Probing the surface properties of a polymer glass with macroscopic friction

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Abstract. We show how macroscopic friction can be used as a sensitive probe of chain dynamics at the surface of a glassy polymer. We present experiments in which a smooth poly(methylmethacrylate) (PMMA) solid slides on flat surfaces presenting different densities of pinning sites available for polymer/substrate bond formation. These experiments indicate that: (i) at high pinning level, frictional dissipation occurs through the sudden flips of molecular-sized bistable regions localized in a nm-thick layer of confined chains, which responds to shear as an elasto-plastic solid, and (ii) in situations of weak pinning, dissipation appears to be governed by a process akin to that proposed for rubber friction. This suggests that some “glass-to-rubber” transition occurs at the polymer surface when its interaction with the substrate goes from strong to weak. The temperature-dependence of friction provides further support for the presence of a nm-thick layer at the polymer surface, which exhibits a rubberlike response in situation of weak interaction with the countersurface. This behavior results from the interplay between viscous flow in this surface layer, and shear induced depinning of adsorbed surface chains. Moreover, a quantitative analysis of the results indicates that the pinning dynamics of polymer chains is controlled by localized $\beta$ rotational motions at the interface.

1. Introduction

Polymers are employed in many situations in which their tribological properties are of paramount importance, e.g. for solid lubrication using polymer coatings [1, 2, 3] or in applications involving sliding of rubber components [4, 5, 6]. Understanding the basic mechanisms responsible for polymer friction therefore lies at the heart of a number of studies over the past fifty years. The following two main pictures, developed for two classes of polymeric materials, emerge from these works.

In his pioneer study of rubber friction [4], Grosch showed that energy dissipation resulted from the combination of bulk viscoelastic losses and of an interfacial molecular process. The latter was described by Schallamach as the thermally activated formation and breaking, under the applied shear stress, of molecular bonds between the rubber and the countersurface [7]. Such a pinning/depinning mechanism is consistent with the velocity-dependent friction reported in experimental studies of rubbers sliding on smooth substrates [4, 5].

On the other hand, friction of glassy polymers is usually related to bulk plasticity [1, 8]. It has been recently shown that, in the absence of ploughing of the material, i.e. in the absence of bulk dissipation, friction is governed by the yield properties of a nanometer-thick polymer layer confined at the interface between the solids [9, 10, 11, 12, 13].
Now, in connection with questions related to the physics of glass transition, the issue of surface properties of glassy polymers has attracted much attention in the last decade [15, 16, 17, 18, 19]. Studies of the thermal [16, 20, 21] and mechanical [22, 23, 24] properties of thin films indicate that a glassy polymer exhibits a nanometer-thick surface layer in which the chain mobility differs from that of the bulk. Moreover, the dynamics in this layer appears to be strongly influenced by the nature of the chemical interactions between the polymer and the substrate: mobility is enhanced near a free polymer surface or an interface with a low energy substrate, whereas chain dynamics seems to be slowed down in the case of strong polymer/substrate interactions [20, 25, 26].

In the present paper, we review recent results from macroscopic single-contact friction experiments [10, 27, 28], in which a smooth lens of polymer is pressed, under low contact pressure, on a rigid flat substrate, which allows to probe the shear response of the polymer surface without inducing bulk dissipation during sliding. The surface of the substrate is modified by grafting organic monolayers, in order to adjust the density of pinning sites available for polymer/substrate bond formation.

We thus show that the above-mentioned dependence of surface chain mobility on interactions has a clear signature on friction, suggesting that some “glass-to-rubber” transition occurs at the polymer surface when its interaction with the substrate goes from strong to weak [27]. Moreover, from the temperature dependence of friction in the rubberlike regime, we identify the molecular mechanism which controls the pinning dynamics at the interface. Finally, we present results showing how the contact pressure affects the response of the polymer/substrate interface.

2. Experiments

We use a homebuilt tribometer (see [10, 28] for a detailed description) in which a smooth lens of glassy poly(methylmethacrylate) (PMMA, $T_g \approx 110^\circ$C) is in contact with a flat silicon substrate. Under constant normal load $F_N$, we simultaneously monitor the contact area $A$ and the tangential force $F_T$ while the substrate is driven at constant velocity $V$. We thus have access to the mean shear stress $\sigma = F_T/A$ as a function of the applied contact pressure $p = F_N/A$ (in the range 10—100 MPa) and the driving velocity $V$ (in the range 0.03—300 µm.s$^{-1}$). The silicon substrate is mounted on a temperature-controlled holder, which allows us to perform experiments in the range $T = -20^\circ$C—100$^\circ$C. All measurements are made at relative humidity below 5%, in a glovebox purged with dry argon.

PMMA samples are prepared following a protocol [10] which allows us to obtain lenses of millimetric radius of curvature, and of a root-mean-square roughness of $\sim$3 Å at their apex [28].

Substrates are silicon wafers covered by a nanometer-thick native oxide layer. They are cleaned in a UV/O$_3$ chamber for 30 min, and subsequently exposed to a water saturated oxygen flux in order to prepare hydroxylated silica surfaces, i.e. exhibiting a high number of silanol (Si-OH) groups. The PMMA macromolecules can form hydrogen bonds, via their carbonyl groups, with these silanols, which thus act as pinning centers for the polymer chains. In order to control the density of such pinning sites, the wafer surfaces are grafted with methyl-terminated silane layers according to one of the following procedures:

(i) gaz-phase grafting of trimethylsilane (TMS),
(ii) grafting of octadecyltrichlorosilane (OTS) by immersion of a substrate for 5 min in a solution of OTS in hexadecane/carbon tetrachloride at 18°C (labeled OTS18 in the following),
(iii) grafting of octadecyltrichlorosilane (OTS) by immersion of a substrate for 5 min in a solution maintained at 25°C (labeled OTS25).

The first type of silane (TMS) does not self-assemble and yields a thin ($< 5Å$) disordered submonolayer in which non-passivated Si-OH groups are still available. Changing the grafting temperature of OTS has an impact on the layer morphology, as documented in extensive studies [30]. OTS18 has an average thickness $\sim 21$ Å (as measured by ellipsometry) and exhibits islands
of high areal density of silane molecules (lateral size $\sim 10-100$ nm), separated by regions of much lower coverage density or even bare substrate (of lateral dimension $\sim 10$ nm)\[27]. On the other hand, OTS25 has an average thickness $\sim 15\text{Å}$, but presents a more uniform coverage density [27].

We therefore expect the density of available silanol groups to be low on OTS25 (low pinning level), slightly higher on OTS18 (intermediate pinning level), and much higher on TMS coated wafers (high pinning level).

3. Effect of pinning level on friction

We first present the velocity dependence of the shear stress, measured in steady sliding at $T = 22^\circ\text{C}$ and $p = 25$ MPa, for the three substrates described above.

It is seen on Fig. 1 that in the situation of high pinning level, the shear stress $\sigma$, which lies in the range 30–40 MPa, exhibits a logarithmic increase with velocity: $\sigma \approx \sigma_0 + \alpha \ln(V)$. Such a $\ln(V)$ dependence of $\sigma$ has been shown to result from thermally-assisted stress-induced structural rearrangements. These rearrangements involve zones of $\sim \text{nm}^3$ (from the log-slope of $\sigma(V)$, we compute an activation volume $v_{\text{act}} = k_B T/\alpha \sim 1-2 \text{ nm}^3$) localized in a nanometer-thick polymer layer, which, under shear, behaves as an elasto-plastic glassy medium [10, 11, 14].

![Figure 1. Shear stress as a function of velocity for PMMA sliding on a substrate presenting a high number of pinning sites. Velocity plotted on a log scale. Experiment performed at $p = 25$ MPa and $T = 22^\circ\text{C}$.](image1)

At low pinning level, $\sigma$ is found to be roughly one order of magnitude lower than in the previous case, and displays a power-law dependence on velocity: $\sigma \sim V^\beta$, with $\beta \approx 0.1-0.2$ (see Fig. 2). Such a power-law behaviour is qualitatively similar to the shear-thinning response of strongly confined melts [31, 32]. Moreover, as mentioned in the introduction, recent studies of

![Figure 2. Shear stress as a function of velocity in the case of low pinning level. Velocity plotted on a log scale in the main panel. Inset: same data plotted on log-log scales. Experiment performed at $p = 25$ MPa and $T = 22^\circ\text{C}$.](image2)
the properties of ultrathin polymer films indicates that at its free surface, or at the interface
with a low energy substrate, a glassy polymer exhibits a nanometer-thick layer in which the
chain mobility is enhanced with respect to the bulk one. This leads us to propose that the
frictional response observed in the low pinning level situation results from viscous dissipation
in a liquidlike nm-thick polymer layer at the surface of the PMMA sample. Such a picture is
further supported by the fact that increasing the contact pressure (see Fig. 3a) or decreasing
the temperature (see Fig. 3b) both result in an increase of the shear stress. This is consistent
with a mobility of surface chains which is lower at higher \( p \) or lower \( T \). A more quantitative
analysis, in order to estimate the effective viscosity of this nanometer-thick layer, would however
require the precise knowledge of the slip boundary condition at the wall, \textit{i.e.} the slip-length [33],
a quantity that cannot be accessed in our experiments.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(a) \( \sigma(V) \) measured at \( T = 20^\circ C \) and (\( \bullet \) \( p = 10 \) MPa, (\( \circ \) \( p = 19 \) MPa, (\( \triangle \) \( p = 38 \) MPa, (\( \square \) \( p = 63 \) MPa. (b) \( \sigma(V) \) measured at \( p = 43 \) MPa and (\( \triangle \) \( T = 40^\circ C \), (\( \blacksquare \) \( T = 30^\circ C \),
(\( \square \) \( T = 20^\circ C \), (\( \bullet \) \( T = 10^\circ C \), (\( \circ \) \( T = 0^\circ C \).

In the case of intermediate pinning level, the \( \sigma(V) \) curve displays a minimum. For the
dataset plotted on Fig. 4, the shear stress is found to increase when the velocity increases for
\( V > V_c \simeq 0.3 \mu m.s^{-1} \), but is a decreasing function of velocity for \( V < V_c \). This velocity-
weakening regime below \( V_c \) is the source of unstable sliding, which manifests as stick-slip
oscillations which are observed at \( V < 0.1 \mu m.s^{-1} \). We propose, in the spirit of Schallamach’s
model [7, 6, 11], that friction at such an interface is the result of two combined mechanisms
[27, 28]:

(i) Viscous dissipation in the nm-thick polymer layer made of chain ends and loops, which
yields a velocity-strengthening contribution to the shear stress.

(ii) Shear induced depinning of surface chains which are adsorbed on the coverage defects of
OTS18 substrate. The dynamics of bond formation is governed by a characteristic pinning time
\( \tau \). Upon sliding, the faster the chain is driven, the smaller the time available for bond formation.
The number of bonds formed at the interface is thus a decreasing function of velocity, which
leads to a velocity-weakening contribution to \( \sigma(V) \). This mechanism is expected to contribute
negligibly to frictional dissipation at sliding velocities above \( V_c = D/\tau \), where \( D \) is an average
capture radius (\( \sim 10 \) nm, the size of the coverage defects on OTS18 substrate).

The position of the minimum in the \( \sigma(V) \) curve thus indicates the crossover between pinning-
controlled and viscosity-controlled friction[34]. In what follows, we show how temperature and
pressure affect this crossover.
4. Temperature-dependent pinning dynamics

The effect of temperature on $\sigma(V)$, in the intermediate pinning level situation, provides support to the above picture. We find that increasing the temperature shifts the stick-slip regime and the position of the minimum ($V_c$) to higher velocities (see Fig. 5a). Conversely, at low enough temperature, $V_c$ lies below the lowest accessible velocity with our experimental setup, and only the power-law “viscous” regime $\sigma \sim V^\beta$ is observed (see Fig. 5b). Such a shift of $V_c$ with temperature is consistent with the expected decrease of the pinning time $\tau$ when $T$ is increased.

Furthermore, if we use $V_c$ to evaluate the pinning time $\tau = D/V_c$, taking $D \simeq 10$ nm, we find: $\tau$ in the range $10^{-3}$–$3 \times 10^{-3}$ s for $T = 40^\circ$C, $\tau \simeq 10^{-2}$ s for $T = 29^\circ$C, $3 \times 10^{-2}$ s for $T = 21^\circ$C, and $\tau$ in the range $10^{-1}$–$3 \times 10^{-1}$ s at $T = 5^\circ$C. Figure 6 shows that $\tau$ follows an Arrhenius temperature dependence, from which we extract an activation energy $E_a \simeq 20$ kcal.mol$^{-1}$. It coincides with that of the $\beta$ relaxation process in PMMA, which corresponds to the hindered rotation of the -COOCH$_3$ side groups [18, 35, 36]. Besides, the values of the pinning time are themselves found to be in good agreement with $\tau_\beta$ (see Fig. 6). This leads us to conclude that pinning of polymer segments on the substrate is governed by $\beta$ rotational motions along the backbone of surface chains. A pinning dynamics controlled by $\beta$ motions is indeed consistent with the fact that -C=O groups have to be favorably oriented with respect to silanols in order to form H-bonds.
5. Role of contact pressure

On Fig. 7 is plotted a set of $\sigma(V)$ curves measured at different contact pressure $p$, in the case of intermediate pinning level. It is clearly seen that increasing $p$ shifts $V_c$ towards lower values, in agreement with the expected increase of $\tau$ (i.e. a slower segment dynamics) when $p$ is larger. Such a pressure effect has been observed at a single temperature, but a more detailed investigation, including measurements at various temperatures, should allow to determine how $\beta$ rotational motions at the interface are affected by the applied pressure.

The contact pressure is thus found to affect the respective weight of viscous dissipation and pinning/depinning in the case of intermediate pinning level.

In situations of high or low pinning level, we observe that an increase in pressure mainly results in an upward shift of the $\sigma(V)$ curves. This indicates that, for PMMA sliding on TMS or OTS25 substrates, the basic mechanism for frictional dissipation (namely plastic flow on TMS and viscous flow on OTS25) is not significantly affected by pressure, in the range of $p$ and $V$ explored in our study. We further investigate the pressure dependence of the shear stress, for PMMA sliding on TMS and OTS25 substrate, by measuring $\sigma(p)$ at given velocity and temperature. Results are plotted on Fig. 8 for both substrates. It is clearly seen that the shear stress increases sublinearly with the mean contact pressure. Although we cannot provide an explanation for this non-linear dependence of the shear stress on pressure, our results highlight the non-trivial role of contact pressure in single contact friction, where the common Amontons-Coulomb proportionality between shear and normal stresses is not the rule.

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**Figure 6.** Natural logarithm of the pinning time as a function of the inverse of the temperature ($\bullet$). The ($\circ$) symbol corresponds to a value of $\tau_{\beta}$ taken from reference [35]. Error bars on ($\bullet$) symbols correspond to the uncertainty on $V_c$ at 5 and 40°C. The line is an Arrhenius fit to our the data.

**Figure 7.** Shear stress as a function of velocity, in the intermediate pinning level situation, $T = 29^\circ C$. ($\blacktriangle$) $p = 50$ MPa; ($\circ$) $p = 25$ MPa; ($\bullet$) $p = 7$ MPa. Unstable sliding is observed for $V < 3 \mu m.s^{-1}$ at $p = 7$ and $V < 0.3 \mu m.s^{-1}$ at $25$ MPa.
Figure 8. Shear stress as a function of pressure, measured at $V = 10 \mu m.s^{-1}$. (a) PMMA sliding on TMS substrate. (b) PMMA sliding on OTS25 substrate.

6. Conclusion
Macroscopic friction can be a very sensitive probe of the dynamics at the surface of a glassy polymer. This requires a contact geometry that allows to avoid bulk mechanical losses during sliding. This is achieved, in our experiments, by using a smooth macroscopic lens of polymer which deforms elastically when it is brought in contact under low pressure with a rigid substrate. This contrasts with previous studies of glassy polymers using friction force microscopy, where indentation of the surface by the scanning tip can be such that friction is entirely attributable to bulk dissipation [18].

We have shown that, when the strength of interfacial interactions is increased, the frictional rheology gradually evolves from that of a highly viscous confined melt to that of a plastically deformed glassy medium. We conclude that the nanometer-thick polymer layer where shear localizes undergoes a “glass-to-rubber transition”. That is, in a situation where molecular mobility at the free PMMA surface is still liquid-like, confinement by a strongly corrugated potential, helped by pressure, is able to quench the interface into a jammed glassy state. This interpretation is fully consistent with the analysis of glass transition shifts in thin supported films in terms of the existence, at the surface of a glassy polymer, of a layer in which chain mobility is all the higher as the interaction with the substrate is weak [20]. Moreover, a quantitative analysis of our data in the rubberlike regime leads us to conclude that the pinning dynamics is governed by $\beta$ rotational motions at the interface.

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