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Enhanced Polymer Segment Exchange Kinetics Due to an Applied Shear Field

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Introduction. Fundamental knowledge about the behavior of polymer melts near solid surfaces is important to many technologies such as electronics packaging, adhesion, coatings, and polymer processing. When polymers are placed under flow, surface effects can be critical in widely used polymer processing methods such as die extrusion and injection molding. Changes in the extrusion die material can suppress or induce instabilities that lead to unsatisfactory products.[1] These results show that the short-ranged interactions between the polymer and the substrate (coupled with the general viscoelastic properties of polymers) have macroscopic impacts. These processing instabilities have been correlated with “wall slip” at the polymer/solid interface where the apparent fluid velocity near the solid surface is no longer zero. Much work has been performed to determine the important physical parameters for wall slip and to understand the underlying mechanisms of the behavior of polymers at solid boundaries with the goal of better designing processing routes.[2−12] However, the effect of flow on the microscopic behavior of polymer chains directly at a solid surface is not well understood. Few experimental data are available for the behavior of polymer melt chains at the solid interface because of the inherent difficulty of distinguishing between surface-bound chains and the melt matrix.[13−15]

In this communication, neutron reflectometry was used to study the effect of a shear deformation on the adsorption/desorption kinetics of an entangled polymer melt at an attractive solid substrate. The high spatial resolution of neutron reflectivity, *O* (Å), provides information directly at the polymer/solid interface. A labeled (deuterated) polymer layer was formed at the surface of a silicon wafer and was welded with a hydrogenated polymer matrix. The fraction of deuterated polymer segments at the silicon surface was monitored with different annealing times with no applied shear and with varying shear rates after a set annealing time. Increases in the shear rate resulted in an increased rate of desorption of the surface-bound polymer chains (or adsorption of the matrix polymers). To the best of our knowledge, this shear-induced adsorption/desorption of an entangled polymer melt at an attractive solid surface was directly observed for the first time. These results provide important experimental evidence of molecular mechanisms which should be incorporated into future models of flow effects on polymer dynamics at surfaces.

Experiment. The surface polymer layer consisted of deuterated poly(methyl methacrylate) (d-PMMA) ($M_w = 135\,000$,[16] $M_w/M_n = 1.10$) spin-coated from an *o*-xylene solution with a d-PMMA mass fraction of 0.4% onto polished silicon wafers to form thin films 80−82 Å thick (as measured by X-ray reflectivity). The silicon wafers (76 mm in diameter and 5 mm thick) were first etched in a buffered hydrofluoric acid solution, then placed in an ultraviolet light−ozone cleaner, forming an oxide layer 15−25 Å thick. The d-PMMA layers were annealed for at least 20 h at 150 °C under high vacuum. The rms roughnesses of silicon oxide and d-PMMA layers are less than 10 Å as measured by X-ray reflectivity. The bulk matrix material consisted of uniform films, 0.7−1.0 mm thick, of monodisperse hydrogenated PMMA ($M_w = 125\,200$, $M_w/M_n = 1.08$). The films were prepared by pressing the powder under vacuum between Kapton sheets with an aluminum spacer at 185 °C. The glass-transition temperature of both polymers is 115 ° C as measured from differential scanning calorimetry.

The shearing apparatus was placed within a hydraulic press for mechanical stability. The silicon wafer with the d-PMMA film was held in a specially designed aluminum sample holder clamped to one plate of the hydraulic press. The shearing plane consisted of an aluminum block attached to a dove-tail sliding assembly with the rate of translation controlled by a lead screw. The sample holder was machined with side walls that come into contact with the shearing plane so that a constant gap height was physically maintained. Cartridge heaters were placed in the aluminum holder and the shearing plate for temperature control (±2 °C). At rest, the variation in the gap height was less than 0.05 mm. It is possible that additional perpendicular velocity components in the shear field may be present in the current experimental setup, as the gap height is not continuously monitored. Since the measurements probe changes within 20 Å of a surface with nano meter roughnesses, the flow field near the polymers of interest can closely be approximated as linear shear. Any additional normal component in the shear field would change the effective shear rates at the surface.

Before imposing the shear field, the h-PMMA film was pressed on top of the d-PMMA layer at 150 °C and allowed to interdiffuse for 60 min. An oscillatory shear deformation was then applied to the sample for 3 min with a translation of 5 mm in each direction at different shear rates. The sample was cooled and maintained at 100 °C, below the glass-transition temperature of the bulk polymer, to effectively halt the interdiffusion process. The aluminum blocks holding the sample were clamped together, to prevent any debonding of the polymer from the substrate due to thermal stresses, and transferred to the instrument to measure the neutron reflectivity. During heating periods, a stream of nitrogen was gently flowed around the sample to prevent polymer degradation. Good adhesion was maintained between the polymeric layers and between the polymer and the silicon substrate during the shearing procedure and the reflectivity measurements. Any macroscopic delamination (adhesive failure) between the polymer and the substrate or poor adhesion between the polymer layers would appear in the reflectivity measurements from the significant change in the neutron scattering length density from polymer segments to air. Samples exhibiting delamination or cohesive failure were removed from the study. The macroscopic void formation or shear fracture effects seen in other studies[17] were not observed in these samples. Adhesive failure on a microscopic scale cannot be completely ruled out. There are no optically observable defects, but the formation of small voids and the subsequent reattachment to the surface would have to occur over the time scale (15 min) of cooling to the measurement temperature. This time scale is much shorter than that necessary to heal any macroscopic void formation (several hours).[17]

Neutron reflectivity measurements were performed at the NG-7 reflectometer at the National Institute of Standards and Technology Center for Neutron Research. The neutron wavelength, λ, was 4.768 Å with $\Delta\lambda/\lambda = 0.025$. The reflectivity is

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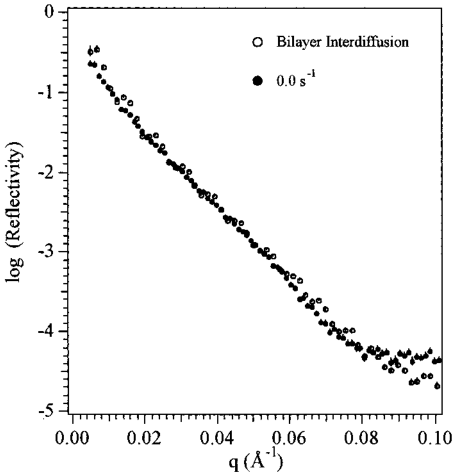

Figure 1. Neutron reflectivity data from a sample (d-PMMA thickness of 80 Å and h-PMMA thickness of 1 mm) in the shearing apparatus after annealing for 60 min at 150 °C and from bilayer (d-PMMA thickness of 70 Å and h-PMMA thickness of 804 Å) interdiffusion after 67 min at 150 °C.

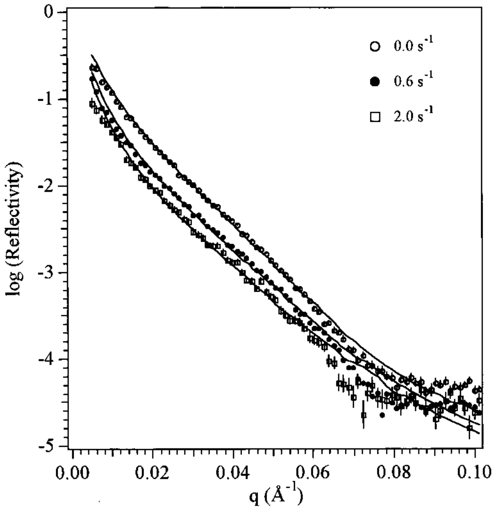

Figure 2. Neutron reflectivity data from samples after 60 min of annealing at 150 ° C then sheared for 3 min with shear rates of 0, 0.6, and 2.0 s^{-1}. The solid lines represent the best fit to the neutron reflectivity data.

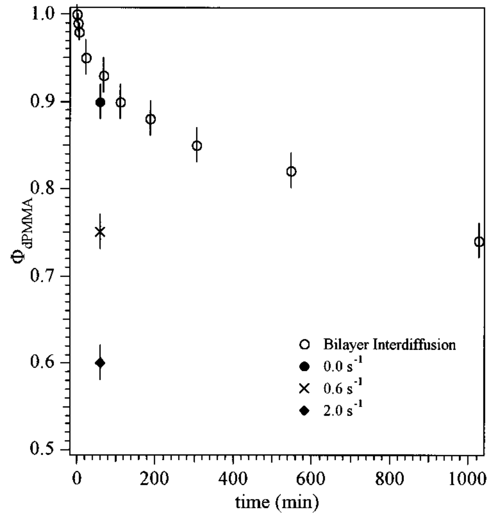

Figure 3. Desorption curve from a bilayer (d-PMMA thickness of 80 Å and h-PMMA thickness of 804 Å) experiment showing the rate at which the deuterated segments are replaced at the solid surface. Also shown are the deuterated surface fractions after shearing.

measured at the specular condition at different angles and is presented as a function of the neutron momentum transfer perpendicular to the surface, $q = (4\pi/\lambda)\sin\theta$, where θ is the incident and reflected angle of the neutron beam. The neutron beam, 30 mm wide, was passed through the silicon wafer with a transmission of $\approx$ 0.90 of the beam intensity as measured through air. In this geometry, the measured reflectivity emphasizes the silicon/d-PMMA interface. The reflectivity data are fit using the multilayer recursive method.[18] The reflectivity data are modeled and fit with a three layer model of silicon, d-PMMA, and h-PMMA with error function profiles between each component layer. The large difference in the neutron scattering length density between the deuterated and hydrogenated components leads to strong contrast between almost chemically identical species and the straightforward determination of the d-PMMA surface fraction. More details about this system are available elsewhere.[19]

Results and Discussion. To measure changes in the surface exchange kinetics due to the shear field, the data from samples in the shear apparatus are compared with data from static bilayer interdiffusion experiments.[19] As a control, the reflectivity data from a sample in the shearing apparatus annealed at 150 °C without shear for 60 min are presented with data from a static interdiffusion experiment in Figure 1.[20] The data from the bilayer sample are from a d-PMMA layer 70 Å thick interdiffusing with an h-PMMA layer 804 Å thick after being annealed at 150 °C for 67 min. The curves overlap, indicating that the rates of desorption or interdiffusion behavior are similar. Small oscillations in the bilayer data arise from the thickness of the h-PMMA layer of the bilayer sample. The sample in the shearing apparatus has an h-PMMA film thickness that results in oscillations with a periodicity smaller than that resolvable by the instrument. The full concentration profiles of the sheared samples could not be uniquely determined because the background intensity (due to incoherent scattering from the large hydrogen content in the h-PMMA matrix) at q values greater than ~0.1 Å^{-1} is comparable to or larger than the reflectivity intensity. The measurement, however, is very sensitive to the surface fraction of the deuterated component, Φ_{dPMMA}, because of the large contrast in the neutron scattering length density between silicon and d-PMMA. In this study, Φ_{dPMMA} is determined from the maximum neutron scattering length density in the concentration profile that best fits the data and is always located at the silicon surface.

Figure 2 shows the reflectivity data from three samples with nearly identical d- and h-PMMA layers, annealed for 60 min at 150 °C, and sheared for 3 min with shear rates, γ^{-1}, of approximately, 0, 0.6, and 2 s^{-1}. As the shear rate increases, a lower overall reflectivity is observed, indicating that the surface concentration of the deuterated component decreases. From the best fits to the data, Φ_{dPMMA} values were determined to be 0.90 ± 0.02, 0.75 ± 0.02, and 0.58 ± 0.02, respectively. For comparison, the bilayer interdiffusion experiment resulted in $\Phi_{dPMMA} = 0.93 \pm 0.02$ after 67 min of annealing at 150 °C. The magnitude of the effect of the shear field on the surface exchange kinetics can be seen in Figure 3, which shows the sheared Φ_{dPMMA} (after 60 min annealing) with the d-PMMA desorption curve as determined from the data obtained from bilayer interdiffusion experiments.[19] In the static experiment, a surface concentration of the deuterated component greater than 0.70 is present even after more than 15 h at 35 °C above the polymer glass-transition temperature. After 3 min of a shear deformation, Φ_{dPMMA} is significantly less than Φ_{dPMMA} from the static interdiffusion data even after long annealing times.

To better quantify changes in the apparent surface exchange kinetics, effective diffusion coefficients, D_s, can be determined from the measured Φ_{dPMMA} and using the solution for Fickian diffusion of a slab of material from a surface. For shear rates of 0, 0.6, and 2 s^{-1}, the D_s values were determined to be 0.2×10^{-16}, 9.5×10^{-16}, and 21.0×10^{-16} cm^2 /s, respectively. For comparison, diffusion experiments have determined the bulk self-diffusion constant for this polymer to be in the range of $(0.03-0.3) \times 10^{-16}$ cm^2/s.[19,21] An enhancement by more than an order of magnitude of the apparent diffusion constant from the surface due to the imposed shear for both shear rates is clearly observed. It should be noted that pure Fickian diffusion is not directly applicable for PMMA layers near an attractive surface over these time scales[19] and that a single D_s value does not fit all data points for the static interdiffusion case. The value of D_s decreases with time, suggesting that the rate of d-PMMA desorption is dependent upon the configurations of the remaining chains at the surface.

The enhanced desorption of the d-PMMA segments is due to the highly entangled nature of high-molecular weight polymeric materials, which gives rise to both the high viscosity of the material and the slow interdiffusion rates near solid surfaces.[19] In contrast, significant desorption of PMMA chains adsorbed on Ge by solvent (carbon tetrachloride) flows is *not* observed even at shear rates of up to 2.5×10^4 s^{-1}.[22] Entanglements between the bulk matrix and the surface-adsorbed polymers lead to large effective shear forces on surface-adsorbed chains.[3,23] The high viscosity of these polymers results in large shear stresses at the polymer/solid interface that can account for the enhanced desorption rates observed at relatively low shear rates. Although the shear stress is not quantitatively measured in this experiment, the shear stress can be estimated, given the molecular characteristics of the PMMA used in this study, from the viscosity[24] and shear rate to be on the order of 1 MPa. It has been calculated that the frictional forces for other systems (polystyrene on stainless steel) can be comparable to the segment attachment energy.[23] In addition, molecular dynamics simulations of oligomers in confined geometries under shear also show enhanced desorption/adsorption kinetics from attractive surfaces.[25,26]

The large shear stresses at the silicon surface can account for the enhanced desorption/adsorption kinetics, but several details of the observed enhancement in the kinetics are not fully resolvable. For example, the enhanced desorption/adsorption kinetics do not clearly indicate that wall slip is occurring in this system. Although there are no studies measuring wall slip velocities for the polymer and substrate used in this study, massive slip is not expected because of the high interaction energy, 4 kT per segment, for PMMA and silicon oxide where k is Boltzmann's constant.[27] If there is some wall slip behavior, the enhanced kinetics observed here are not necessarily inconsistent with the scaling models describing wall slip as the disentanglement of polymer tails from the bulk matrix.[3,10] Some disentanglement of tails from adsorbed polymers may occur, but cannot be resolved from this experiment. The important observation is that the exchange kinetics of *segments* at the surface are increased due to the imposed shear flow, but at any given time, tails from the adsorbed layer could disentangle from the matrix. The composition of the adsorbed layer changes with time, and the original layer is continuously replaced by matrix polymers.

In summary, direct measurements of shear-induced enhanced polymer melt adsorption/desorption kinetics at an attractive surface have been made for the first time. These results provide new insight into the physical mechanisms of polymeric materials under flow at solid surfaces. Additional experiments are clearly needed to better understand and quantify the behavior of entangled polymers near surfaces under flow. Many issues remain to be addressed, including the dependence of shear-induced desorption on the matrix molecular weight, surface energy, and shear rate over varying time periods. An important parameter in this problem is the degree of interpenetration of the h-PMMA with the d-PMMA layer as well as the initial structure of the d-PMMA chains. The interfacial structure deformed in this study is not at equilibrium as the two layers are not completely mixed. Differing levels of interpenetration between the bulk and the surface adsorbed chains may lead to different levels of d-PMMA desorption. Although great progress has been made in theoretically describing grafted chain systems, more detailed theoretical models taking into account entanglements between an adsorbed polymer structure and the matrix as well as the kinetics of shear-induced adsorption/desorption are needed to better understand the molecular behavior of polymers near surfaces.

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