Hydrodynamic Slip: Polymer Adsorption and Desorption at Melt/Solid Interfaces

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Hydrodynamic slip due to lack of molecular interfacial interactions is demonstrated rheologically as a function of molecular weight and temperature, by comparing poly(dimethyl siloxane) (PDMS) suspensions of bare and silane-treated glass spheres. The magnitude of interfacial slip between treated spheres and PDMS matrix increases with the applied stress and with the molecular weight of PDMS matrices. The onset stress for slip drops sharply with temperature and PDMS molecular weight.

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Highly entangled polymeric melts are a class of liquids that exhibit unique flow behavior. In particular, it has been theoretically proposed that, under certain conditions, such fluids may not maintain the usual stick boundary condition at a solid wall [1,2], thus providing an exception in the field of hydrodynamics. Under stress, two distinct situations may arise: (a) interfacial polymer chains become debonded from a weakly adsorbing wall and (b) disentanglement occurs between the adsorbed chains and the surrounding free chains at strong melt/wall interfaces. Although these theoretical studies were originally motivated by experimental observations [3–7], more experimental data are desired to provide indisputable evidence for hydrodynamic slip that arises from lack of interfacial interactions at the molecular level. Also more experiments are necessary to further elucidate the nature of boundary condition at melt/solid interfaces.

In reality, polymer chains often adsorb fairly strongly at metallic surfaces such as the inner wall of capillary dies and parallel plates in conventional rheometers, making it impossible to observe interfacial slip under relatively low stresses. A recent experimental study recognized this point and made a conscious effort to minimize chain adsorption of poly(dimethyl siloxane) (PDMS) on glass plates by a careful silane treatment of the glass plates [8]. By applying an innovative combination of optical techniques, a slip transition was revealed in the parallel-plate geometry and the actual slip velocity was measured as a function of the applied shear flow. A subsequent study on PDMS suspensions of glass spheres also produced evidence for slip by comparing samples containing bare spheres and treated spheres, respectively [9]. However, Refs. [8] and [9] appear to suggest different mechanisms for hydrodynamic slip at the polymer/solid interfaces [10]. In a more recent communication, another molecular mechanism for slip was experimentally revealed to involve a stress-induced *disentanglement* transition between adsorbed and free chains of polyethylene (PE) in capillary flow where the interfacial interactions between PE and steel are very strong and rather high stress (≈0.3 MPa) is necessary to produce the transition [11].

In this Letter, we present the first description of molecular weight and temperature dependence of the intriguing hydrodynamic slip behavior of high molecular weight PDMS in contact with nearly nonadsorbing solid surfaces. The noted temperature dependence strikingly elucidates the strong correlation between interfacial interactions, the extent of chain adsorption or desorption, and hydrodynamic slip. The observed molecular weight M dependence qualitatively confirms the theoretical scaling relation [1] between the amplitude of slip and the degree of molecular chain entanglement and reveals new information on the M dependence of chain packing at melt/solid interfaces. The documented stress dependence provides convincing evidence for stress-induced chain desorption.

According to theoretical estimate [1], the extrapolation length b, defined as the distance away from the polymer/wall interface where the velocity of the bulk polymer would be extrapolated to zero, may be on the order of 10 μm in the ideal case of negligible chain adsorption for a high molecular weight ($M = 423\,000$) polydisperse poly(dimethyl siloxane). By definition, such a PDMS will not display any rheologically observable interfacial slip in a parallel-plate geometry with a typical gap distance of 0.5 mm $\gg$ 10 μm. In other words, the hydrodynamic boundary condition (HBC) will appear "stick: unless one examines it on a characteristic length comparable to the anticipated b.

We consider PDMS suspensions of uniform glass spheres with diameter $(2R)$ around 10 μm. Two batches of glass spheres are prepared, one without surface modification and the other with an elaborate chemical treatment to achieve maximum replacement of silanol groups on the glass spheres with (Tridecafluoro-1, 1, 2, 2-tetrahydroctyl)-1-trichloro silane. Detailed description of the silane treatment will be discussed elsewhere [12]. It suffices to note that such a treatment on glass can boost the contact angle of water up to 115°. PDMS chains can establish only van der Waals type interactions with the *fully* silane-treated, strongly hydrophobic glass. Thus the normal stick HBC may not apply for the PDMS suspensions consisting of these treated glass spheres. Whether a violation of the stick HBC can be rheologically measured depends not only on strength and extent of the polymer/solid interfacial interactions and on the level of applied stress, but also on the bulk properties of the PDMS such as the degree of chain entanglement. This is a unique example of interfacial phenomena where the interfacial properties are directly related to the bulk properties. To illustrate this point, three PDMS of increasing molecular weight are selected as the matrix for the glass sphere suspensions The viscosity-average molecular weight M for the three PDMS, to be referred to below as PDMS1, PDMS-G, and PDMS-FG, are, respectively $M \cong 423\,000$, $763\,600$, and 1.06×10^6. PDMS1 is from United Channel Technologies, Inc., PDMS-G is a gum received from Rhoné Poulenc, and PDMS-FG is obtained from PDMS-G by fractionation in our laboratory.

In terms of the exptrapolation length b, we expect to find the following expression for the suspension viscosity in the Einstein limit of infinite dilution of spheres [13]: $\eta(\phi) = \eta_m[1 + 5(1 + 2b/R)\phi/2(1 + 5b/R)]$, where R is the sphere radius, η_m is the medium viscosity, and b is the extrapolation length characterizing the sphere-medium interfacial interactions. It is easy to show that $b = \eta_m/\beta_i = (\eta_m/\eta_i)a$ [1,2,13], where a is a characteristic molecular length, η_i is an effective interfacial viscosity, and $\beta_i = \eta_i/a$ is an interfacial "friction coefficient," relating the slip velocity v_s at the interface to the shear stress σ, $\sigma = \beta_i v_s$. In the complete slip limit, $b/R \gg 1$ and $\eta(\phi) = \eta_m(1 + \phi)$, i.e., the viscosity increment due to the spheres would be significantly smaller than the Einstein result which is valid only under the stick HBC. No theoretical results are available for *concentrated* suspensions of spheres displaying hydrodynamic slip at the sphere/medium interfaces. However, we expect the reduced viscosity $\eta_r(\phi, b/R) = \eta(\phi, b/R)/\eta_m$ to be an explicit and monotonically decreasing function of the slip parameter b/R. When b/R is of order unity, we expect the reduced viscosity $\eta_r(\phi, b/R)$ at a finite volume fraction ϕ to be considerably smaller than that of a uniform suspension at ϕ to which the stick HBC applies.

Uniform nonaggregating dispersions of spheres all share one universal property, i.e., they all have the same reduced viscosity $\eta_r(\phi)$ vs volume fraction ϕ [14], provided the stick HBC applies and the dispersing medium is Newtonian. For $\phi \leq 0.2$, the contribution from the particle Brownian motion is negligible and, at $\phi = 0.28$, $\eta_r(\phi)$ attains $\eta_r(\phi) = 3.0 \pm 0.2$ in absence of the Brownian motion contribution [15]. Mixing equal weights of the bare glass spheres with the three PDMS, respectively, we obtain three perfectly dispersed suspensions at $\phi = 0.28$. Throughout this work, only this concentration of 50% weight fraction is considered. The phenomenon at other concentrations was found to be qualitatively the same and data at other ϕ will be reported elsewhere [12]. Three additional suspensions are prepared at the same volume fraction using the silane-treated glass spheres. The shear viscosity of these six suspensions and the three pure PDMS matrices are measured in the steady-shear mode using a parallel-plate Rheometrics Mechanical Spectrometer (RMS-800). We have avoided applying oscillatory shear which causes ordering of the spheres in viscoelastic suspensions [16,17].

In Fig. 1 the reduced viscosity η_r at $\phi = 0.28$ is plotted against the applied shear stress σ at room temperature $T = 25$ °C. Consistent with the literature results [15], η_r reaches 3.0 for all the three samples containing $\phi = 0.28$ of *bare* glass spheres in the low shear rate limit. The small decrease of η_r with the applied stress σ arises from the enhanced shear thinning of the non-Newtonian PDMS matrices due to the presence of the glass spheres. The same uniform structureless suspensions of the silane-treated glass spheres exhibit increasingly lower viscosity $\eta_r < 3.0$ as the matrix varies from PDMS1 to PDMS-G to PDMS-FG. For the PDMS-FG matrix, $\eta_r < 2.0$ at a level of stress σ as low as 100 Pa. Clearly grafting the glass spheres with a monolayer of the fluoro-silane has completely weakened chain adsorption. A sufficiently high stress can remove most adsorbed chains to create a sharp contrast in the fluid structures across the treated-sphere/PDMS interfaces. Under this condition, a sizable extrapolation length b arises: $b = N(N/N_e)^2 a$ [1], where N is the number of monomers per chain and N_e is the number of monomers between entanglements. It is reasonable to expect b to vary from below 1 μm to perhaps above 100 μm as a function of the PDMS molec-

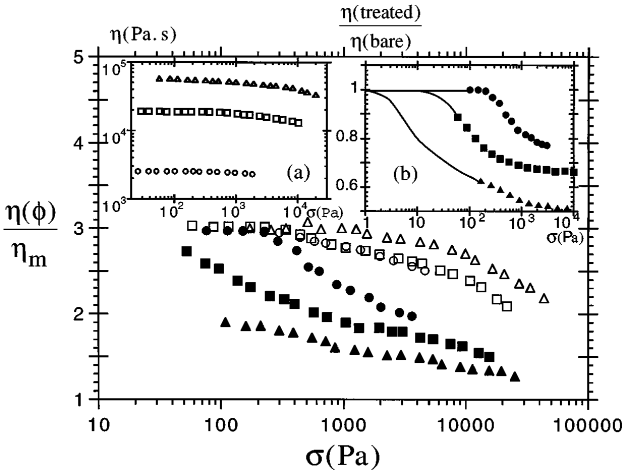

FIG. 1. Reduced viscosity $\eta(\phi)/\eta_m$ of six suspension vs the applied stress σ at $T = 25$ °C. Open and full symbols, respectively, represent the suspensions of bare glass spheres and treated glass spheres. In both the figure and insets (a) and (b), circles denote PDMS1, squares correspond to PDMS-G, and triangles designate PDMS-FG. Inset (a) presents the shear viscosity of the three pure PDMS as a function of stress. Inset (b) normalizes the viscosity η(treated) of suspensions containing treated spheres with that η(bare) of the respective suspensions containing the bare glass spheres, as a function of stress σ. The lines in inset (b) are the extrapolation of actual data and are supposed to guide our eyes.

ular weight and the applied stress. For example, we find no difference in $\eta_r(\phi)$ between the treated sphere (full circles) and bare sphere (open circles) suspensions for $\sigma < 300$ Pa, implying the slip parameter b/R for the sphere/PDMS1 interfaces is much smaller than unity. On the other hand, the treated sphere/PDMS-FG interfaces probably satisfy $b/R \gg 1$ even below $\sigma = 100$ Pa. Inset (a) of Fig. 1 shows the non-Newtonian behavior of the PDMS matrices. Expressing the viscosity ratio $\eta(\text{treated})/\eta(\text{bare})$ of the silane-treated sphere suspension to the bare sphere suspension as a function of stress, inset (b) of Fig. 1 not only clearly illustrates the enhancement of interfacial slip by stress but more importantly depicts the molecular weight dependence of the slip phenomenon.

While the molecular weight dependence of the interfacial slip is quite revealing, the temperature dependence is even more intriguing. The PDMS-G suspension were taken down to $T = -30$ °C in the RMS-800 rheometer which is about 9 °C above the crystallization temperature of PDMS. Notice the PDMS-G suspension containing the silane-treated glass spheres displayed appreciable slip at $T = 25$ °C at a stress $\sigma = 100$ Pa. The same sample no longer indicates any measurable slip even at $\sigma = 1000$ Pa at -30 °C as shown in Fig. 2. With the shear stress increasing beyond 1000 Pa, η_r of this suspension begins to deviate downward, signifying the onset of stress-induced interfacial slip. The PDMS-G suspensions were also brought up to 80 °C and the viscosity ratio $\eta(\text{treated})/\eta(\text{bare})$ is presented together with those at 25 and -30 °C in the inset of Fig. 2. The PDMS-FG suspensions showed a similar temperature dependence to that shown in Fig. 2. For clarity we omitted data for the PDMS-FG suspensions in Fig. 2.

By comparing the slip behavior at different temperatures, we find from the inset of Fig. 2 that the onset stress σ_c for the interfacial slip is significantly higher at a lower temperature. This trend suggests that the cause for the interfacial slip is stress-induced chain desorption and is not the previously proposed disentanglement of sparsely populated adsorbed chains from the surrounding free chains [8]. (If the disentanglement mechanism would operate here, σ_c should be proportional to k_BT and be lower at a lower temperature [2].) According to standard activation theories, it is sensible that chain desorption requires higher interfacial stress at a lower temperature. Reference [11] shows that chain disentanglement transition is possible only for strong interfaces. Thus the presented data, which are consistent with the notion of stress-induced chain desorption, are among the first *experimental* evidence for a new molecular mechanism for interfacial slip.

The onset stress σ_c for chain desorption decreases not only with temperature from $\sigma_c \cong 1300$ Pa at -30 °C to an estimated $\sigma_c \cong 20$ Pa at 25 °C for the PDMS-G suspension as shown in Fig. 2, but also with the molecular weight M_w from $\sigma_c \cong 200$ Pa for PDMS1 to an estimated $\sigma_c \cong 10$ Pa for PDMS-G at $T = 25$ °C as shown in Fig. 1. To confirm this somewhat unexpected M dependence of σ_c, the remaining four suspensions involving PDMS1 and PDMS-FG were also taken down to -30 °C, where their viscosities were measured as shown in Fig. 3. Consistent with experiments conducted at room temperature (25 °C) and presented in Fig. 1, Fig. 3 demonstrates the *same* strong molecular weight dependence of not only the magnitude of hydrodynamic slip but also the onset of the slip. At -30 °C, the onset stress σ_c drops from an estimated 10^4 Pa for PDMS1 to $\sigma_c \cong 1000$ Pa for PDMS-G to an estimated $\sigma_c \cong 100$ Pa for PDMS-FG as shown in Fig. 3. Such a molecular

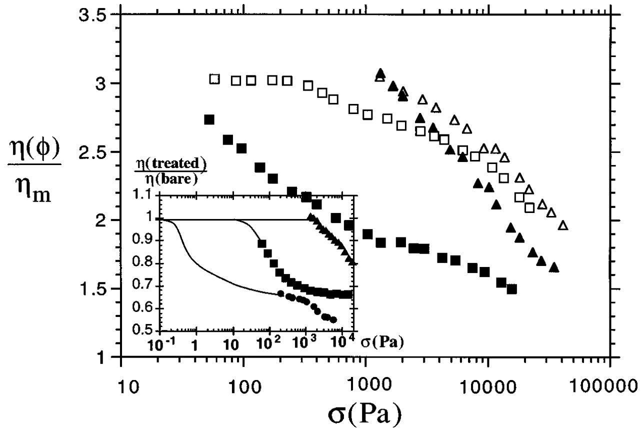

FIG. 2. Reduced viscosity $\eta(\phi)/\eta_m$ of the PDMS-G suspensions vs the applied stress at two different temperatures: $T = 25$ °C (symbolized by squares) and $T = -30$ °C (represented by triangles). Inset: the normalized viscosity $\eta(\text{treated})/\eta(\text{bare})$ vs the applied stress σ for the PDMS-G suspensions at $T = 80$ °C (denoted by circles), $T = 25$ °C, and $T = -30$ °C.

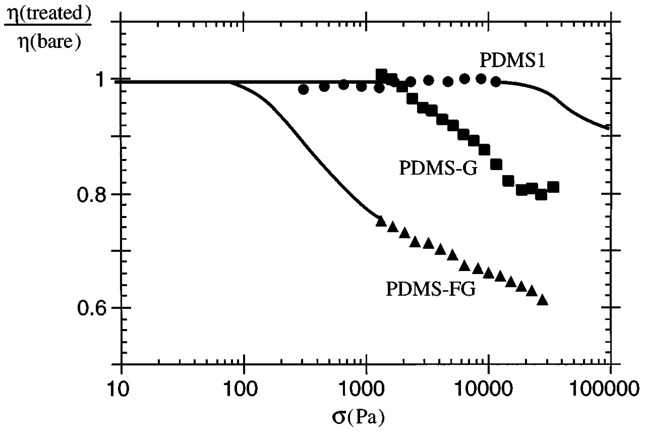

FIG. 3. Normalized viscosity $\eta(\text{treated})/\eta(\text{bare})$ vs the applied stress σ at $T = -30$ °C, which is calculated from the viscosity of the six suspensions involving all the three PDMS, respectively.

weight dependence of σ_c indicates that the PDMS chains of higher M_w desorb more easily, given the same stress. With a nearly perfect coverage of the glass spheres by the fluoro-silane molecules, not many interacting sites on the spheres are exposed to the strongly polydisperse PDMS matrices. Each stress-bearing interfacial (SBI) chain rarely has more than one segment adsorbed onto the treated glass spheres at any given moment. Furthermore, there are fewer SBI chains per unit area for a higher molecular weight PDMS matrix, as the short non-SBI chains saturate a large portion of the available adsorption sites. Thus under the same stress, each SBI chain experiences more force in the case of a higher M PDMS matrix. Conversely, chain desorption should occur at a lower onset stress for a PDMS suspension of higher molecular weight. Comparison between Fig. 1 and Fig. 3 also shows that this molecular weight dependence of σ_c is quantitatively *invariant* with respect to temperature, revealing a peculiar feature of a very weak melt/solid interface.

By measuring the internal hydrodynamic slip at the treated glass sphere/PDMS interfaces in terms of the reduced suspension viscosity η_r, we can also indirectly examine kinetics of the desorption and readsorption processes at melt/solid interfaces. Few experimental data exist on this subject [19] and new experimental methods remain to be developed. We found that the interfacial slip, as measured by the diminished suspension viscosity, occurs instantaneously and recovery from slip to stick also takes place immediately upon lowering the applied stress [17]. This implies that both stress-induced chain desorption and readsorption require a negligible amount of time to complete instead of hours long [19]. In other words, upon applying a high enough stress, *sufficient* chain desorption takes place instantaneously to cause interfacial slip. Similarly, upon lowering the stress level, *sufficient* chain readsorption occurs instantaneously to restore the stick boundary condition.

In conclusion, by studying the viscometric properties of stable uniform suspensions made of poly(dimethyl siloxane) and 10-μm-sized glass spheres, we have experimentally demonstrated that significant interfacial slip may occur at weak melt/solid interfaces as a result of stress-induced chain desorption. This chain desorption mechanism for slip is supported by the striking temperature dependence of the onset stress σ_c for slip. For example, we found that σ_c increases by an estimated 4 orders of magnitude as the temperature changes from 80 to -30 °C for the PDMS-G suspension. Without an analytical theory, we cannot explicitly relate σ_c to the local interfacial stress experienced by the spheres. However, it suffices to say that slip and chain desorption are induced and determined by and grow with the applied shear. The characteristics of slip behavior also depend strongly on the polymer molecular weight M. The magnitude of slip, as measured by the reduced suspension viscosity η_r, increases monotonically with M, as expected from [1]. The onset of slip also varies with M. We found that the onset of the sphere-matrix interfacial slip is at a stress 2 orders of magnitude higher in the PDMS1 suspension than the onset stress required to produce interfacial slip in the PDMS-FG suspension at both 25 and -30 °C.

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