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Slip in Entangled Polymer Melts. 2. Effect of Surface Treatment

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ABSTRACT: The influences of various physical and chemical characteristics of solid substrates on apparent slip violations in entangled polybutadienes are investigated in plane-Couette shear flow. Slip measurements are reported for a range of substrates: (i) clean silica glass, (ii) uncleaned silica glass, (iii) fluorocarbon-coated silica, (iv) clean roughened silica, and (v) polybutadiene-grafted silica. Though the magnitude and details of the measured slip velocities vary dramatically from substrate to substrate, our findings all appear consistent with a shear-induced polymer disentanglement explanation for apparent slip violations in entangled polymers. On uncleaned silica, at shear stresses beyond the critical shear stress σ^* for macroscopic slip, we find extensive void and/or shear fracture formation near the polymer−silica interface. We show that these observations result from nonuniform slip velocities on the heterogeneous, unclean substrate. On clean roughened silica glass surfaces, no evidence is found of the stick-slip instabilities reported in Part 1 for smooth silica. This difference in slip dynamics is attributed to differences in the surface relaxation dynamics of polymer chains on the two substrates. On low-energy smooth silica, very large slip velocities are found over the entire range of shear stresses investigated. These slip velocities are, however, at least an order of magnitude lower than current expectations for slip over ideal nonadsorbing surfaces. Finally, slip velocity versus shear stress diagrams obtained for polybutadiene-grafted silica are found to be remarkably similar to those observed on bare silica. This finding provides additional support to an earlier contention that surface friction characteristics of long polybutadiene molecules spontaneously adsorbed onto a neutral substrate are reasonably approximated by those of entangled, end-grafted polymer chains.

1. Introduction

In the previous paper[1] we discussed results from slip measurements using a series of narrow molecular-weight distribution polybutadienes subjected to plane-Couette shear flow over clean silica glass surfaces. The objective of that paper was to illustrate the basic features of slip in entangled polymers sheared over a well-defined surface. Tracer particle velocimetry coupled with simultaneous measurement of shear stress using a force transducer facilitated our previous study. Although only microscopic slip was detected for polybutadienes with $\bar{M}_n \leq 86500$, a sequence of weak slip, alternating stick slip, followed by strong slip was observed in the higher molecular-weight samples as the shear rate was increased. These experimental observations were found to be in good-to-excellent agreement with a recently proposed scaling model, even though the model assumed tethered, nonoverlapping surface chains with a surface density $\nu = (Na^2)^{-1}$.[2] We contended that the good correspondence between theoretical predictions and experimental results lends support to a polymer adsorption model in which a single macromolecule spontaneously attaches to numerous surface sites, yet offers a sufficiently long tail to resist relative motion of the bulk polymer.[3,4]

In this paper we wish to focus in greater detail on the influence of the wall surface material on apparent slip violations. Macroscopic investigations of polymer slip have shown that the onset condition and magnitude of slip depends on the physical and chemical nature of the wall surface.[5−8] For certain polymer/surface combinations macroscopic slip is not observed at any level of stress, whereas in others slip is detected above a well-defined critical stress value. For example, polystyrene melts extruded through stainless steel slit dies appear to show no macroscopic evidence of slip at any stress level.[5] Shidara and Denn[5] attributed this observation to possible π-bonding between aromatic groups and the metal die surface, resulting in enhanced adhesion of the polymer to the die. However, Vinogradov et al. observed that beyond a well-defined critical wall shear stress polybutadiene melts require a much lower pressure drop to sustain a given flow rate through poly(tetrafluoroethylene) (PTFE) capillaries, compared to stainless steel ones.[6] Recently, Kissi et al. analyzed flow of undiluted poly(dimethylsiloxane) extruded through stainless steel and fluorinated dies.[7] They found that fluorinated dies delayed the flow rate required to cause extrudate distortion by a factor of 3.5 compared to dies constructed from stainless steel. This increase was attributed to enhanced slip of poly(dimethylsiloxane) over the fluorinated surface. In another study, Hatzikiriakos and Dealy analyzed the flow of polyethylenes in a sliding plate rheometer with plates uniformly coated with a fluoropolymer (Dynamar).[8] Their results show that apparent slip (evidenced by lower transient stresses at the wall) is triggered at lower stress levels for fluoropolymer-coated plates, compared to plates made of stainless steel. In a recent study, Wang and Drda investigated the effects of surface topology and the chemical nature of capillary walls on the stick-slip transition in capillary flow of polyethylene melts.[9] These authors found that surface roughness increased the critical stress for the stick-slip transition. Also, they found that coating the die wall with fluoropolymer eliminated the stick-slip transition completely and yielded massive slip at all flow rates.

In this study we wish to employ the direct slip measurement technique described in part 1 to quantify the effects of the nature of the wall surface on slip. Such direct, quantitative measurements of polymer slip using well-characterized materials on well-defined surfaces

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are clearly needed to adequately understand the phenomenon. Specifically, we investigate here in detail the slip behavior of narrow molecular-weight distribution polybutadiene melts for a wide range of wall surface conditions. We believe that the experiments reported here are unique for at least three reasons. First, simultaneous tracer particle velocimetry and shear stress measurements facilitate direct and accurate estimation of slip on any surface (transparent or opaque). Second, slip measurements were conducted in plane-Couette shear where the shear rate is the same at all locations. This situation could be contrasted with the more popular capillary flow measurements where the shear rate and hence polymer rheological properties (viscosity and relaxation time) are only locally defined. Third, slip measurements were conducted using a wide spectrum of surfaces, namely, a (i) cleaned, smooth silica surface, (ii) uncleaned, smooth silica surface, (iii) low-energy, smooth silica surface, (iv) cleaned, rough silica surface, and (v) polymer-grafted, smooth silica surface, providing a fairly thorough understanding of surface effects.

2. Experimental Section

2.1. Materials. All entangled polymer melts studied consisted of narrow molecular-weight distribution (MWD) polybutadienes (PBD) (1,4 addition >90%). The polymers were purchased from Polymer Source, Inc. and had molecular weights ranging from $\bar{M}_w = 6.73 \times 10^4$ to $\bar{M}_w = 6.50 \times 10^5$. The molecular characteristics and rheological properties of interest for all the test samples are summarized in Table 1 of ref 1. Samples for tracer particle slip measurements were prepared by first dissolving the PBD melt in toluene and then adding a small amount of 1.5-μm diameter spherical silica tracer particles to the solution. A small amount (2−5 ppm) of antioxidizing agent (Irganox 1010; Ciba-Geigy) was also added to inhibit the oxidation of PBD. The toluene was allowed to evaporate at room temperature for several days. The last traces of toluene were vacuum evaporated at 50 °C for about 48 h. Samples were subsequently heated in a nitrogen environment to remove any trapped air bubbles.

2.2. Methods. Slip measurements were performed using a plane-Couette shear flow cell described in part 1. The flow cell allowed us to measure simultaneously the shear stress, using a force transducer, and the slip velocity, using tracer particle velocimetry. Gaps of 250 and 500 μm were employed in all the measurements. Sample aspect ratios (gap/width) never exceeded 0.02, and all tracer particle measurements were performed close to the center of the shear cell to eliminate the effects of secondary flow on slip measurements.[10] For details, please refer to section 2.2 of ref 1.

3. Results and Discussion

3.1. Slip on a Cleaned, Smooth Silica Surface. Prior to the slip experiments silica surfaces were cleaned thoroughly using the procedure described in part 1 (see section 3.1). Apparent slip velocities were deduced from the motion of tracer particles close to the stationary bottom surface. Slip velocities were determined from the long-time slope of the displacement versus time plot at different nominal shear rates $\dot{\gamma}_{app}$. Slip measurements conducted on clean, smooth silica surface for all the test samples are presented in Figure 5, parts a−g, of part 1.[1]

3.2. Slip on an Uncleaned, Smooth Silica Surface. In this part of the study we conducted slip experiments with uncleaned (without performing the cleaning procedure described in the section 3.1 of part 1), smooth silica glass surfaces (water contact angle ≈ 30°). At low shear stresses no unusual observations were made, except that slip lengths were slightly higher ($b_m = 13.6$ μm for PBD176) than those measured on a cleaned silica surface ($b_m = 12.5$ μm for PBD176). However, for shear stresses close to the critical shear stress we observed wholesale formation of voids near the polymer−silica interface. These voids grew up in time with steady shearing. Figure 1, parts a−f, shows a typical sequence of real-time microscope images of voids formed near the polymer−silica interface for a PBD176 sample sheared at a nominal rate of 5 s^{-1}. Figure 1a displays irregular-shaped voids formed during the steady shearing just before the cessation of flow. Figure 1, parts b−f, shows the microscope images during subsequent relaxation taken at 5, 10, 15, 30 s, and 60 s (1 min), respectively, following the cessation of shearing. It is apparent that the size and number of voids decreases with time and after about 1 min the voids disappeared completely and the polymer sample appeared perfectly homogeneous. Similar observations of shear-induced void formation have been reported recently by Archer et al. during steady shearing of a low molecular polystyrene ($\bar{M}_w = 13000$) melt.[11] In another study, Chen et al. reported shear fracture and bubble formation during oscillatory torsional shearing of polystyrene melts and solutions.[12] Since we did not observe surface voids/shear fracture in any of the samples sheared over carefully cleaned silica surfaces, we suspected that the origin of surface void formation during shear could be the inhomogeneous nature of the substrate.

Crudely, uncleaned silica surfaces should have patches of low surface energy and high surface energy regions, which would result in the nonuniform distribution of surface-adsorbed chains, more adsorbed chains in high-energy regions and less on low-energy ones. Assuming noninteracting surface chains, the shear stress at the surface is just the force per adsorbed chain times the number of adsorbed chains per unit area. We propose that for a given wall shear stress, polymer chains adsorbed in the low-energy regions will experience more force than their counterparts absorbed in higher energy regions. As a result, when the critical stress required for slip over clean silica is approached, a condition will arise in which polymer molecules adsorbed in the low-energy regions are disentangled from the bulk fluid (strong slip) while molecules in the high-energy regions remain entangled (weak slip). This imbalance in slip velocities could result in the observed surface voids. In extreme cases (high rates and very heterogeneous surfaces) such surface voids could lead to shear fracture of the polymer.

To check this proposed mechanism for void formation/shear fracture, we deliberately created a dual surface energy substrate in which half of a cleaned silica glass plate was grafted with a low-energy perfluoro polymer (see details in the next section) and the other half was left bare. Subsequent shearing of PBD176 over this heterogeneous surface resulted in the formation of large voids/shear fracture almost exactly at the boundary between the fluorinated and bare silica substrate, in agreement with expectations for the proposed mechanism. Microscope images illustrating this result are shown in Figure 2.

3.3. Slip on a Low-Energy, Smooth Silica Surface. To study the effect of the chemical nature of the wall surface in detail, a perfluorosilane, (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane, was grafted

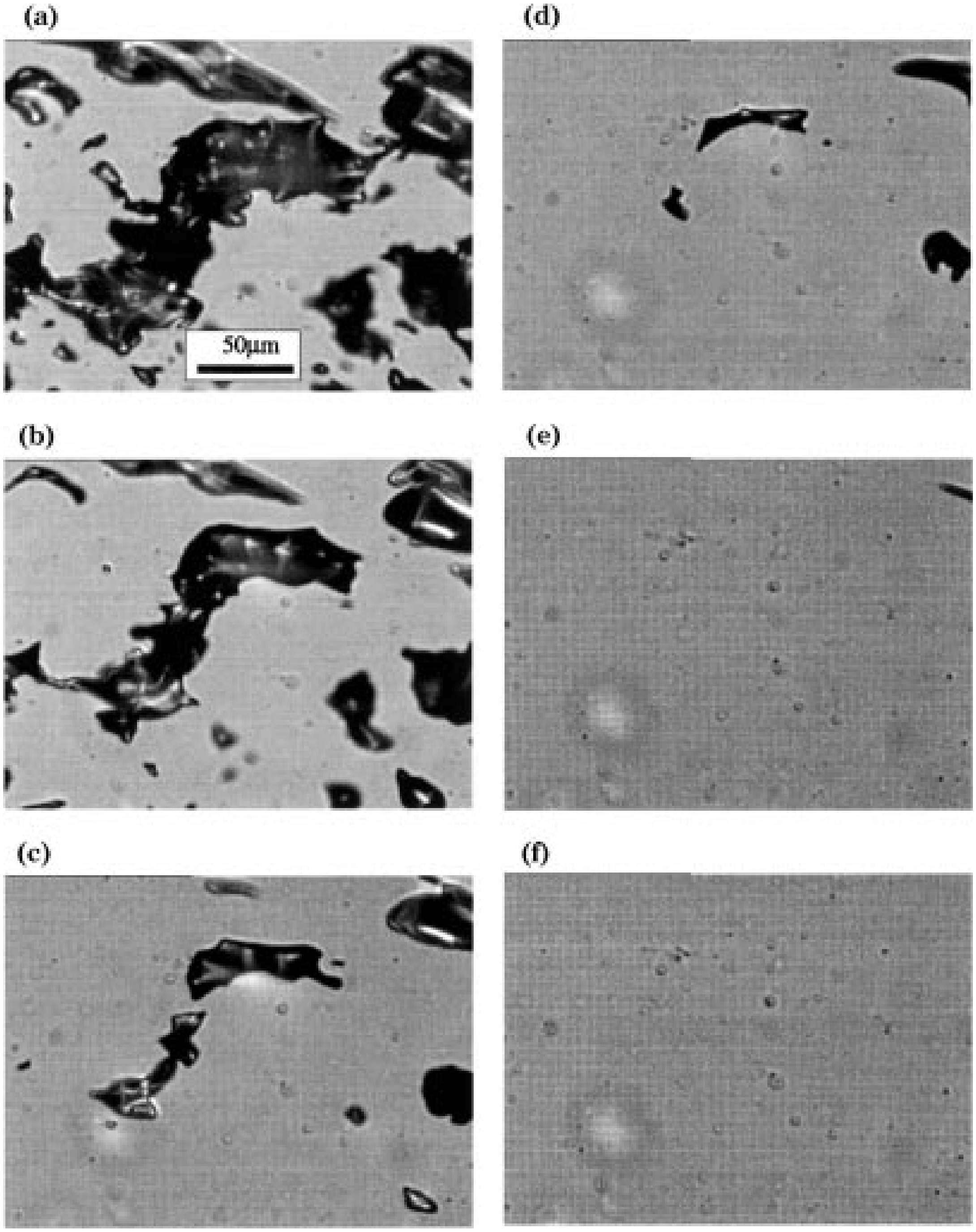

Figure 1. Light microscopy images of voids formed near the polymer−silica interface during and after cessation of steady shearing of PBD176 at a nominal rate of 5 s^{-1}. (a) At steady state, just before the cessation of the flow. Large irregular-shaped voids are apparent. (b) 5 s after cessation of shearing. (c) At 10 s after cessation of shearing the sizes and number of voids are seen to be significantly decreased. (d) 15 s after cessation of shearing. (e) 30 s after the cessation of shearing. (f) At 60 s after cessation of shearing voids are no longer apparent and the polymer sample appears completely homogeneous.

onto silica. As the trichlorosilane groups of the perfluorosilane molecules react with silanol groups on silica, it produces a stable uniform layer of fluorocarbons and thus minimizes the adsorption of polybutadienes onto the silica surface. The recipe used for grafting perfluorosilane onto silica was as follows: a solvent consisting of 70 mL of hexadecane, 10 mL of carbon tetrachloride (CCl_4), and 2 mL of a water-saturated chlorinated solvent was prepared, to which about 0.2 mL of perfluorosilane was added. Precleaned silica surfaces were soaked into this freshly prepared solution for about 2 min. Silica surfaces were then sonicated in a chloroform bath to remove unreacted species. The contact angle of deionized water on the perfluorosilane-grafted surfaces was found to be 121 ± 4°, compared to hydrophilic silica (spontaneous spreading of water) used in the earlier part of the study.

Figure 3 compares stress−velocity diagrams for PBD176 measured on a perfluorosilane−treated silica surface with that measured on bare silica. The magnitude of slip velocities are seen to be larger by a factor of 29 for the perfluorosilane-grafted surface. Furthermore, over the entire range of shear stresses studied, extrapolation/slip lengths on the fluorinated silica surface are seen to be constant, independent of the shear stress ($b_m = b_\infty = 358.7 \pm 33.12\ \mu$m). Importantly, we

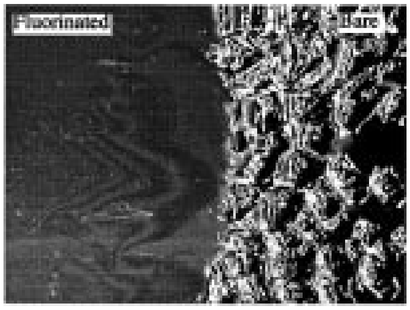

Figure 2. Fracture near the polymer–solid interface for a PBD176 sample sheared at a nominal shear rate of 2 s^{-1} over a dual surface energy silica substrate. Half of the substrate was grafted with a low-energy perfluoropolymer and the other half was maintained as a clean bare silica.

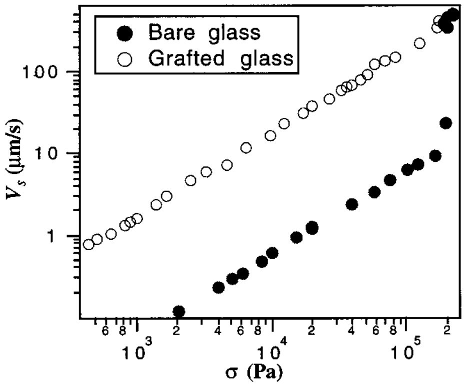

Figure 3. Effect of a low-energy coating on a stress-slip velocity diagram for PBD176. Slip velocities on this surface are seen to be about 30 times higher than those measured on bare silica. Also, no stick-slip flow is observed in the case of fluorinated silica.

did not observe any stick-slip instability at any level of imposed stress. For an ideal, nonadsorbing surface the theoretical extrapolation length is $b_\infty \approx (\eta_p/\eta_{\text{monomer}})a$,[13] which is of the order of a millimeter (theoretically, $b_\infty \approx 6.95$ mm for PBD176) and is at least an order of magnitude higher than the experimentally observed values on perfluorosilane-grafted silica ($b_{\infty,\text{Theory}}/b_{\infty,\text{Experiment}} = 17.4$ for PBD176). It appears that even weak van der Waals interactions between polybutadiene and a fluoropolymer-grafted surface gives rise to a friction coefficient that is much higher than the ideal monomer friction coefficient η_{monomer}/a.

3.4. Slip on a Cleaned, Rough Silica Surface. Although the effect of surface roughness on polymer slip has not yet been studied directly, indirect measurements do show that surface roughness has a profound effect on slip.[14] A threaded die used in extrusion experiments has also been reported to significantly delay the stick-slip transition.[9] Here, we study the effect of wall surface roughness on slip of PBD176 using commercially available, roughened silica glass. Prior to the slip experiments, the silica pieces were thoroughly cleaned using the procedure described in section 2.1. Roughness of the substrate was measured using a Stylus profilometer (Surfanalyzer 5000; Federal Products). The root-mean-square value of the measured roughness profile height deviations about the mean line was found to be 5.6 μm, which is much larger than the coil size of the polymer chain, $R = \sqrt{N}a \approx 17$ nm.

Figure 4 compares stress-slip–velocity diagrams for the PBD176 sample obtained on a rough surface with that obtained on a smooth silica surface. Several observations can be made: (1) The slip velocities on the rough surface are lower (corresponding extrapolation length $b_m = 8.3$ μm) than on a smooth surface (corresponding extrapolation length $b_m = 12.5$ μm). The decrease in slip length suggests an increase in friction between the polymer and the surface. As suggested by Wang and Drda,[9] because of the roughness of the surface, some polymer chains can become trapped in surface regions between the “hills and valleys”, which replaces (moving polymer)–(solid surface) interactions by (moving polymer)–(stagnant polymer) interactions. A penetrable polymer–polymer interface is more favorable for the adsorption of bulk chains than an impenetrable polymer–solid surface; the former should therefore support a higher number of interpenetrating chains per unit area (i.e., larger ν). The slip length b_m is inversely proportional to ν, so the rough surface would be anticipated to yield a decrease in b_m. (2) The critical shear stress σ^* for macroscopic (strong) slip on the roughened silica surface was found to be about 2.1 times higher than that on smooth silica. This observation is consistent with the first because $\sigma^* \sim \nu^{-1}$, ν being higher in the case of a rough surface. (3) No stick-slip instability was observed in the rough surface case. Slip velocities displayed a sharp transition between weak slip and strong slip. As discussed above, polymer–surface interactions are replaced by polymer–polymer interactions on a rough surface. We have already seen in part 1 that at a polymer–solid interface polymer chains absorb by forming small loops and trains in contact with the surface and long tails that extend into the bulk. These chains can therefore be crudely represented as end-tethered chains to describe friction between bulk and surface–polymer molecules in shear. Further, the relaxation dynamics of an end-tethered polymer chain is not simple reptation but rather involves arm retraction and constraint release. In contrast, at a polymer–polymer interface caused by surface roughness, interfacial polymer chains have both their ends free and can undergo the usual reptational diffusion. Unlike end-tethered chains, such chains lack the mechanism of disentanglement–re-entanglement responsible for stick-slip flow, and are simply convected by the bulk flow. This could explain why a stick-slip instability is not observed in shearing experiments over roughened silica.

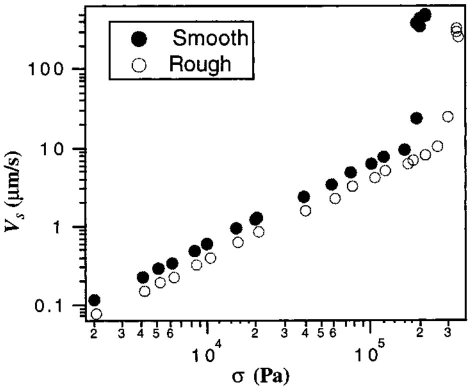

Figure 4. Effect of surface roughness on a stress-slip velocity diagram for PBD176. Slip velocities on a roughened surface were slightly lower than those on a smooth surface. A stick-slip flow regime was not observed in the case of the roughened silica surface.

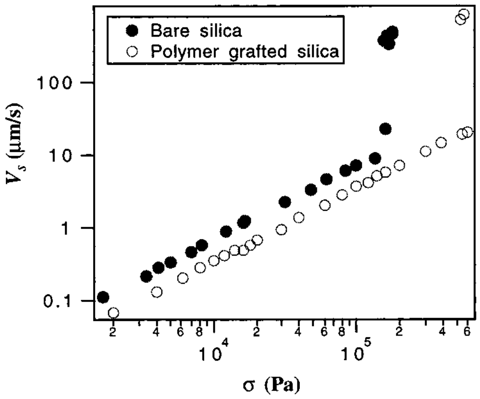

Figure 5. Slip velocity−shear stress plot for a PBD176 sample sheared over polymer-grafted and bare silica glass.

3.5. Slip on a Polymer-Grafted, Smooth Surface. An important parameter governing slip behavior is the number of adsorbed/grafted chains per unit area. Although the agreement between the experimental results of slip over a clean silica surface [see part 1] and the theoretical predictions is excellent, there are some important uncertainties in the theoretical and experimental situations. The theoretical description is based on slip of an entangled polymer over a surface grafted with chemically identical polymer chains whereas experiments involve slip over spontaneously adsorbed chains. Although our understanding of the structure of the adsorbed chains is still incomplete,[15] the agreement between theory and experiments suggest that, for the purpose of computing the frictional drag on the bulk polymer, adsorbed polymer chains can be crudely represented as end-tethered ones. Nonetheless, it is of interest to construct experiments where the experimental conditions are more closely matched with those in the theoretical situation.

Slip experiments were therefore conducted on silica grafted with end-functionalized polybutadiene chains. The polymer used was a narrow molecular-weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.04) diblock copolymer, polybutadiene($\bar{M}_n$ = 90300)−polydimethyl siloxane($\bar{M}_n$ = 7600). The polydimethyl siloxane (PDMS) block had a terminal hydroxyl group ($-Si(CH_3)_2-OH$) which reacts with the silanol groups on silica, resulting in an end-tethered polymer brush. The grafting procedure involved (i) physisorption of the block copolymer (from its dilute, $c \sim 10^{-3}$ g/mL, solution in toluene); (ii) heating the silica substrate under nitrogen to 150 °C to produce chemisorption; and (iii) redispersion of the grafted surface in a large volume of toluene to remove excess (ungrafted) polymer.

Figure 5 compares stress−velocity diagrams for PBD176 sheared over polymer-grafted and bare silica surfaces. The qualitative similarity between the two curves is immediately apparent from the figure. This observation is very important as it not only implies that the friction exerted by spontaneously adsorbed surface−polymer chains is rather similar to that exerted by end-grafted chains but also provides convincing support for a shear-induced disentanglement mechanism for polymer slip. The slip length for the polymer-grafted surface $b_m = 7.1$ μm was found to be lower by about a factor of 2 compared to the slip length on a bare silica surface, $b_m = 12.5$ μm. Also, the critical stress for the transition to a macroscopic slip on the polymer-grafted surface was found to be $\sigma^* = 7.1 \times 10^5$ Pa which is higher, roughly by a factor of 3, than that in the case of bare silica ($\sigma^* = 2.3 \times 10^5$ Pa). Both observations are in excellent agreement with the theoretical predictions of $b_m \approx 10.8$ μm and $\sigma^* = 9.4 \times 10^5$ Pa for slip of *P*-mers (PBD176) over end-tethered *N*-mers ($\bar{M}_n = 90300$, $N = 1672$) with $\nu = 1/Na^2$.

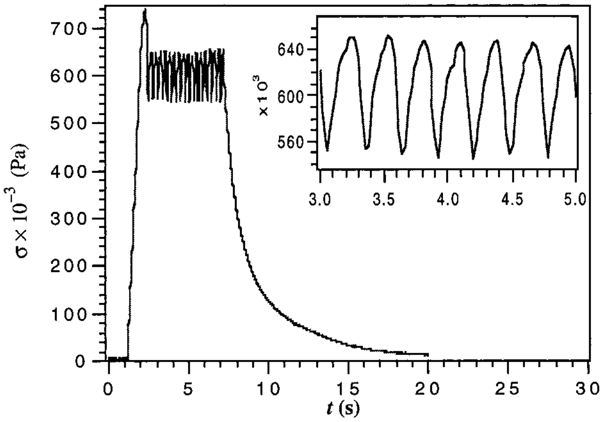

Figure 6. Transient shear stress during start-up of steady shearing of PBD176 over polymer-grafted silica. A nominal shear rate of 3 s^{-1} was used in this experiment. Inset shows expanded view of the curve in the stick-slip region.

Figure 6 shows transient shear stress for the PBD176 sample being sheared at a nominal rate of 3 s^{-1} over a polymer-grafted surface. The shear stress is seen to undergo periodic oscillations. The periodicity of oscillations was found be about 0.3 s which is remarkably close to the longest relaxation time of the bulk polymer τ_{Rep} = 0.46 s. This last observation confirms our previous results [see section 3.1 of part 1] that at low rates the characteristic frequency of oscillations in the stick-slip flow regime is a function of the relaxation time of the bulk polymer.

4. Summary

We have investigated the influence of surface conditions on the slip behavior of entangled polybutadienes sheared over well-defined surfaces. Our observations can be summarized as follows: (i) On uncleaned silica substrates, shear-induced voids/shear fracture formation near the polymer−silica interface was observed at shear stresses approaching the critical value required for macroscopic slippage of polybutadiene melts over clean silica surfaces. Under prolonged shearing, voids grew up in time and increased in number. Remarkably, following the cessation of shearing, the voids completely disappeared over a period of several minutes. Surface voids/shear fracture were not observed in any of the polybutadiene samples sheared on carefully cleaned silica surfaces. It was proposed that, in the case of uncleaned silica, nonuniform slip velocities at different locations result in surface voids/fracture. The validity of this proposed mechanism was confirmed by performing slip experiments on dual surface energy silica (see Figure 2).

(ii) Experiments performed on clean, roughened silica surfaces yielded a small decrease in limiting extrapolation lengths (for PBD176: $b_{m,Rough} = 8.3$ μm; $b_{m,Smooth} = 12.5$ μm), but revealed no signs of stick-slip instability at high stresses. This last was attributed to differences in the relaxation dynamics of surface−polymer chains on smooth and rough surfaces.

(iii) The effect of the chemical nature of the wall surface on slip was studied by employing perfluorosilane-, (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane-, grafted silica. Slip velocities on these surfaces were found to be significantly higher (by a factor of 29 in the case of PBD176), compared with those measured on bare silica. No signs of stick-slip flow were observed on perfluorinated silica surfaces at any level of stress. Over the entire range of shear stresses studied, extrapolation lengths were in fact found to be large and constant, but nonetheless still at least an order of magnitude lower than those of theoretical predictions for an ideal, nonadsorbing surface.

(iv) To create experimental conditions closer to those assumed in our recent scaling theory for polymer slip,[2] polybutadiene/poly(dimethyl siloxane) diblock copolymers were grafted to silica. In this case, the slip velocity−shear stress diagram was observed to be similar to that observed on a bare silica surface and in excellent agreement with the scaling theory prediction. This observation is important for three reasons. First, it implies that, for the purpose of drag calculations, spontaneously adsorbed polymer chains can indeed be represented as end-grafted ones. Second, it supports a shear-induced disentanglement of end-grafted (or surface-adsorbed) mechanism for slip and disfavors a mechanism based on shear-induced desorption, at least for the case of slip over bare silica. Third, it confirms the physics embodied in our scaling theory for slip in entangled polymers.

5. Conclusion

In a series of two papers, apparent slip violations were studied in several well-characterized polybutadiene melts over a range of experimental conditions. Direct measurements of slip velocity and shear stress, plus careful manipulation of wall surface conditions, allowed us to demonstrate key molecular, rheological, and interfacial characteristics of slip in entangled polymers.

Specifically, in Part 1, we determined (i) the magnitude of slip over a wide range of shear stress, (ii) the molecular-weight dependence of the slip length and the critical shear stress for stick-slip flow, (iii) the frequency of oscillations in stress and slip velocity and its dependence on the longest relaxation time of the bulk polymer, and (iv) the magnitude of slip and its molecular-weight dependence in the strong slip regime. In Part 2, we investigated the slip behavior of polybutadiene melts over surfaces with carefully varied physical and/or chemical characteristics. This facilitated detailed study of the effect of surface physical (i.e., surface roughness) and chemical (surface energy, surface inhomogeneities, and polymer grafting) characteristics on polymer slip. In a future article we will extend this work to cover apparent slip violations over polymer-grafted surfaces with known graft densities, as well as over specialty polymer-grafted surfaces where the assumption of noninteracting surface chains should not hold.

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