Cite this: *Soft Matter*, 2011, **7**, 8535

www.rsc.org/softmatter

PAPER

Incidence of the molecular organization on friction at soft polymer interfaces

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Received 11th May 2011, Accepted 16th June 2011

DOI: 10.1039/c1sm05874f

Polymer molecules strongly anchored to a solid substrate and interdigitated into bulk crosslinked elastomer have been shown recently to efficiently promote adhesion and friction between substrate and elastomer. Concerning friction, the regime of low surface coverage in surface anchored chains has been fully and quantitatively accounted for by the pull off mechanisms, where individual chains are dynamically extracted from the elastomer. Then, the stretching energy of these chains dominates the friction losses. We focus here on the dense surface coverage regime. We present systematic experiments performed on the polydimethylsiloxane (PDMS) – silica system, and determine molecular weight and sliding velocity dependences of the friction stress. We show that the friction is dominated by the shear thinning of the grafted layer confined between the elastomer and the substrate, and responding to the shear solicitation like a melt, but with very long relaxation times. We also show that the friction stress appears highly sensitive to the molecular organization inside the surface anchored polymer layer, comparing end grafted and strongly adsorbed layers having otherwise the same molecular characteristics (molecular weight of the chains, and thickness of the surface anchored layer).

Introduction

The friction properties at interfaces between polymers are strongly influenced by the presence of bridging chains. Disentanglement and pull-out of these chains during sliding has been pointed out as a major contribution to energy dissipation and friction losses.^{1,2} We focus here on the *a priori* simple case of soft polymers, with neutral chains, well above their glass transition temperature.

A number of experimental approaches have been developed to try to identify the detailed molecular mechanisms of friction in such systems. Early experiments were conducted using the surface force apparatus, in order to characterize brush – brush and brush – solution or melt friction.^{3–7} The interpretation of these experiments in terms of molecular mechanisms is however not trivial, for two reasons: if rather densely grafted brushes are used, the relative degree of interdigitation, and thus the possibility of developing entanglements between chains grafted on antagonist surfaces is not easy to predict and control, and secondly, the surface pressure in the contact of a SFA machine is usually quite high, which may deeply affect the local molecular behavior. Friction properties at grafted brush/melt interfaces are more directly reflected in flow properties, and especially in the boundary condition for the flow velocity at interface. Various systematic sets of experiments have been conducted in order to access directly (local velocity measurement at the solid wall) or

indirectly (overall flow properties) the boundary condition for the flow velocity at the wall.^{8–22} If sufficient interdigitation between the surface anchored chains and bulk melt is achieved, it has been shown that various friction regimes could develop when the shear velocity was progressively increased, due to the progressive stretching of the surface anchored chains under the effect of friction forces. This stretching of the surface chains was shown able to induce disentanglement between surface and bulk chains, strongly reducing the friction coefficient. As a result various non linear friction regimes were identified. For weak enough surface coverages, when the surface chains were contributing independently to the friction, these friction regimes were qualitatively well accounted for by the pull out model proposed by de Gennes and co-workers.^{23–27}

More recently, direct measurements of the friction force have been reported, using a JKR like experiment,²⁸ where a microlens of soft crosslinked PDMS elastomer was put into contact with silicon wafer surfaces covered with end grafted PDMS chains, and then slide at controlled velocity, while the friction force was measured. These direct friction force measurements have put into evidence two regimes in terms of dependence of the friction force *versus* the surface density of grafted chains. For weakly dense grafted layer, the friction force increases linearly with the surface grafting density. This indicates a friction behavior dictated by independent surface anchored chains. In this regime, it was then possible to extract a friction force per grafted chain, which could directly be compared to predictions by models at the molecular level. The absolute value along with the velocity and the molecular weight dependences of the friction force have been quantitatively accounted for by the pull off mechanism

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developed by M. Rubinstein *et al.*^{29,30} A second regime was also identified by these early PDMS/PDMS friction experiments: at higher grafting densities, the friction force was becoming independent of the grafting density. In this regime, a more collective response of the chains inside the grafted layer to shear solicitation is thus expected.

We report here systematic experiments conducted on the same JKR like friction apparatus, on the same PDMS/grafted PDMS system as in ref. 28, but now focused on this densely grafted regime. In order to gain a better insight in the molecular characteristics of this friction regime, and provide guide lines to the development of molecular models, we shall compare in a systematic manner the friction behavior of end grafted and irreversibly adsorbed surface layers.

Materials and method

The details of the friction experiment and of the sample preparation have already been reported.²⁸ We just recall here what is necessary for the understanding of the presented data.

Sample preparation

Crosslinked elastomer microlenses are obtained using the following method: chains of α - ω vinyl terminated PDMS chains (molecular weight 18 kg mol⁻¹, polydispersity index 1.17) are crosslinked in the presence of Karstedt catalyst on SiH tetra functional crosslinker. The crosslinking reaction is optimized in order to control the quality of the network and minimize the amount of pending chains: first the ratio of hydride to vinyl function is adjusted, and second the crosslinking is conducted in strictly controlled humidity (glove box, and dry argon atmosphere) in order to keep the hydride amount under control. In order to keep a large enough open time before crosslinking in order to form the small elastomer lenses, the reactive mixture is kept at -20 °C, until all lenses are formed, with the help of a Peltier cooled thermal chamber. Small convex microlenses of crosslinked elastomer are obtained by depositing droplets of the reactive mixture on a glass slide, treated with a perfluorinated silane, in order to obtain a non totally wetting substrate for PDMS.³¹ After reaction at 110 °C for 12 h, all networks are washed for 9 days in toluene, in order to extract all unattached chains, and dodecane thiol is added to the final rinsing bath, in order to deactivate any remaining catalyst. It is worthwhile to notice that the mode of elaboration of these small elastomeric lenses leads to quite smooth surfaces, (as can be seen through AFM imaging of the upper part of the crosslinked drops, with a typical RMS roughness of 0.3 nm). The surface has been smoothened before crosslinking by the surface tension of the liquid. With the optimized crosslinking reaction used, the step of washing of all unreacted chains out of the elastomer does not affect the surface roughness of the lenses, because the amount of extracted chains remains small, of order of 3% by weight.³²

Grafted PDMS layers were formed as follows: first a just cleaned silicon wafer surface (UV-ozone cleaning during half an hour) was covered by a self assembled mono layer of a short PDMS oligomer with one chlorosilane and one SiH extremity, in order to form a dense carpet of SiH reactive sites on the silicon wafer. Then this surface was incubated with a mixture of

terminated PDMS melt and Pt catalyst, and let to react overnight. Five monovinyl terminated PDMS samples were anionically polymerized for the present study, with molecular weights respectively 5 kg mol⁻¹, 50 kg mol⁻¹, 74 kg mol⁻¹, 107 kg mol⁻¹ and 187 kg mol⁻¹, and polydispersity indices smaller than 1.1. The substrate was then rinsed in toluene, again with a last rinsing bath containing dodecane thiol, to deactivate any remaining catalyst, and finally dried in an oven at 80 °C. The dry thicknesses of the grafted layers were measured by ellipsometry. The surface grafting density was deduced from this dry thickness, h , and the molecular characteristics of the grafted chains through $\Sigma = h/Na^3$, with N the polymerization index of the grafted chains, and a the size of the monomer.³³

Dense strongly adsorbed PDMS layers were fabricated by incubating freshly cleaned silicon wafers with di-OH terminated PDMS melts of chosen molecular weights. The monodisperse di-OH PDMS were obtained by a classical fractionation process of a commercial PDMS mixture kindly provided by Rhodia Silicones. In order to allow easy spreading of the highly viscous high molecular weight melts, 20% solutions in octane were prepared, spread on the silicon wafer, and the octane was rapidly evaporated under vacuum, to keep a thin layer of melt spread on the surface. After annealing for a night at 110 °C, the layers were rinsed in five successive toluene baths, and then dried, quite similarly to what was done for the grafted layers. The dry thickness was measured by ellipsometry, and used to deduce the surface density of adsorbed chains, with the same formula as for grafted chains.

The above grafting or adsorption procedures lead to surface anchored layers corresponding to either grafted brushes or surface attached pseudo-brushes. This has been demonstrated by

Fig. 1 Schematics of the friction experiment. A semi-spherical elastomer lens, L, attached to a rigid mechanical holder, H, is put into contact with the substrate, S. The substrate is translated at a chosen velocity, V, through a double beam cantilever, K. The deflection x of K, monitored through the position sensor, C, gives the friction force. The contact area is optically controlled through a microscope, O.

characterization by neutrons reflectivity of the concentration profile inside these surface layers, when swollen by a good solvent.³⁴

Friction force measurements

The friction measurements have been performed on a set up designed on purpose by L. Bureau,²⁸ and schematically presented in Fig. 1.

A microlens of elastomer is adhered to a glass plate inserted into a mechanical holder, which can be translated vertically with a micrometric screw, with a μm resolution. This lens is brought into contact with the substrate covered with the polymer layer to be investigated. The substrate is fixed at the free end of a double cantilever spring (stiffness $k = 240 \text{ N m}^{-1}$), able to slide with respect to the lens, as driven at chosen velocities by a microstep motor connected to the other extremity of the spring. The range of available velocities is $3 \text{ nm s}^{-1} < V < 330 \mu\text{m s}^{-1}$. A capacitive displacement gauge (model S601-0.2 from Micro-Epsilon, France, equipped with DT610 electronic control) measures the spring bending, and allows one to access the friction force, in the range $50 \mu\text{N}$ to 50 mN . The linearity of this capacitive sensor is better than 1% on the full range used in the present experiments, so that no linearity corrections need be implemented, contrary to what is usually done in the case of piezoelectric actuators in AFM or SFA machines. The normal force cannot be measured directly in this set up, but, as an indication of the normal load, the size of the contact area between the lens and the substrate is monitored optically, through a long working distance microscope (Questar N°QM100). During a sliding experiment, the sphere/substrate indentation depth is fixed. The contact is first observed to obey the JKR description of the mechanics of contact, when no sliding is applied. Secondly, when sliding, the

friction force appears characteristic of a monocontact, as shown in Fig. 2, where the friction force is reported as a function of the contact area.

The observed linear relationship is indeed indicative of a friction force growing (non linearly, due to JKR contact mechanics) with the normal load, which is very different from what is usually observed for solid contacts obeying Amonton's law, with a friction force independent of the apparent contact area, as a result of contact roughness.^{35,36} In the following, all the friction data will thus be presented in terms of friction stress (measured friction force divided by the contact area) *versus* sliding velocity. For the range of sliding velocities used in the present series of experiments, the contact area which is continuously monitored during the sliding experiment, appears to be independent of the sliding velocity, and identical to the static one. Then, the friction force divided by the area of contact yields a true shear stress.

Typical raw sliding data are shown in Fig. 3, where the friction force is reported as a function of the sliding distance, for a contact between an irreversibly adsorbed layer ($M_w = 330 \text{ kg mol}^{-1}$) and a given elastomer microlens. After an initial transient step, steady sliding occurs, and is characterized by the final plateau in the force *versus* distance curve. The transient initial response is indicative of a static stiction peak, and the amplitude of the maximum force depends both the molecular characteristics of the adsorbed layer and on the time spent under static contact before starting the sliding motion. In the present paper, we shall focus on the steady sliding regime. A systematic analysis of the transient regime, which contains information on the kinetics of the interdigitation process between the surface anchored chains and the elastomer will be reported in a forthcoming paper.

Fig. 2 Linear relationship between the sliding friction force and the contact area, for a typical experiment: elastomer lens on an irreversibly adsorbed layer of PDMS with molecular weight $M_w = 330 \text{ kg mol}^{-1}$, and a sliding velocity $V = 8.72 \mu\text{m s}^{-1}$.

Fig. 3 Typical evolution of the friction stress as a function of the displacement for a typical sliding velocity $V = 3.05 \mu\text{m s}^{-1}$ and an irreversibly adsorbed layer ($M_w = 330 \text{ kg mol}^{-1}$). The three different curves correspond to three separate sliding runs, on the same zone of contact on the substrate.

The three curves reported in Fig. 3 represent separate sliding runs on the same contact zone of the substrate. The high reproducibility of the friction data indicates that the sliding does not cause any significant damage to the layer. In particular, the adsorbed PDMS chains are not desorbed by the sliding friction force. This is true too for end grafted chains.

Results

End grafted chains

Data obtained on end grafted layers, for various molecular weights in the range 5 to 187 kg mol⁻¹ are reported in Fig. 4 which represents the evolution of the friction stress as a function of the velocity.

The data for the 5 kg mol⁻¹ dense layer are fully consistent with those yet reported in Bureau *et al.*²⁸ on layers with the same molecular weight, below the entanglement molecular weight of PDMS (9 kg mol⁻¹). In particular, the high velocity part of the curve shows a linear dependence of the friction stress *versus* the velocity, with a friction coefficient indicative of monomer–monomer friction.²⁸

When the molecular weight of the grafted chains is increased, keeping the grafting density high enough to remain in the regime of collective response of the grafted layer to friction solicitation, the friction for a given velocity significantly increases with molecular weight, while the velocity dependence evolves to become a power law, with an exponent much smaller than one, close to 0.2.

Remarkably enough, for large enough molecular weights (50 to 187 kg mol⁻¹), the friction stress becomes independent of the molecular weight of the grafted chains, contrary to what was observed, for the same range of molecular weights, in the low

Fig. 4 Evolution of the friction stress as a function of the velocity for end grafted chains with molecular weights ranging from below the entanglement molecular weight (5 kg mol⁻¹ compared to 9 kg mol⁻¹) to well above.

grafting density regime.²⁸ In order to gain a better insight on how the friction, inside this high surface density regime is sensitive to the internal organization, we have performed similar friction force measurements on dense irreversibly adsorbed PDMS layers, and compared the results obtained on grafted and adsorbed layers having similar thicknesses.

Irreversibly adsorbed chains

The friction stress measured on irreversibly adsorbed layers is reported in Fig. 5, as a function of the sliding velocity, for various molecular weight of the chains in the surface layer.

Trends quite similar to what was observed on grafted chains appear: the friction stress at a given velocity increases with molecular weight, and for large enough molecular weights and velocities, all curve tend to merge in a unique curve, whatever the molecular weight. The evolution towards this molecular weight independent regime appears however more progressive, and occurs at higher velocities than for end grafted chains, as can be seen comparing data in Fig. 4 and 5. Reaching the molecular weight independent high velocity regime of friction is more difficult for dense adsorbed layers than for end grafted ones.

Comparison between end grafted and adsorbed chains

A more precise comparison between end grafted and adsorbed chains is reported in Fig. 6, for two series of layers made of chains having the same molecular weights (respectively 50/43 and 105/107 kg mol⁻¹), and having almost the same dry thickness (respectively for 107 kg mol⁻¹, 17 nm for end grafted & 14 nm for 105 kg mol⁻¹ irreversibly adsorbed, and for 50 kg mol⁻¹ 14 nm end grafted and 11 nm irreversibly adsorbed 43 kg mol⁻¹).

For both kinds of layers, similar power law dependences *versus* velocity are observed, but the absolute value of the friction stress appears systematically 20% smaller on adsorbed layers compared to end grafted ones. It is also clearly apparent in Fig. 6 that the

Fig. 5 Evolution of the friction stress as a function of the velocity for irreversibly adsorbed layers with different molecular weights and dry thicknesses.

Fig. 6 Comparison between the friction stress on end grafted chains and irreversibly adsorbed chains. The filled symbols corresponds to grafted chains. The open symbols correspond to irreversibly adsorbed chains. ● 43 kg mol⁻¹ grafted, ○ 50 kg mol⁻¹ adsorbed ■ 107 kg mol⁻¹ grafted □ 105 kg mol⁻¹ adsorbed.

convergence towards the molecular weight independent high velocity regime is slower on adsorbed layers compared to grafted ones. The present experiments clearly demonstrate that the level of friction at surface anchored polymer layers/crosslinked elastomers interfaces is highly sensitive to details in the molecular organization of the chains inside the surface anchored layer.

Discussion

To summarize the above presented results, we have essentially shown that the steady sliding friction stress between an elastomer and either end grafted or irreversibly adsorbed chains of high enough molecular weights is molecular weight independent, contrary to what is observed at low surface densities where the surface chains act independently of each other on the friction. In this molecular weight independent regime, the friction, follows a power law dependence *versus* the sliding velocity over more than two decades in velocities. Since for both the adsorbed and grafted layers used in the present investigation, the surface density of chains inside the layer is quite high, it is expected that these chains should essentially be rejected from the elastomer, due to the swelling elastic energy penalty of the elastomer associated to the interdigitation process.³⁷ The friction between an elastomer and a chain pulled out from the elastomer at a chosen velocity, v , has been modeled by Ajdari *et al.*^{29,30} and recently revisited by T. Vilmin and E. Raphaël.³⁸ The process is qualitatively easy to describe: if at rest, the surface chain tends to penetrate into the elastomer (if both are of the same chemical species) in order to maximize its entropy. When subjected to the sliding motion, the surface chains which have penetrated inside the elastomer need to be extracted in order to allow for the sliding displacement. The friction then results from a competition between penetration and

extraction of the portions of chain which have succeed in penetrating inside the elastomer, during the time it takes to a mesh of the network to travel by a mesh size. As pointed out first by T. C. B. McLeish and K. P. O'Connor,³⁹ the penetration process, without sliding, should be very slow, because, starting from a situation where a surface chain is fully out of the elastomer and thus confined between the elastomer and the substrate, the first penetration steps involving the free end of the chain will most probably occur far from above the grafting point. The chain then needs to go out and in the elastomer in order to let the distance d between the grafting point and the position at which the penetration into the elastomer takes place relax to zero, so that the chain can fully recover its gaussian configuration inside the elastomer. With sliding, this relaxation is even more difficult, as the sliding friction tends to stretch the chain in the sliding direction, thus competing the tendency towards relaxation of d . In fact, three characteristic times play an important role and rule the competition between penetration and extraction of the surface chain during sliding: the relaxation time of the part of the chain extracted out of the elastomer,³⁹ the time the chain spends fully out of the elastomer before hopping again inside the elastomer, and the time needed for sliding the elastomer over a mesh size. The modeling of the friction done in ref. 29, 30 and 38 consists in evaluating these characteristic times as a function of the sliding velocity to finally predict the evolution of the friction force as a function of the imposed sliding velocity. This friction force is composed of an elastic part, associated to the stretching of the surface chain, and of a friction contribution associated to the relative motion between monomers pertaining to the extracted chain and to the elastomer. Indeed, the value of the time needed to slide over a mesh size fixes the amount of relaxation a surface chain can undergo during the sliding, and thus its average stretching. Except for very very slow sliding velocities, out of the range attainable in the present experiments, a surface chain has never enough time to fully relax its elongation along the sliding direction, and the average penetration inside the elastomer is partial, and depends on the sliding velocity. Both the non linear velocity dependence of the friction force, and the level of friction force observed experimentally in the low grafting density regime were found to be fully compatible with these ideas,²⁸ both for the dependences in grafting density and in molecular weights of the grafted chains. T. Vilmin and E. Raphaël,³⁸ have revisited this approach and extended it to high grafting densities, when the portions of chains stretched out of the elastomer are close enough to each other so that they can entangle. Taking into account these entanglements between partly stretched chains, confined between the elastomer and the substrate, and thus trapped, Vilmin and Raphaël were first able to predict the onset, in terms of grafting density, of a high grafting density regime in which the friction stress should no longer depend on the grafting density. They also predicted that the friction stress, in this high grafting density regime, should be independent of the molecular weight of the surface chains, due to the entanglements between the stretched chains, which impose an equal loading condition of the surface chains, whatever their length. The rough estimate of the friction stress made in ref. 38 appears to be in quite good agreement with the experimental data presented above, not only for the molecular weight independence, but also for the order of magnitude of that friction stress, which should be in the range of 40 kPa, according to

equation 7 in ref. 38 with typical values of $N = 10^3$, $a = 0.5$ nm and $N_e = 10^2$ for PDMS. The estimate of the friction stress given in ref. 38 is however too crude to precisely predict the velocity dependence. As we expect the grafted chains to be essentially out of the elastomer, confined between the elastomer and the substrate and possibly stretched, it is interesting to analyze the measured friction in terms of an effective viscosity of this sheared confined layer. The shear stress associated with this situation can easily be evaluated as $\sigma = \eta_{\text{eff}} \dot{\gamma}$ with η_{eff} an effective viscosity of the confined entangled layer of partly stretched chains, for the shear rate $\dot{\gamma}$. The actual shear rate experienced by the film is $\dot{\gamma} = V/h$ with V the sliding velocity and h the thickness of the film, when squeezed between the elastomer lens and the solid substrate and sheared. This thickness is *a priori* smaller than the dry thickness of the film (measured by ellipsometry, without any contact with the lens). It is however possible to evaluate how different are those two thicknesses: the polymer chains inside the film are strongly attached to the surface (by adsorption or end grafting), so that they cannot escape the contact zone when squeezed by the elastomer lens. The films inside the contact zone is then submitted to a compression, in a way somewhat similar to a isothermal compression of a bulk liquid. The maximum pressure inside the contact is at the center of the contact and can be evaluated through the JKR analysis⁴⁰ as:

$$\sigma_{\text{JKR}} = \frac{3}{2\pi a^2} \frac{Ka^3}{R} - \frac{1}{2\pi a^2} \sqrt{6\pi a^3 WK}$$

For the typical parameters of the systems (radius of contact $a = 100$ μm , radius of the lens $R = 1$ mm, rigidity constant of the lens $K = 4$ MPa and thermodynamic work of adhesion for PDMS – PDMS contact $W = 43$ mJ m⁻², one obtains a maximum pressure of 0.16 MPa. Using the data for the isothermal compressibility of PDMS,⁴¹ this gives an overestimate for the relative change in volume of the film under the contact of 1%. Due to the lateral constraints associated with the anchoring of the polymer chains to the substrate, this change in volume will be associated to a comparable change in thickness. This means that the thickness of the sheared squeezed layer should differ from the rest one by less than 1%. This is below the accuracy of the thickness determination, and we shall use the rest thickness of the films to evaluate the shear rate. The data reported in Fig. 4 allow one to evaluate this effective viscosity as shown in Fig. 7 for the four large molecular weights of grafted chains, 50, 74, 107 and 187 kg/mol.

It is particularly striking to notice that the effective viscosity associated with the sliding friction at the grafted layer/elastomer interface follows exactly the same shear thinning behavior as the bulk polymer melts, at high shear rates: this is not only true for the shear thinning exponent, close to 0.8, but also for the absolute value of the effective viscosity, which is observed to exactly join the shear dependent viscosities of the melts. This comes in strong support of the picture of a sheared grafted layer in which the grafted chains are entangled and deformed by the friction force in a way very similar to what happens in a melt submitted to large enough shear rates, so that the chains are elongated, thus inducing the shear thinning. The strong difference between the response of the grafted layer and that of a melt to shear, comes from the relaxation time of the elongation, which has to be related to a terminal relaxation time in the case of a melt, and is

Fig. 7 Effective viscosity of sheared grafted layers as a function of the shear velocity, for three different molecular weights of the grafted chains. For comparison, the shear rate dependent viscosity of the corresponding bulk melts are shown as the full lines (data from ref. 42).

expected to be much longer, (rather the retraction time of an arm of a star molecule, depending exponentially on the arm polymerization index) in the case of grafted chains. This explains why the onset of a shear independent velocity (Newtonian plateau) at low shear rates is out of the range of the present experiments, and not visible in curve 7. It is interesting to notice that the same exponent, for the shear rate dependence of the effective viscosity was measured by Yamada *et al.*⁴³ for highly confined PDMS melts in a SFA experiment, again with no indication of the Newtonian regime at low sliding velocities. It is well plausible that in these SFA experiments two irreversibly adsorbed layer had spontaneously formed on the two mica surfaces, leading to a shear response very similar to the one observed in the present experiments. An important question then is to try and understand in detail why even if not sensitive to the over all molecular weight of the surface anchored chains, as a consequence of the entanglements between the chains inside the surface layer, the friction keeps track of the detailed organization of these chains, leading to different levels of friction for end grafted or irreversibly adsorbed chains. What is the exact role of the polydispersity of the loops and tails in this later case? Detailed modeling of the shear response of a surface anchored soft polymer layer is needed to try to shine more light in the molecular process responsible for friction at such interfaces. This is of particular importance, not only from a fundamental point of view, but also for practical applications, as the most frequent situation when a polymer melt is put into contact with a solid wall is the spontaneous formation of a surface anchored polymer layer, which resembles the irreversible adsorbed layers used in the present study.

Conclusion

We have conducted a systematic investigation of the friction behavior of surface anchored PDMS layers put into contact with a crosslinked PDMS elastomer, in the dense surface coverage

regime where the surface chains respond collectively to shear solicitation. These experiments show that for high enough molecular weights of the surface chains and high enough sliding velocities, the friction stress becomes independent of the molecular weight of the chains in the surface anchored layer. For end grafted polymer chains, we have shown that the grafted layer shows the same shear thinning behavior than the one observed for a melt of PDMS, except that, due to the different relaxation time of a end-grafted chain and a free chain, no Newtonian plateau can be observed. Moreover, comparing grafted and adsorbed layers, with the same molecular weights of surface chains, it was possible to show that friction, in the molecular weight independent regime, remains sensitive to the details of the molecular organization of the chains inside the surface layer. For adsorbed chains, which are made of dense short loops and few (two on average per surface chain) long polydisperse tails, the friction stress is smaller by 20% than for end grafted chains. This is a subtle effect, as for the chains used, the friction appears independent of the molecular weight, and the average factor by 2 in length of the long tails for the adsorbed layer cannot account for the observed smaller friction. The present data call for detailed modeling of the molecular mechanisms of friction at such interfaces, when the chains in the surface layer are essentially rejected from the elastomer and confined and sheared under the effect of sliding the elastomer.

Acknowledgements

C. Cohen thanks the "Triangle de la physique" for financial support. We are grateful to D. Brunello for his help in all the experiments.

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