrapolation length, $l_e$, as a measure of the apparent slip between a polymer melt and a solid surface [de Gennes (1979)]. This concept was extended to measure the interfacial slip at a polymer–polymer interface. As shown in Fig. 1, $l_e$ is defined as the distance to extrapolate the velocity at the interface back to zero, so that

$$l_e = \left( \frac{a_I}{2} \right) \frac{\eta_{\text{bulk}}}{\eta_I}. \quad (3)$$

where $\eta_{\text{bulk}}$ and $\eta_I$ are the bulk and interfacial viscosities. For symmetric pair, $\eta_{\text{bulk}}$ is the same for both polymers. The deviation of the apparent viscosity of A/B bilayers, $\eta_{\text{app}}$, from the bulk viscosity, $\eta_{\text{bulk}}$, is
\[
\frac{\eta_{\text{bulk}} - \eta_{\text{app}}}{\eta_{\text{app}}} = \frac{2l_e}{L} \left(1 - \frac{\eta_I}{\eta_{\text{bulk}}}\right),
\]  

(4)

where \( L \) is the length scale of the layers. It is assumed the same for each layer.

Goveas and Fredrickson (1998) modeled symmetric bilayers under simple one-dimensional shear with shear stress parallel to the interface (Fig. 1). They derived expressions for \( l_e \) in the case of entangled bulk phases and a Rouse-like interface \((a_I < bN_e^{1/2})\):

\[
l_e = \frac{\sqrt{6\chi R_g^2(N/N_e)^2}}{2b}. \tag{5}
\]

They also give a phenomenological relation for the case of entangled bulk and interface \((a_I \gg bN_e^{1/2})\):

\[
l_e = \frac{\sqrt{6\chi R_g^2}}{2b}. \tag{6}
\]

Substituting Eq. (5) or (6) into Eq. (3) with \( a_I = 2b/\sqrt{6\chi} \) [see Eq. (11)], the ratio of interfacial viscosity to bulk viscosity for \( a_I \ll bN_e^{1/2} \) is

\[
\frac{\eta_I}{\eta_{\text{bulk}}} = \frac{(a_I/R_g)^2}{2(N/N_e)^2}, \tag{7}
\]

and for \( a_I \gg bN_e^{1/2} \) is

\[
\frac{\eta_I}{\eta_{\text{bulk}}} = \frac{1}{2} \left(\frac{a_I}{R_g}\right)^2. \tag{8}
\]

Note that Eq. (7) differs from Eq. (8) by the factor \((N/N_e)^2\). According to Eqs. (7) and 8, for systems with \( \chi \gg 1/N \) (i.e., \( a_I < R_g \)), the interfacial viscosity is always lower than the bulk viscosity, thus the apparent interfacial slip is an intrinsic property of incompatible blends. When the layer thickness of bulk phases is of the same order of magnitude as the extrapolation length, i.e., \( L \sim l_e \), Eq. (4) predicts an apparent viscosity deviation about 200%. The extrapolation length of the blends listed in Table I is estimated using Eq. (5) assuming a Rouse-like interface. They have values on the order of 10 \( \mu \text{m} \), which, assuming \( a_I \sim 2 \text{ nm} \) and applying Eq. (5), implies that interfacial viscosity could be \( 10^4 \) times lower than that of the bulk phases.

The rheological measurements obtained from melt blends cannot be easily used to measure the apparent interfacial slip, due to the interplay between rheology and morphology [Doi and Ohta (1991); Macosko (2000)]. A layered composite structure is an ideal model system for this purpose. Miroshnikov and Andreeva (1987) and Cohen and Schroeder (1990) created multilayer composites of polystyrene–polymethyl methacrylate (PS/PMMA) and PS/PP in a capillary rheometer by stacking alternating disks of each homopolymer in the barrel. Under constant stress, the disks were pushed down through a capillary die, forming a telescopic layered structure in the die channel. They measured the mass flux of the layered composite and found that it was larger than that of the homopolymers, and increased as the number of layers increased (or, equivalently, the layer thickness decreased), therefore, indicating interfacial slip. However, in their experiment, the layered structure was not well controlled. The number of layers and layer thickness kept changing during extrusion. Layers were broken at the center and interfaces were not
parallel to the flow direction in the entrance region. Therefore, their data cannot be used quantitatively to study interfacial slip.

Coextruded multilayers with the number of layers ranging from tens to thousands have been made in our laboratory using layer multiplication dies. One of the unique features of these coextruded multilayers is that a large amount of well-defined interfacial area is generated without the influence of rheology and interfacial properties up to the point of layer breakup. This provides an excellent model system to test interfacial slip. In this paper, we quantitatively studied interfacial slip by rheological measurement on coextruded multilayers. The interfacial slip velocity was calculated and compared with theoretical predictions. The role of block copolymer in suppressing slip was also examined.

II. EXPERIMENT

Conventional multilayer coextrusion using a manifold die can make multilayer sheet or film with up to about 10 layers [Johnson (1976)]. Manifold dies which can make more than 100 layers were also designed [Schrenk and Alfrey (1978)], but they are too complicated and costly for practical and laboratory use. However, using layer multiplication dies a sheet with hundreds to thousands of layers is possible [door Sluijters (1965); Schrenk and Alfrey (1969); Schrenk and Alfrey (1978)]. Figure 2 shows the schematic of the layer multiplication process.

Initially, two polymer melts are brought together in a feed block and arranged into two (or more) layers. When these layers flow through the die, they first split into two parts, and each part subsequently is compressed, rotated, restretched to the original width, and finally restacked together with the number of layers being doubled. If the initial number of layers is $N_0$ and the number of multiplication dies is $n$, the final number of layers is simply $N_0 \cdot 2^n$. A coextrusion line interfaced with up to 10 layer multiplication dies has been set up in our laboratory, as shown in Fig. 3 [Saito and Macosko (1998); Zhao (2001)].

Either a bilayer or a four layer feed block can be used in our setup, so the final number of layers is $2^{n+1}$ or $2^{n+2}$, respectively. The layer thickness ratio of the two polymers is determined by the flow rates of each melt, which is controlled by two gear pumps (Zenith PEPII). Pressure pulsations from the two extruders are also isolated from the downstream flow by the two gear pumps. A neutral spacer die (no flow division) is added between...
every two multilayer dies to evenly distribute the flow in the die channel for better layer thickness uniformity [van der Hoeven et al. (2001); Zhao (2001)]. A fish tail sheeting die is attached to the end of the multilayer die assembly to transform the square flow into a 51-mm-wide by 2-mm-thick rectangular flow. The multilayer melt is then fed into a slit die channel, 51 mm-wide by 102 mm long and either 2 mm or 1 mm thick. Two pressure transducers are mounted 51 mm apart, flush to the slit wall. Upon exiting the slit die, a water cooled double chill roll quenches the multilayer melt.

The materials we choose for this study are polystyrene (Styron 666D, Dow Chemical) with $M_w = 200$ kg/mol and $M_w/M_n = 2.0$, and isotactic polypropylene (Exceed 4062, Exxon) with $M_w = 140$ kg/mol and $M_w/M_n = 2.4$. According to the manufacture, there are no additives in these polymers. At 200 °C, the viscosities of both polymers

FIG. 3. (a) Multilayer coextrusion setup. A 1 in. and a 3/4 in. single screw extruder are used to melt the polymers and deliver them to two gear pumps. A two or four layer feed block is interfaced with the two gear pumps, and up to 10 layer multiplication dies can be mounted in the line. A sheeting die is attached to the end of the multiplication dies to form the square multilayer flow into rectangular flow. The multilayer melt is quenched by two water chill rolls upon exiting the sheeting die. (b) A slit die can be attached to the end of the sheeting die. Two pressure transducers are mounted flush to the slit wall.

FIG. 4. Complex viscosity of PP and PS homopolymers at 200 °C. They are well matched in the frequency range from 0.1 to 500 rad/s. The maximum deviation is 20% at 5 s$^{-1}$. The steady shear viscosity are similarly matched, see Fig. 6(a). The solid and dashed lines are calculated with the Ellis model using the parameters listed in Table II.
closely match each other, as shown in Fig. 4. The lines in Fig. 4 are calculated viscosities using the Ellis model [see Eq. (15)]. The fitting parameters of the Ellis model are listed in Table II. The other materials listed in Table II will be discussed later.

To eliminate the effect of processing history, all of the polymers were given the same processing as the multilayers, i.e., the melt viscosities reported in Fig. 4 were measured after coextrusion. Melt blends of PS and PP with 30, 50, and 70 wt % PS were made in a 16 mm co-rotating twin screw extruder (Prism TSE16TC) at 200 °C and 40 rpm. Multilayer samples of PP and PS were made using our multilayer coextrusion setup at 200 °C. The number of layers in this study is either 8, 32, or 64. The layer thickness distribution of the multilayer samples were measured using a video-enhanced light microscope (Nikon Optiphot-Pol) and are shown in Fig. 5. Listed in Table III is a summary of the thickness distributions in our multilayer samples. The last sample in Table III was made before the feed block was redesigned to improve thickness uniformity.

To study the effect of block copolymer on interfacial slip, melt blends and multilayers with block copolymer were also made. A symmetric diblock copolymer polystyrene–block–ethyl ethylene [P(S-b-EE)] with $M_n = 200$ kg/mol and $M_w/M_n = 1.05$ was synthesized in our laboratory, as described by Jones (2000). Small-angle neutron scattering showed polyethylethylene is fully miscible with PP [Weimann et al. (1997)]. At 200 °C, P(S-b-EE) 2.0% by weight was preblended in PS matrix in our twin screw extruder at 40 rpm and pelletized. The pellets were then coextruded with PP into samples with 32 layers.

Rheology tests were done at 200 °C in a capillary rheometer (Göttfert Rheo-Tester 1500) using a φ1 mm × 20 mm die, or in a rotational shear rheometer (DSR, Rheometrics Scientific) using φ25 mm parallel plates. Both dynamic and steady shear measurements were performed. For all the steady shear rheology tests shear rate correction was done

<table>
<thead>
<tr>
<th></th>
<th>PP</th>
<th>PS666</th>
<th>PS685</th>
<th>PMMA</th>
<th>aPA</th>
<th>PP</th>
<th>PP–MA$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_0$ (Pa s)</td>
<td>7800</td>
<td>7000</td>
<td>3900</td>
<td>6800</td>
<td>6100</td>
<td>3800</td>
<td>3800</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>2.1</td>
<td>2.4</td>
<td>2.25</td>
<td>2.1</td>
<td>1.94</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>$k \times 10^{-3}$ (Pa)</td>
<td>8.0</td>
<td>14.0</td>
<td>19.0</td>
<td>58.0</td>
<td>186.7</td>
<td>7.6</td>
<td>5.8</td>
</tr>
<tr>
<td>$T$ (°C)</td>
<td>200</td>
<td>200</td>
<td>235</td>
<td>235</td>
<td>225</td>
<td>225</td>
<td>225</td>
</tr>
</tbody>
</table>

$^a$Blends of 90 wt % PP with PP–MA (0.25 wt % MA).

![FIG. 5. Optical micrograph of 32 layer PP/PS multilayers (a) before and (b) after steady shear to a maximum strain of 50. Multilayer samples were cast in epoxy and cryomicrotomed. The apparent black layers in (b) are delaminated regions between the polymer layers which occurred during removal from the parallel-plate rheometer.](image-url)
For PP and PS in the capillary rheometer entrance pressures were measured by using \( \phi 1 \text{ mm} \times 10, 20, \) and 30 mm dies. Entrance pressures were found negligible in the shear rate range up to 500 s\(^{-1}\). For dynamic measurements, the strain amplitude was controlled at 5\% to insure that the tests were done in the linear viscoelastic region. For steady shear measurements in parallel plates, edge failure limited the shear stress \( \tau < 10^4 \text{ Pa} \) or shear rate \( \dot{\gamma} < 2 \text{s}^{-1} \). Below these levels the layer structure even at the perimeter of the plates was undisturbed, as shown in Fig. 5(b). The parallel layers observed in Fig. 5 indicate that there was rectilinear flow with little secondary flow in both the slit die and parallel plates.

### III. RESULTS AND DISCUSSION

#### A. Rheology of melt blends

We first examined the anomalously low viscosity of PP/PS melt blends at three concentrations. Their steady shear viscosity was measured and plotted in Fig. 6(a). Data with shear rate \( \dot{\gamma} \geq 10 \text{s}^{-1} \) were obtained using the capillary rheometer, and \( \dot{\gamma} \leq 2 \text{s}^{-1} \) were obtained with the parallel plates. It can be seen that the steady shear viscosity of the three blends is consistently lower than that of the homopolymers in the shear rate range 0.3 < \( \dot{\gamma} < 500 \text{s}^{-1} \), or in the shear stress range \( 2000 < \tau < 10^5 \text{ Pa} \). This confirms what Han and Yu (1972) have reported. When \( \dot{\gamma} < 0.3 \text{s}^{-1} \), or \( \tau < 2000 \), blend viscosity is even higher than that of homopolymers, and that is understood as the pronounced elasticity from drop deformation [Riemann et al. (1997)].

In the shear rate range of our tests, since the viscosities of the two polymers are so similar, any volume mixing rules (linear or nonlinear) should predict similar blend viscosity, i.e., \( \eta_{av} \approx \eta_{pp} \approx \eta_{ps} \). Using Eq. (1), the deviation of the measured blend viscosities from \( \eta_{av} \) was calculated and plotted in Fig. 6(b). The deviation appears to be the function of the shear rate (or rather shear stress) and has maximum value about 50\% at 10 \text{s}^{-1} for all three blends. However, the deviation seems to approach zero at high shear rates. This has not been reported before.

![FIG. 6](image)

(a) Steady shear viscosity of PP/PS melt blends and both homopolymers measured at 200 °C. (b) Deviation of blend viscosity from the average value of the two homopolymers.
B. Rheology of multilayers

To more quantitatively test interfacial slip, PP and PS homopolymer melts and multilayer melts from the multilayer setup were fed into the slit die, and pressure drops at different volume flow rates were measured. Since the viscosities of the two homopolymers match each other, their pressure drops through the slit die should match that of multilayers if there is no slip. The measured pressure drops are plotted in Fig. 7a. Indeed, the pressure drops of the two homopolymer melts fall nearly on one line. The pressure drops of multilayer melts with 8 layers agrees with that for the homopolymers within the uncertainty of the measurement ($\pm 5\%$). With 8 layers the interfacial area seems to be too small to contribute any significant effect even if there is interfacial slip. However, a significant pressure drop reduction is measured for 32 layers, and an even greater reduction is shown for 64 layers. This result is strong evidence for apparent slip at the melt interfaces of PP and PS. From the pressure drop measurements, the apparent viscosities of homopolymers and multilayer melts were calculated [Macosko (1994)], and plotted in Fig. 7b. Compared with the homopolymers, about a 30% reduction in apparent viscosity is observed for 32 layers, and about a 60% reduction for 64 layers.

One could argue that the slip of polymer melts on a solid wall is the cause of pressure drop reduction. Wall slip is well documented [Denn (2001); Wang (1999)]. It can be caused by stress-induced chain desorption off low surface energy walls. For most polymer melts, the shear stress level for this to happen is normally higher than $10^5$ Pa. In our experiment, the slit die surface is untreated carbon steel. The surface energy of carbon steel is normally high enough to adsorb polymer chains. More importantly, the maximum wall shear stress here is only about $0.2 \times 10^5$ Pa, as we will see below apparent interfacial slip seems to onset at much lower stress, about 1000 Pa, so chain desorption off the wall is unlikely to happen. Wall slip can also be caused by the coil stretch transition at the interface between chains adsorbed on the wall and adjacent chains, but again a stress level of about $10^5$ Pa is required. An indication of this type of wall slip is oscillation in the flow. This was not observed in our experiments. Typically, for most polymer melts there is a break in the stress–shear rate curve from the no-slip to slip region. In our pressure–flow rate curve (wall stress–shear rate), such a break was not observed. Moreover, wall slip should occur for homopolymers, 8 layers as well as the higher multilayers. Thus, we have ruled out wall slip as a cause of pressure drop reduction.

The flow in the slit die is inhomogeneous. The stress is maximum at the wall, and zero somewhere near the middle of the slit die. Each interface is subjected to a different level of stress. If the interfacial slip depends on stress then it varies at each interface, so the
contribution of each interface to the apparent slip is different. This allows the evaluation of interfacial slip over a wide range of shear stress, but the analysis is more complicated as will be shown in the next section.

To simplify the analysis and observe the slip more directly, the multilayer samples were also sheared in the parallel-plate rheometer. 25-mm-diam disks were cut from samples which had been prepared via the multilayer setup. Due to draw down by the chill rolls and the shrinkage in cooling, the samples were about 0.7 mm thick (see Fig. 5 and Table III). Steady shear viscosity of homopolymers and multilayer samples were measured and plotted in Fig. 8(a). As with the measurements in the slit die rheometer, the apparent viscosity of 8 layers is very close to that of the two homopolymers. For 32 layers and 64 layers, when shear stress is above 1000 Pa, the apparent viscosity is consistently lower than the mean value of the two homopolymers. The deviation increases with number of layers and with shear stress as observed in the slit die.

C. Interfacial slip velocity

In multilayer coextrusion, the morphology of layers is well controlled and can be clearly defined by the number of layers and layer thickness, therefore, the multilayer flow dynamics in the slit die or parallel plates can be well described. This allows us to calculate interfacial slip from apparent viscosity measurements.

As discussed in the Introduction, the apparent slip is caused by a low interfacial viscosity, \( \eta_I \). Let \( \dot{\gamma}_I \) be the shear rate in the interfacial region,

\[
\dot{\gamma}_I = \frac{\Delta V_I}{a_I},
\]

where \( a_I \) is the interfacial width, and \( \Delta V_I \) is the velocity difference across the interface. Let \( \tau_I \) be the stress in the interfacial region,

\[
\tau_I = \eta_I \frac{\Delta V_I}{a_I},
\]

\( a_I \) can be estimated from [Helfand and Tagami (1972)]:

\[
a_I = \frac{2b}{\sqrt{6\chi}}.
\]
For PP/PS, $\chi = 0.042$ (Table 1) and $b_{PS} = 0.64$ nm, $b_{PP} = 0.57$ nm [Fetters et al. (1999)]. Using an average $b = \sqrt{b_{PS} b_{PP}} = 0.60$ nm, gives $a_I = 2.4$ nm. Since the average thickness of PP, PS bulk layers is $10–20$ μm, i.e., about 10 000 times thicker than the interfacial width, so mathematically the interfacial width can be treated as zero and the velocity as discontinuous across the interface. An alternative approach is to analyze slip in terms of an interfacial viscosity [Zhao (2001)] but this requires knowing $a_I$ or estimating it by fitting the experimental data. It is preferable to obtain only one slip parameter from the data. Thus, we define an interfacial slip coefficient $b_I = h_I/a_I$, so Eq. (10) becomes

$$\tau_I = \beta_I \Delta V_I.$$

This is a similar expression to the Navier slip boundary condition for a fluid on a solid wall [Silliman and Scriven (1980)]. However, $\beta_I$ here is a strong function of interfacial shear stress. A constitutive equation for $\beta_I(\tau_I)$ is needed to solve the flow in the slit die. In the parallel-plate measurements, the shear stress is constant across each layer and controlled in the experiments. This allows $\Delta V_I$ to be directly calculated from apparent viscosity measurements.

1. **Interfacial slip velocity in the slit die**

The flow in the slit die is pressure driven multilayer flow, as depicted in Fig. 9. The aspect ratio of the width to height of the slit die channel is about 25, so the melt flow in the die channel can be well approximated as one-dimensional plane Poiseuille flow. The distance of the first pressure transducer from the die entrance is about 20 times the channel height, so the flow is also fully developed when it reaches this pressure transducer. Assuming isothermal and one-dimensional creeping flow, the Navier–Stokes equation for the $j$th layer can be simplified to

$$0 = \frac{d\tau_j}{dy} - \frac{dP}{dx},$$

where $\tau$ is the shear stress on the $xy$ plane and $P$ the pressure. Shear stress is continuous across the interfaces, but velocity is different across the interfaces when there is slip. Thus, the boundary conditions are
\[ \tau_j = \tau_{j+1} \text{ at } y = y_{j,j+1}. \]

\[ v_{j+1} - v_j = \frac{\tau_j}{\beta_j} \text{ at } y = y_{j,j+1}. \]

\[ v = 0 \text{ at the walls } y = 0 \text{ and } y = 2 \text{ mm}. \]

The Ellis constitutive equation [Matsuhisa and Bird (1965)] was used to model the viscosity in each \( j \)th layer:

\[ \eta_j = \frac{\eta_0^j}{1 + \frac{\tau_j^{s_j}}{k_j^{s_j}}}. \]

The parameters of Ellis model for PP and PS were found by best fitting the data in Fig. 4. The values are listed in Table II.

A modified four parameter Ellis model was used to describe the constitutive relation of \( \beta_I \) to the interfacial stress \( \tau_I \).

\[ \beta_I = \beta_0 + \frac{\beta_0}{1 + \frac{\tau_I^{s_I}}{k_I^{s_I}}}. \]

The above flow problem was solved analytically. The velocity in the \( j \)th layer at position \( y \) is

\[ v_j(y) = v_j(y_{j-1,j}) - \left( \frac{\Delta P/L}{2 \eta_0} \right)^{s_j-1} \left[ (y - y_c)^2 - (y_{j-1,j} - y_c)^2 \right]^{s_j-1} \left( \frac{\Delta P/L}{k_j} \right)^{s_j-1} \frac{2}{s_j+1} \times \left( |y - y_c|^{s_j+1} - |y_{j-1,j} - y_c|^{s_j+1} \right), \]

where \( y_c \) is an integration constant. Physically, \( y_c \) is the position of zero shear stress in the flow field. The value of \( y_c \) is determined by the following equation:

\[ 0 = \sum_{j=1}^n \frac{y_{j,j+1} - y_c}{\beta_0 + \beta_0 \left[ 1 + \left( \frac{\Delta P/L}{k_j} \right)^{s_j-1} \right]} \left[ 1 + \left( \frac{\Delta P/L}{k_j} \right)^{s_j-1} \right] \left[ |y_{j,j+1} - y_c|^{s_j-1} \right] \]

\[ - \frac{1}{2 \eta_0} \left[ (y_{j+1,j} - y_c)^2 - (y_{j-1,j} - y_c)^2 \right]^{s_j-1} \left( \frac{\Delta P/L}{k_j} \right)^{s_j-1} \frac{2}{s_j+1} \left[ |y_{j,j+1} - y_c|^{s_j+1} \right] \]

\[ - |y_{j-1,j} - y_c|^{s_j+1} \right). \]

Integration of velocity over each layer gives the total volume flow rate of multilayer melt through the slit die:

\[ Q = \sum_{j=1}^n \int_{y_{j-1,j}}^{y_{j,j+1}} v_j(y) w dy, \]
where $w$ is the width of the slit die. Equations (17)–(19) form a four-dimensional nonlinear minimization problem. The objective function is

$$\text{error} = \sum \frac{|Q_i^{\text{cal}}(\beta_0, \beta_\infty, k_I, s_I) - Q_i^{\text{exp}}|}{Q_i^{\text{exp}}},$$

(20)

where $\beta_0$, $\beta_\infty$, $k_I$, and $s_I$ are Ellis model parameters for interfacial slip velocity. The constraints for these parameters are

$$0 < \beta_0, 0 < \beta_\infty,$$

$$0 < k_I,$$

$$1 < s_I.$$

A down hill simplex algorithm was used to solve this problem [Press et al. (1992)].

The thickness of each PP and PS layer was measured from micrographs like Fig. 5(a). The position of each interface was then mapped for 8-, 32-, and 64-layer samples. By best fitting the pressure drops versus volume flow rates for 8, 32, and 64 layers, the Ellis model parameters for the interfacial slip velocity are found and listed in Table IV.

The calculated pressure drops versus volume flow rates for 8, 32, and 64 layers are plotted in Fig. 7(a) with experimental data. The final residual error of Eq. (20) is less than 5%.

The pressure drops of the multilayers change for different number of layers [recall Fig. 7(a)], but the interfacial slip velocity is a material property and should not change with the number of layers. Indeed, one set of parameters fits all the pressure drop measurements from 8, 32, and 64 layers, as plotted in Fig. 7(a), which supports the validity of the measurements and computation. Using the parameters in Table IV, the interfacial slip velocity is plotted in Fig. 10.

Three distinct regions are observed: (1) At low shear stress, $\tau < 1000\,\text{Pa}$, the slip velocity is of order 1 nm/s and is a weak function of the interfacial stress. (2) When shear stress is above 1000 Pa, the slip velocity increases rapidly and shows a power-law dependence on shear stress. The power-law index, 1/s, is 0.5 and 0.4 for the viscosity of PP and PS compared to 0.2 for the slip velocity. This power-law behavior may indicate that chains are still entangled in the interfacial region, but the degree of entanglement is lower than that of bulk phases. (3) At high shear stress, $\tau > 10^4\,\text{Pa}$, the slip velocity appears to asymptotically approach a constant value of order of 1 mm/s.

Migler et al. (2001) observed slip of LLDPE on the surface of a thin layer of fluoropolymer on a capillary die wall. They measured a slip velocity of 4 mm/s at $\tau = 5 \times 10^4\,\text{Pa}$. This is about 100 times larger than our results and typical of polymer melt-solid slip velocities [Wang (1999)].
These results can also be compared to theoretical prediction by Goveas and Fridrickson ~1998!. For PP and PS in this study, \( N(\text{PP}) = 1400, N(\text{PS}) = 1000, \) and \( N_e = 130 \) for both PP and PS [Fetters et al. (1999)], so \( N/N_e(\text{PP}) = 11 \) and \( N/N_e(\text{PS}) = 8 \). Taking the arithmetic average, \( N/N_e = \sqrt{11 \times 8} \approx 10 \). Using Eqs. (5) and (6), the theoretical prediction of extrapolation length for Rouse-like and entangled interfaces are about 10 and 0.1 \( \mu \text{m} \), respectively. Using Eqs. (3) and (10), the slip velocity was calculated and plotted in Fig. 10. For our experiments \( a_I < bN_e^{1/2} \) (2.4 nm, 6.8 nm), thus a Rouse-like interface is predicted. We see reasonable agreement between theory and experiment at high stresses, but the theory gives a simple linear relation for \( \Delta V_I \) vs \( \tau \) over the whole stress range and significantly over predicts \( \Delta V_I \) at low \( \tau \) where the theory is expected to be more valid.

### 2. Parallel plates

In a parallel-plate rheometer the multilayer sample is subjected to shear parallel to the layers, and the shear stress is constant across the layers at a fixed radius. For a PP/PS multilayer sample with total thickness \( H \) and each PP, PS layer thickness \( h_{\text{pp}}^i, h_{\text{ps}}^i \), the apparent shear rate is

\[
\dot{\gamma}_{\text{app}} = \frac{\Delta V}{H} = \frac{i \Delta V_{\text{pp}}^i + i \Delta V_{\text{ps}}^i + (n-1) \Delta V_I}{H},
\]

(22)

where \( \Delta V \) is the total velocity difference across the whole multilayer sample, \( \Delta V_{\text{pp}}^i \) and \( \Delta V_{\text{ps}}^i \) are the velocity difference across each PP and PS layers, respectively. The shear rate in each layer is

\[
\dot{\gamma}_{\text{pp}} = \frac{\Delta V_{\text{pp}}^i}{h_{\text{pp}}^i}, \quad \dot{\gamma}_{\text{ps}} = \frac{\Delta V_{\text{ps}}^i}{h_{\text{ps}}^i}.
\]

(23)

Substituting into Eq. (22) gives

\[
\dot{\gamma}_{\text{app}} = \dot{\gamma}_{\text{pp}} \left( \frac{i h_{\text{pp}}^i}{H} \right) + \dot{\gamma}_{\text{ps}} \left( \frac{i h_{\text{ps}}^i}{H} \right) + \frac{n-1}{H} \Delta V_I.
\]

(24)
Equation (24) can be written in terms of apparent viscosity as

$$\tau = \frac{(n-1)/H}{\eta_{\text{app}}} - \frac{1}{\eta_{\text{pp}}} \left( \frac{\sum h_{\text{pp}}^j}{H} + \frac{\sum h_{\text{ps}}^j}{H} \right) \Delta V_I,$$

(25)

where $\eta_{\text{app}}$, $\eta_{\text{pp}}$, and $\eta_{\text{ps}}$ are apparent viscosity of multilayers, and viscosity of PP and PS homopolymers at stress $\tau$. Using Eq. (25), the slip velocity at stress $\tau$ can be directly calculated without applying any constitutive equation. The stress at the rim of the plate, $\tau_R$, is evaluated from the total torque, $M$, of the materials acting on the plates. The total torque is an integration of all the stresses from $r = 0$ to $r = R$ [Macosko (1994)]. Then, the total torque generated by a multilayer sample sheared at $\dot{\gamma}_R$ (evaluated at $r = R$) is

$$M(\dot{\gamma}_R) = 2\pi \int_{0}^{R} \sum_{j=1}^{n} r \tau_j(r) r dr$$

(26)

and the shear stress at $R$ is

$$\tau_R = \frac{M}{2\pi R^2} \left[ 3 + \frac{d \log M}{d \log \dot{\gamma}_R} \right].$$

(27)

Due to the sample edge failure at high shear stress, the shear stress was limited to < 5000 Pa. Also, because of the instrument resolution, at low shear stress, the experimental error in $\eta_{\text{app}}$ can exceed 10%.

Again, the thicknesses of each PP, PS layer in 32 layer and 64 layer samples were measured from micrographs like Fig. 5(a). Inserting the values of $h_{\text{pp}}^j$, $h_{\text{ps}}^j$ into Eq. (25) along with $\eta(\tau)$ of the two homopolymers and $\eta_{\text{app}}(\tau)$ from the 32 and 64 layer experiments, the slip velocity was calculated and plotted in Fig. 10. The slip velocity calculated from 32 layers and 64 layers agree with each other and with the slip velocity calculated from the slit die measurements within the experimental error.

Using Eqs. (26) and (27) and the slip velocity obtained from the slit die, the apparent viscosity of 8 layers in the parallel-plate rheometer is calculated and compared in Fig. 8(b) with experimental measurements. The calculated values fit the experimental data within experimental error. This calculation supports the 8 layer data in Fig. 7 and 8(a) which show that 8 layers is not sufficient to distinguish slip. The concord of $\Delta V_I$ calculated from two different rheological methods and different number of layers shown in Fig. 8(b) and, especially, Fig. 10 supports the accuracy of our experiment measurements, the validity of the computations and the presence of slip.

D. Slip in other systems

The theory predicts that slip velocity should increase with $\chi$, i.e., polymer pairs with greater immiscibility. This is demonstrated in Table I. In addition to the PP/PS system we have limited data on a pair with a lower $\chi$ value and higher one.

Multilayers of PS (Styron 685, Dow Chemical) with PMMA (Plexiglas VA26-100, Atofina) and PP with an amorphous, aromatic nylon, aPA (Zytel 330, Dupont) were made for investigating adhesion in polymer–polymer layer structure [Cole and Masoko (2000)]. The pressure drops of these two pairs were also measured, and interfacial slip was calculated.

The pressure drop measurements of PMMA/PS 32 layers in the slit die are plotted in Fig. 11(a). Since the viscosity of the PMMA is about four times that of PS, the pressure...
drops of these two homopolymers are very different from each other. The pressure drops of the multilayers are in between the two homopolymers. Although they are below the average pressure values, the slip is not as obvious as that in PP/PS pair. However, using the model developed in Sec. III C 1, the pressure drops without slip can be calculated. The viscosities of PMMA, PS homopolymers were first fit to the Ellis model with the parameters listed in Table II, then the pressure drops of the multilayers were calculated using Eqs. (17), (18), and (19). The calculated pressure drops are plotted in Fig. 11(a). The calculations are close to the measured values at low volume flow rates, i.e., low shear stress, and are significantly higher than the measured values at high volume flow rates. This indicates slip between the PMMA and PS layers at higher shear stresses. Applying slip boundary conditions and using Eq. (20) to fit the measured pressure drops of the PMMA/PS 32 layers gives good agreement with experiment, as shown in Fig. 11(a). The fit interfacial slip parameters are listed in Table IV.

The pressure drops of the aPA/PP 32 layers in the slit die were also measured and plotted in Fig. 11(b). The viscosity mismatch for this aPA and PP pair is even larger than the PMMA/PS pair. Although the pressure drops of the aPA/PP 32 layers are lower than the average value of the aPA and PP homopolymers, it is still not obvious to conclude that slip occurs in the aPA/PP pair. As for the PMMA/PS pair, the pressure drops of the aPA/PP multilayers were calculated applying no-slip boundary conditions. The fitting parameters of the Ellis model are listed in Table II. The calculated pressure drops are plotted in Fig. 11(b). On average they are higher than the measured values, indicating interfacial slip. Applying slip boundary conditions and fitting the measured pressure drops of the multilayers, the interfacial slip velocity of the aPA/PP pair was calculated. The interfacial slip parameters are listed in Table IV.

The slip velocity versus the interfacial stress for PMMA/PS, PP/PS, and aPA/PP are plotted together in Fig. 12. These three curves show similar behavior to each other. Three zones are observed as described before for the PP/PS pair. The critical stresses where significant slip is observed for PMMA/PS, PP/PS, and aPA/PP are $4 \times 10^3$, $8 \times 10^2$, and $2 \times 10^2$ Pa. They scale inversely with $\chi$ parameters as expected, because for immiscible pairs with larger $\chi$ parameter the slip should happen at a lower stress. The power-law index for these three systems are similar. The high stress end plateau values for these three systems are in the order of magnitude of 100 $\mu$m/s but do not scale correctly with $\chi$. That is probably the inaccuracy in our data fitting due to limited experimental data.
However, the $\alpha$PA/PP pair reaches the high stress end plateau value at a lower stress than PP/PS, and PP/PS lower than PMMA/PS, which does scale with their $\chi$ parameters.

**E. Block copolymers suppress slip**

If the interfacial slip is caused by less chain entanglements in the interfacial region, block copolymers which span the interface and promote chain entanglements are expected to suppress the apparent slip, as proposed by Levitt and Macosko (1999). To test this hypothesis we added block copolymer P(S-b-EE) to the same system described above. The molecular weight of each block is about 100 kg/mol. The radius of gyration of each block is about 9 nm, which is greater than the interfacial width ($a_I = 2.4$ nm) so that each block of the block copolymer chains at the interface should be entangled with its miscible homopolymer.

PP homopolymer and PS/P(S-b-EE) [PS premixed with 2.0 wt% P(S-b-EE)] were separately extruded through the slit die with 1 mm channel thickness, and the pressure drops were measured at various volume flow rates. Adding 2.0 wt% of P(S-b-EE) to PS did not notably change the rheology of PS. Then pressure drops of the PP/PS 32 layers and the PP/[PS/P(S-b-EE)] 32 layers through the slit die were measured. The data are plotted in Fig. 13(a). Both sets of data fall on one line. The pressure drop is significantly lower than homopolymers showing interfacial slip, as demonstrated in Fig. 7(a). Since the channel thickness used in this experiment is half of the slit die used before, the shear rate at the same volume flow rate is approximately doubled. Thus, the slip is stronger as indicated by 15% pressure drop reduction at a volume flow rate of 25 cm$^3$/min compared to the 10% pressure drop reduction in Fig. 7(a). However, the pressure drops for the PP/[PS/P(S-b-EE)] 32 layers are almost the same as that for the PP/PS 32 layers.

First, it appears that adding block copolymer has no effect on the interfacial slip. However, we need to consider whether enough block copolymer was present at the interfaces. The residence time of the layers in the coextrusion dies was less than 45 s. Within that short time period, block copolymers dispersed in PS matrix have to diffuse to the interfaces. The concentration of the block copolymer in the PS matrix is only about 2.0 wt%. It is in the dilute limit, so the block copolymers exist in the matrix as disordered free chains and micelles. Kinning et al. (1989) studied the morphology of poly(styrene-b-butadiene) block copolymer in the PS matrix. They measured a critical
micelle concentration (CMC) of 0.1 wt% for symmetric P(S-b-B) of 160 kg/mol at 115 °C in PS. This value decreases when the molecular weight of the block copolymer and the interaction parameter $\chi$ increase. The molecular weight of our block copolymer is 200 kg/mol, and the $\chi$ of PS/P EE is greater than PS/PB, so the CMC should be lower than 0.1 wt%. The concentration of the P(S-b-EE) in the P(S-b-EE)/PS mixture in our experiment is much higher than the CMC, thus nearly all the block copolymer resides in micelles. In the dilute limit, Yokoyama et al. (1999) demonstrated that micelles of poly(styrene-b-2-vinylpyridine) block copolymer in PS homopolymer follow Stokes–Einstein diffusion,

$$D^* = \frac{k_B T}{6 \pi R_h \eta},$$

where $k_B$ is Boltzman’s constant, $T$ is temperature, $R_h$ is the hydrodynamic radius of micelles, and $\eta$ is the viscosity of PS matrix at $T$. $R_h$ can be approximated as the micelle core radius and corona thickness. Using data reported by Kinning (1989) for P(S-b-B) micelle sizes in PS, $R_h$ of the P(S-b-EE) micelles in PS is about 40 nm. The steady shear viscosity of PS at $\dot{\gamma} = 10$ s$^{-1}$ is about 2000 Pa s (see Fig. 4). Using Eq. (28), the diffusion coefficient of P(S-b-EE) micelles in PS is about $4 \times 10^{-14}$ cm$^2$/s. Assuming all of the block copolymer is in micelles, the amount of block copolymer diffused to the interface in 1 min only yields a surface coverage of about $8.6 \times 10^{-8}$ chains/nm$^2$, which is less than 1% of the saturation value [Macosko et al. (1996)]. We expect that such a small amount of block copolymer at the interface is insufficient to promote appreciable chain entanglement.

To allow time for a significant amount of block copolymers to diffuse to the interfaces, a PP/[PS/P(S-b-EE)] 32 layer sheet was loaded into the parallel-plate rheometer at 200 °C with nitrogen gas protection. The sample was then sheared dynamically at 5% strain and 10 rad/s frequency for 45 min. After that, the steady shear viscosity was measured. As a control, a PP/PS 32-layer sample was treated in the same way. The dynamic viscosity of the multilayer samples measured before and after the 45 min annealing showed no thermodegradation. The steady shear viscosity data of both samples are plotted in Fig. 13(b). While the viscosity of the PP/PS 32 layers is still lower than that of the homopolymers, the viscosity of PP/[PS/P(S-b-EE)] is very close to the mean value of the two homopolymers, indicating the slip is suppressed.
Beside using premade block copolymer, block copolymers can also be formed by reactive coupling at the interfaces. In this way, no annealing is needed to allow block copolymers to diffuse to the interfaces. PP with 0.25 wt % grafted maleic anhydride (PP–MA, Aristech) was blended with 90 wt % PP in a twin screw extruder and pelletized. The PP/PP–MA blend was then coextruded with a PA into 32 layers. During coextrusion, the maleic anhydride on PP can react with the terminal amine on a PA at the interface to form graft copolymers. The pressure drops through the slit die were measured and plotted in Fig. 14. Applying the no-slip boundary condition, the pressure drops of the multilayers were calculated and also plotted in Fig. 14. The calculated values agree well with the measurements, indicating that slip is suppressed and that amine anhydride coupling is very fast [Orr et al. (1997), Orr et al. (2001)].

These two experiments demonstrate that the slip can be suppressed by block copolymers (premade or formed in situ) if it is present at the interfaces. This result supports the hypothesis that the mechanism for polymer–polymer slip is reduced chain entanglements in the interfacial region.

F. Dynamic shear rheology

The dynamic shear viscosity of the blends and homopolymers was also measured and plotted in Fig. 15(a). No negative deviation is observed for all the blends in the frequency range 0.3 < ω < 500 rad/s, where deviation is measured in steady shear. In the low-frequency range ω < 0.3 rad/s, the complex viscosity of the blends is even higher than that of the homopolymers due to the pronounced elasticity from drop deformation and recovery in the matrix [Riemann et al. (1997)]. The linear viscoelastic properties of the blends can be described by the model of Paliere (1990). For the blend PP/PS(70/30), using an interfacial tension Γ = 4.5 mN/m and drop diameter of 6 μm, the complex viscosity was well fit over the whole frequency range using Paliere’s model, as shown in Fig. 15(a).

The dynamic shear viscosities of the multilayers (32 layers) with and without adding block copolymers were measured and plotted in Fig. 15(b). As with the blends, no
negative deviation was seen over the whole frequency range. In layered structures, parallel to the shear direction, the morphology stays unchanged. Thus, unlike drop emulsions, elasticity from the interface does not play a role in the low-frequency range. Therefore, we do not see a much higher complex viscosity of multilayers than homopolymer in the low-frequency range.

Unlike in steady shear, the dynamic shear rheology of both blends and multilayers does not show interfacial slip. This result is not unreasonable, since the maximum shear stress in the dynamic tests was about 1000 Pa, below the level which appears to cause a strong decrease in $\eta_I$. This may also explain why most rheological studies of blends have not observed slip since they focused on linear viscoelastic measurements. It would be interesting to explore large strain dynamic shear.

IV. CONCLUSIONS

We have coextruded PP and PS with closely matched viscosity into 8, 32, and 64 alternating layers and measured the pressure drop as they flow through a slit die. The pressure drop for 8 layers was the same as for the homopolymers within experimental error but the 32 layers showed a lower pressure and 64 layers even lower. These differences increased with flow rates. The coextruded multilayers were also sheared in a parallel-plate rheometer and for stresses above 1000 Pa the viscosity of 32 layers was lower than 8 layers, which agreed with the homopolymers. The viscosity for 64 layer sample was even lower and the deviation increased with shear stress. All these data are strong evidence for apparent slip, i.e., a thin, low-viscosity layer between the PP and PS interfaces.

The pressure drops were analyzed applying slip boundary conditions at the interfaces, so the velocity is discontinuous across the interfaces. Similar to Navier slip boundary conditions for fluids against a solid wall, an interfacial slip coefficient, $\beta_I$ is defined, and it is a strong function of interfacial shear stress. A sigmoidal function described the constitutive relation between $\beta_I$ and $\tau$. The same function fit all 8, 32, and 64 layer pressure measurements and parallel-plate results. This demonstrates that the interfacial slip coefficient is a material property.

Slip was also observed in PMMA/PS and aPA/PP systems with highly mismatched viscosities. The stress at the onset of slip increases from aPA/PP, PP/PS, to PMMA/PS, which inversely scales with their $\chi$ parameters.
In dynamic shear measurement within the linear viscoelastic region, the complex viscosity of the multilayer samples agreed with the homopolymers. No negative deviation was observed. This is reasonable considering that the maximum stress in these dynamic tests is $\leq 1000$ Pa.

Theory based on chain dynamics predicts lower entanglement density near interfaces between immiscible polymers, and thus a low-viscosity region near interfaces. The prediction of interfacial slip by Goveas and Fredrickson is in qualitative agreement with our experimental observation, although they predicted a much stronger slip and the dependence of the slip velocity on stress is linear. Adding premade block copolymers to the interfaces suppressed the slip given enough time for block copolymers to diffuse to the interfaces. Graft copolymers formed by in situ reaction at the interfaces were shown to be able to suppress interfacial slip as well. These copolymer results support the role of interfacial entanglements in controlling slip.

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