Nanofriction of polymers: the complex role of adhesion

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Abstract
The objective of this work is to compare adhesion properties and nanoscale friction behaviour of model elastomers. Two polydimethylsiloxane elastomers, varying in their cross-linking density, are studied before and after extraction of free chains. Adhesion is measured by using a Johnson, Kendall and Roberts (JKR) experiment and nanofriction is quantified by using atomic force microscopy in contact mode. JKR experiment results indicate a higher adsorption ability of elastomers containing free chains. However, the interface created has a lower resistance to separation. In contrast, elimination of free chains allows an increase of adherence, despite a lesser wetting of the substrate. Nanofriction results are also very sensitive to the presence of free chains, with a higher friction before extraction of free chains. The influence of the cross-linking density is also discussed and interfacial molecular mechanisms are proposed for explaining the evolution of both nanoscale friction and adhesion properties.

1. Introduction

Polymer adhesion and friction properties are of prime interest in many applications such as for coatings, adhesives, lubricants, biomaterials, and tyres. The mechanisms governing the friction of polymers are complex and involve surface properties (interfacial interactions) of materials, as well as mechanical and rheological properties [1–10]. They are indeed involved in energy dissipation processes occurring during friction. Dissipation may be located in the vicinity of the interface or assign a larger volume. Viscoelastic dissipation is activated by interfacial interactions which transfer the mechanical stress to the bulk materials.

Due to, among other things, their low glass transition temperature, elastomers are able to exhibit tack properties which can be defined as the resistance to the separation of the polymer in contact with a substrate under a light pressure and for a short time [11–15]. Tack ability can be quantified by different methods, like a peel test or tack experiment (measurement of separation force, at a given speed). Another possibility for quantifying the adherence between an elastomer and a rigid substrate is a Johnson, Kendall and Roberts (JKR) experiment, which consists in compressing a soft elastomer hemisphere against a flat rigid surface and in just measuring the contact area. The relationship between the contact area and the

normal applied force (JKR equation) allows the determination of the work of adhesion between the two materials [16]. The JKR approach is an extension of the Hertz elastic theory [17] to the case where adhesion forces cannot be neglected. The JKR equation is usually well adapted to soft solids like elastomers.

Two kind of experiments can be performed using the JKR test: a 'static' contact experiment during which a constant load is applied to the substrate in contact with the elastomer hemisphere and a 'dynamic' experiment with a loading/unloading step inducing a partial separation. The first case allows one to determine the adhesion energy, and also mechanical properties (modulus) of the elastomer. The second experiment induces a mechanical separation of the interface and can therefore better underline adherence level, through a possible hysteresis phenomenon.

The advantage of the JKR test is the possibility of investigating, during the static step, the chain ability of adsorption onto the substrate (closely linked to chain mobility) and also, during the dynamic step, the strength of the interface previously obtained during the static contact. The efficiency of chain adsorption can then be estimated.

The development of atomic force microscopy (AFM) to probe the mechanical response of a surface has provided a new capability for characterizing local properties of polymer such as surface stiffness, adhesion and friction. Lateral force microscopy (LFM) allows us to measure the lateral

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Table 1. PDMS characteristics: initial molecular weight M_w, sol fraction, molecular weight between cross-links M_c, and Young modulus E before and after extraction of free chains.

| PDMS	M_w (g mol^{-1})	Sol fraction (%)	M_c (g mol^{-1})	E (MPa) with free chains	E (MPa) without free chains
S1	6 000	4	7 500	1.40 (sample S1)	1.20 (sample S1′)
S2	17 200	14	18 500	0.42 (sample S2)	0.24 (sample S2′)

(or friction) force between a polymer surface and a sliding probe tip [18–20].

Elastomers, due to their softness, usually exhibit interesting tack and friction properties. There are generally cross-linked, in order to assure elastic behaviour and a sufficient cohesion. Cross-linking reaction also allows us to modulate properties, especially mechanical properties, by varying the cross-linking density, i.e. the molecular weight between chemical nodes. Polydimethylsiloxane (PDMS) elastomers offer attractive advantages: a very low glass transition temperature (−123 °C), and also the possibility of easily obtaining a cross-linked network in ambient conditions. PDMS can also be end-functionalized, which allows one to control the cross-linking density (or molecular weight between cross-links) by varying the initial molecular weight. However, cross-linking reactions are usually incomplete, leading to an imperfect network. Some chains will be chemically bonded to the networks, through both extremities. Other chains can be linked to the network only by one extremity, the other one being pendant (or dangling). And some chains (named free chains) are not chemically bonded to the network. Increasing the initial molecular weight of PDMS induces in fact two major consequences: a lower cross-linking density (lower modulus), but also a greater quantity of free chains (non-chemically linked to the network) and pendant chains (chemically linked to the network by only one extremity). Free chains can be eliminated by extraction during immersion in a good solvent. Networks were also studied after extraction of free chains in toluene.

The aim of this work is to compare nanoscale friction and adhesion properties of model elastomers. Two different PDMS (varying in their initial molecular weight, i.e. final cross-linking density) will be studied, before and after extraction of free chains. Adhesion will be quantified by using JKR experiments and nanofriction will be investigated by AFM in contact mode. The objective is to analyse the influence of cross-linking density and presence of free chains on adhesion and friction and to attempt to find a correlation between the two properties. The comparative analysis of the adhesion and friction results should help us to propose molecular interfacial mechanisms involved in adhesion and friction.

2. Materials and techniques

Two polydimethylsiloxanes, vinyl terminated, are used (provided by Gelest). The two samples vary in their initial molecular weight M_w: $M_w = 6000$ g mol^{-1} for the sample called S1 and $M_w = 17\,200$ g mol^{-1} for the sample called S2. The PDMS are cross-linked with tetrakis(dimethylsiloxy)silane using a platinum catalyst at
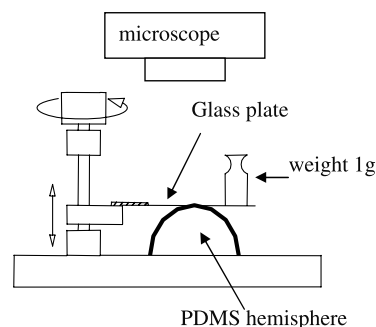
Figure 1. Scheme of the JKR experiment.

room temperature (cross − linker/PDMS stoichiometry ratio equal to 1.1). Networks have been also studied after extraction of free chains in toluene (corresponding samples are called S1′ and S2′, without free chains). Sol fraction and cross-linking degrees have been determined by using the swelling method, performed by immersion in toluene. The glass transition temperature is close to −123 °C for all PDMS samples.

The initial molecular weight M_w, sol fraction, molecular weight between cross-links M_c, and Young modulus E before and after extraction of free chains are given in table 1.

Low values of surface energy ($\gamma_s = 26$ mJ m^{-2}, determined from equilibrium contact angles) are obtained for all PDMS, with a dispersive component γ_s^D equal to 26 mJ m^{-2} with a non-dispersive (or polar) component γ_s^{ND} equal to zero. PDMS lenses are obtained by flowing the liquid reactive mixture in a hemispheric mould (diameter = 1.6 cm). The substrate is a smooth glass plate (microscopy applications), cleaned with ethanol in an ultrasonic bath and dried (roughness = 2 nm, measured by AFM).

During JKR experiments, a PDMS hemisphere is in contact with the glass plate, as shown in figure 1. The contact area is directly measured with an optical microscope equipped with a video camera. Experiments can be performed at 'zero load' (only the weight of the cover-glass, 0.1 g), and by loading the glass plate with calibrated weight (1 g).

For the zero-load experiment, the contact area radius (called $R0$) is just measured at apparent equilibrium (obtained for a time equal to 30 min).

For the loading experiment, two steps are considered. The equilibrium contact area radius (named RL) is first measured during the loading step, the weight (1 g) being applied on the glass substrate. The weight is then removed (the unloading step) and the contact area radius (called RU) is measured at equilibrium (30 min), under a 'zero load', but after a loading/unloading phase. Figure 2 illustrates the different phases of the JKR experiment.
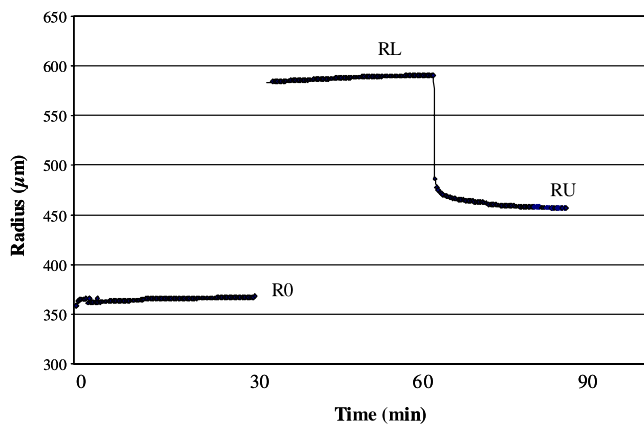
Figure 2. Evolution of the contact area radius between a PDMS hemisphere and a glass plate, during the different steps of the JKR experiment.

Nanoscale friction of PDMS films is quantified by using an atomic force microscope (AFM D3000 from Digital Instruments), in contact mode with a commercial silicon nitride tip on a 100 μm triangular cantilever (spring constant = 0.58 N m^{-1}).

All data (adhesion and friction) are collected in ambient conditions (20 °C).

3. Results and discussion

The contact area radius values will be directly discussed, without calculating the adhesion energy with the JKR equation. Indeed, for a given sample, the mechanical properties and surface energy do not vary during the experiment: contact radii can then be directly compared.

Moreover, the mechanical properties of the elastomers surfaces are able to differ from the bulk modulus measured during a tensile test. There is also the question of the relevance of the JKR equation application which remains a purely elastic (not viscoelastic) approach. For these reasons, the discussion will be focused on the values of the contact radius.

Table 2 reports initial contact area radius at zero load $R0$, contact area radius (RL) during loading (1 g), contact area radius RU after unloading, and hysteresis ($RU - R0$), for PDMS before (S1 and S2) and after extraction of free chains (S1′ and S2′).

It will be fruitful to compare the initial contact area radius ($R0$) and the final radius obtained after unloading (RU). The two radii do indeed correspond to a 'zero-load' state, and should consequently be theoretically identical. However, the RU radius is obtained after a loading step, during which a higher contact area is formed. The created interactions are able to be partly conserved after unloading, especially if these interactions are strong enough (efficient). The objective of the loading step is just to create a new interface. The unloading step will give information on the strength of this interface.

The initial contact radius values $R0$ of S1 and S2 (before extraction) will be first analysed.

Table 1 shows that $R0$ increases with the molecular weight ($R0$ for S2 > $R0$ for S1). This increase is linked on the one

Table 2. Initial contact area radius at zero load $R0$, contact area radius (named RL) under loading (1 g) step, contact radius RU after unloading, and hysteresis of PDMS, before (S1 and S2) and after extraction of free chains (S1′ and S2′).

	S1	S1′	S2	S2′
$R0$ (μm)	351 ± 17	287 ± 8	545 ± 21	477 ± 20
RL (μm)	572 ± 17	481 ± 13	869 ± 17	773 ± 18
RU (μm)	453 ± 23	425 ± 21	762 ± 24	771 ± 22
Hysteresis $RU - R0$ (μm)	102	138	217	294
% Hysteresis $(RU - R0)/R0$	30%	50%	40%	60%

hand to the lower modulus of S2 compared with S1 (even if one considers that there is no loading, the glass slide has its own mass and the deformation of the surface may depend on the applied force, especially for these soft polymers). However, the greater area of contact between the glass and S2 hemisphere is certainly induced by a better chain adsorption of PDMS onto the glass surface, due to its longer and more numerous free and pendant chains.

After extraction of free chains (S1′ and S2′), a lower initial contact area radius $R0$ is observed for both samples (compared with S1 and S2), and this despite a decrease of modulus after extraction, especially for S2′. In that case, the decrease of the contact area is directly induced by the absence of free chains. These free chains exhibit a high mobility, allowing a great adsorption onto the glass, before extraction. This result shows the importance of free chains in the adsorption and wetting ability of elastomers. The elimination of these chains results in a less significant contact (which does not mean that it is less efficient).

The values of the contact radii (RL) measured during the loading step will be now discussed.

The radii are measured under a load of 1 g. The major result is that S1′ and S2′ have a still lower radius under load compared with samples before extraction. This means that the higher mechanical deformation (due to the lower modulus after extraction) induced by the applied normal load does not compensate for the loss of adsorption capacity induced by the elimination of free chains.

The values of the contact area radius RU measured after the unloading step will now be discussed. One of the most interesting points from this loading/unloading experiment is the comparison between $R0$ and RL. Indeed, the two radii correspond to a zero-load contact and should therefore be identical. The difference between the two radii is called hysteresis. Table 2 indicates that the values of RU are always superior to the values of $R0$, this before and after extraction.

This difference is more pronounced, on the one hand for S2 (the larger molecular weight between cross-links) compared with S1, and on the other hand, after extraction (whether for S1′ or S2′).

Before extraction, the higher hysteresis (absolute value or expressed in per cent) measured for S2 compared to S1 indicates that the interface created during the loading step exhibits a higher resistance to separation (higher adherence strength) in the case of S2. The longer and numerous free
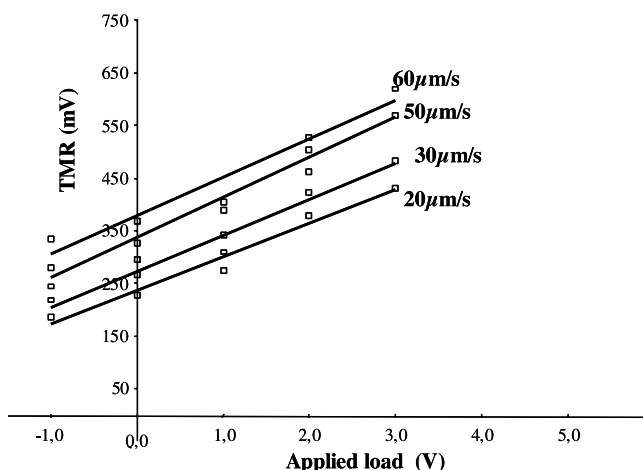
Figure 3. Evolution of nanofriction (TMR value) as a function of applied load, for different friction speeds, for PDMS S1 (before extraction).

Figure 4. Evolution of nanofriction (TMR value) as a function of applied load, for different friction speeds, for PDMS S1′ (after extraction of free chains).

Figure 5. Evolution of nanofriction (TMR value) as a function of applied load, for different friction speeds, for PDMS S2′ (after extraction of free chains).

and pendant chains will be responsible firstly for the higher adsorption (correlated with $R0$) and secondly for the greater dissipation during the partial separation (unloading step).

Extraction of free chains induces a higher hysteresis. The greater hysteresis measured for extracted networks means that the interface created during the loading step is more efficient (higher resistance to separation) when free chains are absent. Free chains are able to better adsorb onto the glass (as shown by the higher $R0$ and RL values before extraction, despite a higher modulus), but the resulting interface is less strong (lower adherence). Free chains act then like a weak boundary layer. They easily adsorb because they are mobile, but they prevent an efficient stress transfer, due to their low cohesion (they are not chemically linked to the network).

After extraction, free chains are absent but pendant chains are still present. Pendant chains have an interesting mobility (one free extremity) for adsorption (even if this ability is lesser than that of free chains), and the created interface exhibits a higher adherence, the mechanical stress being transmitted more efficiently.

The hysteresis value reflects the adherence level, i.e. the resistance to separation of the interface (even if the separation is in that case partial). The results have shown an increase of the hysteresis when the molecular weight increases. In addition, a larger hysteresis is observed after extraction, which underlines the negative effect of free chains on adherence strength. JKR experiment results also show that the surface energy value (identical for all sample) is not a sufficient parameter for predicting adsorption and wetting capacities. Surface chain mobility has to be taken into account.

Tack experiments (total separation of the interface at a controlled speed) performed on PDMS samples, before and after free chain extraction, and for different contact times, normal forces and separation speeds, have evidenced similar behaviours, i.e. an increase of adherence with the molecular weight between cross-links and after elimination of free chains [21–23].

Nanofriction measurements have been performed with AFM in contact mode, for different normal loads (deflection set
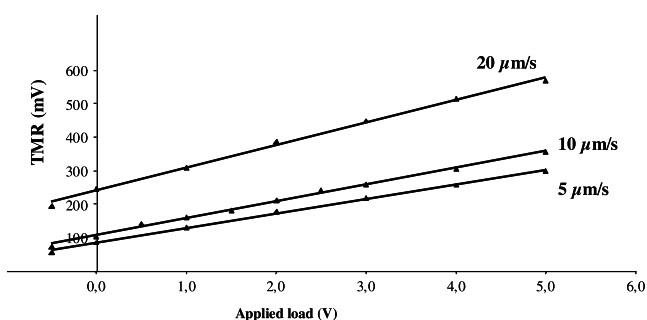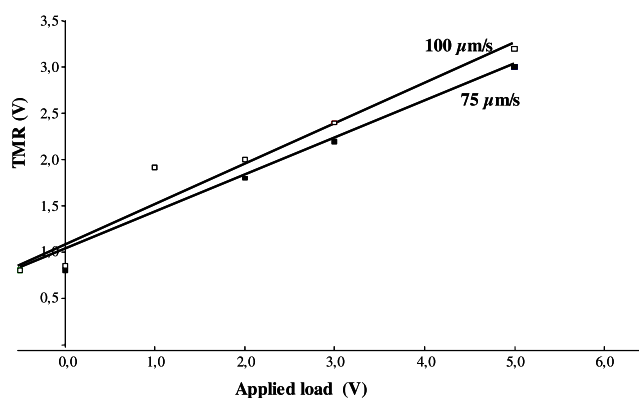
point value in volts) and friction speeds (tip velocity, obtained by varying the scan frequency).

The trace minus retrace value (TMR, in volts), which is directly proportional to the friction force, is determined. The absolute friction force could be obtained with calibration methods but such techniques are not necessary for a comparative study.

AFM experiments (tapping mode) have been performed on PDMS surfaces after nanofriction. The corresponding images do not show any surface damage or wear tracks.

Friction measurements are impossible for sample S2, the AFM tip still being 'trapped' in the surface layer. This effect is attributed to the great adsorption of numerous and long free chains onto the tip, inducing a high friction.

Table 3 reports the TMR values of samples S1, S1′ and S2′, for different applied loads.

Table 3 shows an increase of friction as a function of applied load. Further data allowed us to verify a linear evolution for all samples, indicating a constant friction coefficient (proportional to the slope), as shown on figures 3–5, which illustrate, for different speeds, the increase of friction (TMR) as a function of normal load, for PDMS S1, S1′ and S2′ respectively.

The influence of speed was previously studied [24, 25]. An increase of friction with speed was observed for all PDMS.

Table 3. Friction force (TMR values in volts, ΔTMR $= \pm 0.01$) of S1, S1$'$ and S2$'$ for different applied loads (friction speed $= 20\ \mu$m s^{-1}).

	Applied load (V)		
	0	1	2
S1	0.24	0.31	0.39
S1$'$	0.23	0.30	0.37
S2$'$	1.40	1.80	2.20

This effect was more pronounced for high normal loads, and for samples S1 and S1$'$ (lower effect for S2$'$).

Table 3 indicates close friction levels for S1 and S1$'$, even if a slightly higher friction can be systematically observed for S1. The differences between S1 and S1$'$ become greater at lower friction speeds (5 and 10 μm s^{-1}), with a significantly higher friction for S1 compared to S1$'$ [24, 25]. The adsorption of free chains (for S1) onto the tip was proposed to explain the higher level of friction measured before extraction.

Nanofriction of S2 can be considered as much greater than S2$'$, the tip being trapped (glued) to the S2 surface. Elimination of free chains then reduces nanofriction.

Elsewhere, the friction of S2$'$ is greatly higher compared to those for S1 and S1$'$. A lower modulus (higher contact area between the tip and the PDMS) and the presence of longer and numerous pendant chains (adsorption ability) could be responsible for the more significant friction.

To sum up, nanoscale friction measurements show a higher friction for S2$'$ compared to S1 and S1$'$. The friction level is also higher before extraction, especially for the higher molecular weight PDMS (S2), which contains a greater quantity of free chains.

JKR test results have underlined a higher adsorption ability of free chains, due to their greater mobility. Friction results also evidence the effect of free chains which can adsorb onto the tip and increase the friction. JKR results have shown a greater adsorption for PDMS S2$'$ compared to S1$'$, in correlation with the nanofriction which is also higher for S2$'$. A larger molecular weight between cross-links increases then both adhesion and nanofriction.

However, contact area radius hysteresis values determined after a loading/unloading cycle during JKR tests indicate that the PDMS adherence strength is lower in the presence of free chains, despite their higher adsorption, unlike friction, which is higher with free chains. At the macroscale, free chains reduce adherence, acting like a weak boundary layer, but at the nanoscale, they increase friction and also adhesion, as shown by force curve experiments performed on PDMS to quantify nanoadhesion [24, 25]. Nanofriction and nanoadhesion are very sensitive to chain mobility and adsorption. The free chain layer can also induce capillary effects, which will strongly contribute to nanoscale adhesion and friction. These capillary forces will also contribute to a higher macroscale adhesion (adsorption) as shown by the greater contact radius before and during loading measured for PDMS before extraction. Chaudhury and co-workers have investigated the relation between macroscale adhesion and friction [11, 26], and some interesting relations between interfacial interactions and

friction have been proposed in the literature [27–32]. The role of chain mobility in macroscale adhesion and friction has also been studied in the case of elastomers, but in contact with a silicon wafer covered by a grafted layer [12, 13, 33–35]. The influence of chain length [21, 36], friction speed and normal load [37, 38] on polymer friction has also been investigated in the literature, revealing a significant influence of polymer chain mobility [39]. A surface force apparatus is also often used to investigate tribology of thin films between shearing surfaces [40–43]. However, literature concerning comparative investigation of adhesion and friction of polymers, at nanoscales and macroscales, remains rare. Specific structure and properties of polymers, especially chain mobility, induce complex adhesive and tribological behaviour, which will moreover strongly depend on the contact size.

This study has shown that nanoscale friction depends greatly on the tip wetting by surface chains, the elastomer bulk contribution being minimized in such local probing.

JKR experiments have allowed us to investigate not only chain adsorption onto the substrate, but also the strength of the created interface. Even if this test is macroscopic, unlike AFM, it gives fruitful information on what can appear at the nanoscale. It can therefore provide a complementary test of AFM measurements, bridging the nanoscale and macroscale behaviours.

4. Conclusion

Experimental results have underlined the major role of molecular parameters such as cross-linking degree and presence of free chains in the adhesion and friction of model elastomers.

Nanofriction measurements evidenced that free chains allow a greater adsorption and adhesion on the AFM tip, inducing a consequently higher friction compared to PDMS without free chains. However, the presence of free chains decreases macroscopic adherence, because, even if their adsorption capacity is significant, they constitute a weak boundary layer (low cohesion), preventing the correct stress transmission to the network.

Both JKR and nanofriction tests are then sensitive to the adsorption ability due to chain mobility. Multiscale approaches appear therefore fruitful for better understanding friction behaviour.

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