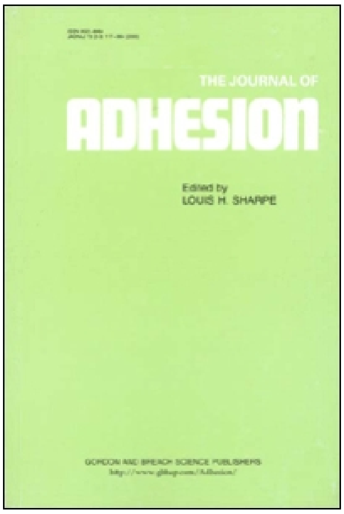

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THE ROLE OF FREE CHAINS IN ADHESION AND FRICTION OF POLY(DIMETHYLSILOXANE) (PDMS) NETWORKS

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The aim of this study is to analyse the influence of some molecular parameters (crosslinking density, presence of free chains) on both adhesion and friction properties of elastomer networks. The polymers used are polydimethylsiloxane (PDMS) networks with different initial molecular weights. Networks were studied before and after extraction of free chains in toluene. The substrate is a smooth glass plate. The experimental procedure uses both friction (pin-on-disk tribometer) and adhesion (tack test) measurements, associated with surface analysis (static and dynamic wetting). Adherence energy increases with PDMS molecular weight. Friction measurements results, however, exhibit a higher friction stress for low molecular weight PDMS. The influence of chain length is discussed and some molecular mechanisms are proposed to explain both friction and adhesion behaviors. The major role of pendant chains is underlined.

Keywords: Friction; Adhesion; Elastomer networks; PDMS; Free chain extraction; Surface properties

INTRODUCTION

Polymer materials exhibit specific properties compared with other materials such as metals. These specificities are mainly due to the molecular structure of polymers, and especially chain mobility, at small or larger scales. This mobility allows relaxation mechanisms and energy dissipation, notably by internal friction. These movements

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are time and temperature dependent. These dependences (generally linked by time-temperature equivalence) are able to affect adhesion and friction levels directly.

Adhesion and friction sciences are both characterized by their multidisciplinarity. Solving an adhesion or a friction problem actually involves several scientific domains, among others polymer chemistry and physics, surface chemistry, rheology, and fracture mechanics.

Basically, it is possible to distinguish the term "adhesion," corresponding to the interfacial interaction energy (substrate/adhesive bonds) and the term "adherence," which represents the energy required to separate the adhesive and the substrate during a mechanical test. Adhesion reflects the total energy of the substrate/adhesive interfacial bonds at a microscopic scale and depends only on the nature and density of these interactions. The adherence value is usually greater than the presumed adhesion value because during separation a part of the energy is dissipated by internal molecular motions (chain extension, disentanglement, etc.).

The correlation between the adhesion level and the measured separation energy becomes, in that case, even more difficult compared with the case of a true interfacial failure.

Others experimental parameters, unfortunately, complicate the solving of adhesion problems. Changing the type of the adherence test or the geometry of the assembly can, for example, influence the adherence value. Adhesion appears, therefore, to be a complex science, simultaneously governed by a great number of molecular and experimental parameters.

Polymer friction is also governed by interfacial interactions and dissipation phenomena located in the interfacial region but that are also able to occur in the bulk, especially in the case of soft materials. The problem with friction is more difficult because both materials are not only in static contact (that is initially the case, at the start of friction test), but also in dynamic contact, during which interactions are built and broken up simultaneously.

Friction then, includes, "adhesion," especially during the first step of friction (also called static friction) corresponding to the debonding step. The inverse link, *i.e.*, "does adhesion include friction," is less evident. However, it exists in two major cases. First, during the lifetime of an adhesive bond, if this bond is submitted to static or dynamic mechanical stress (especially shear stress), this stress is not necessarily able to induce a debonding, but the problem can be considered a friction problem (especially static friction, but also in some cases dynamic friction if the amplitude of the shear movement is low and if broken interfacial bonds are able to rebuild rapidly). The second major case wherein the inverse link is evident is during some adhesion tests, and especially peel tests, during which friction mechanisms can be induced, as shown by Chaudhury and Leger [1, 2].

Adhesion and friction, therefore, constitute two complex domains. The correlation between both properties is then consequently more complicated. However, the challenge is interesting, in order to better predict friction behavior and associated phenomena like wear or lubrication, and to have also the possibility to design smart surfaces able to present predefined properties.

Israelachvili has taken up this difficult challenge [3–9] and he has succeeded in defining some pertinent relations between adhesion and friction. His approach is interesting and original compared with others, mainly due to the fact that it is a phenomenologic approach, combining mechanical, physical, and chemical aspects of adhesion and friction. This overview allows him to propose molecular mechanisms which cannot be predicted from a purely mechanical approach. He shows clearly that friction and adhesion of organic materials and layers can be governed by subtle interfacial phenomena, closely linked to molecular structures.

Other researchers have also underlined the role of chain mobility in adhesion and friction of elastomers. Chaudhury and colleagues have extensively studied dissipation phenomena during adhesion and friction processes of silicone networks [1, 10–12]. Léger and colleagues also investigated silicone adhesion and friction, especially in the case of an elastomer in contact with a silicon wafer covered by a grafted layer, and proposed some interesting structure-properties relationships [2, 13, 14]. Creton et al. [15] and Brown [16] have experimentally studied the effect of chain length in adhesion and have evidenced the role of mobility and internal friction. However, in most cases, previous works study either friction or adhesion, and rarely both properties.

The aim of this work is to compare adhesion and friction behavior of elastomer networks (polydimethylsiloxane, PDMS), investigated at a macroscopic scale.

The crosslinking reaction is 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. And some chains do not react at all. They are called free chains and are not chemically bonded to the network.

Figure 1 presents a scheme of a crosslinked network, with the presence of crosslinked, free, and pendant chains. Free chains, which can play a major role in the adhesion process due to their greater mobility, can be extracted by immersion in a good solvent. Networks have then

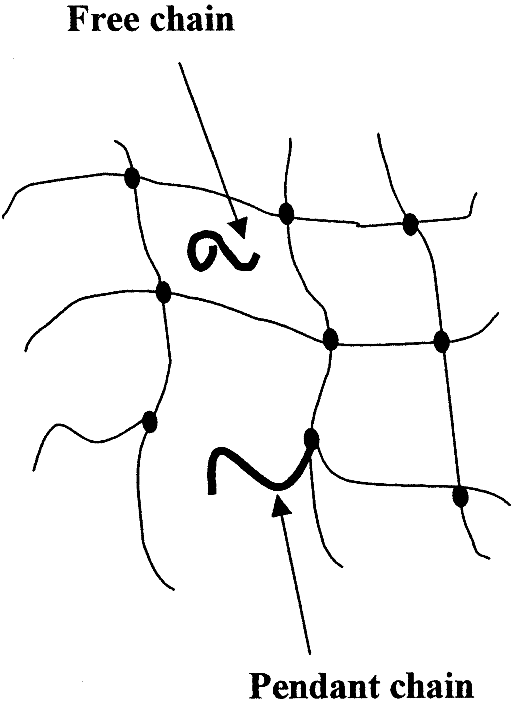

FIGURE 1 Schematic representation of a crosslinked polymer network.

been studied before and after extraction of free chains in toluene. The objective is to analyse the role of free chains both on adhesion and friction properties and to propose some molecular mechanisms able to explain the complex behaviour observed experimentally.

EXPERIMENTAL

Materials and Methods

Two vinyl-terminated polydimethylsiloxanes (PDMS) were used (provided by Gelest, Tullytown, Pennsylvania, USA). Both samples vary by their initial molecular weight Mw (or final crosslinking density): Mw = 6000 g/mol (called PDMS 6) and Mw = 17200 g/mol (called PDMS 17).

A third PDMS (Mw = 28000 g/mol, called PDMS 28) was also used for adhesion and wettability measurements (but it exhibits experimental problems during friction, due to its low stiffness). The PDMSs were crosslinked with tetrakis(dimethylsiloxy)silane, which possesses

TABLE 1 PDMS Characteristics: Initial Molecular Weight, Mw, and Polydispersity Index, Ip, Sol Fraction After Crosslinking (Extraction in Toluene), and Mean Molecular Weight Between Crosslinks, Mc (Swelling Method)

Polymer	Mw (g/mol)	Ip	Sol fraction %	Mc (g/mol)
PDMS 6	6000	1.96	4	7500
PDMS 17	17200	2.35	14	18500
PDMS 28	28000	2.82	24	28600

four functional sites, using a platinium catalyst at room temperature. The stoichiometric ratio (crosslinker/PDMS) is equal to 1.1 (excess of 10% for the crosslinker) to assure a correct reaction. Liquid PDMS mixed with the crosslinker and the catalyst is poured into several hemispheric metallic moulds. The perfectly polished moulds have a surface treatment (TiN), providing a high surface hardness. Sol fraction and crosslinking degrees were determined using the swelling method, performed by immersion in toluene (which is a good swelling solvent of PDMS) for 72 h. The solvent was regularly changed and pure solvent was added. The network was weighed before and after swelling, and also after complete drying. Drying was progressive to avoid hemisphere rupture: adding of ethanol (poor solvent) and then solvent evaporation in ambient air and in an oven at 50°C for 3 days, in order to obtain a constant weight.

Initial molecular weights and polydispersity index (determined by size exclusion chromatography), sol fractions after crosslinking and molecular weights between crosslinks are given in Table 1.

Adhesion and friction properties of the PDMS networks were studied before and after extraction of free chains in toluene. Extraction was achieved by immersion of crosslinked PDMS in toluene for several days (with frequent addition of pure solvent).

The substrate was a smooth glass plate (microscope glide), that was cleaned with ethanol in an ultrasonic bath and dried.

Adhesive behavior of PDMS hemispheres (JKR geometry [17]) was determined with a tack test (Figure 2). During the tack experiment, the polymer hemisphere (diameter = 16 mm) was put into contact (at a fixed approach speed equal to 10 mm/min) with the glass substrate for a given contact time and under a controlled normal load. Both materials were then separated at a given speed, and the separation force was measured. The apparatus determines, simultaneously, the force and the apparent contact area between the substrate and the polymer, using a video camera directly placed under the transparent glass substrate.

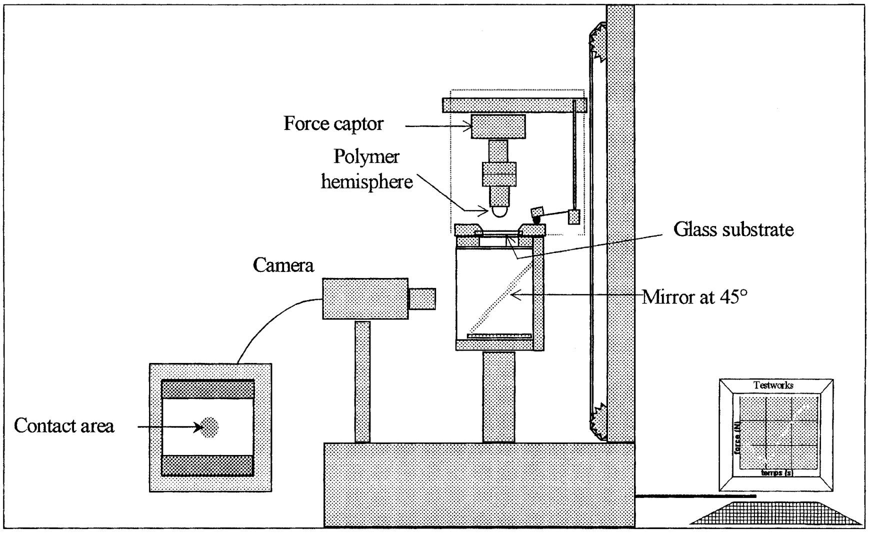

FIGURE 2 Tack apparatus.

Friction properties of PDMS hemispheres were measured using a classical pin on disk tribometer (Figure 3). The PDMS hemisphere was brought into contact with the glass plate, under a given normal load. The glass plate was then rotated at a given speed and the tangential force, which corresponds to the friction force, was measured. An original device was also developed to follow the evolution of the contact

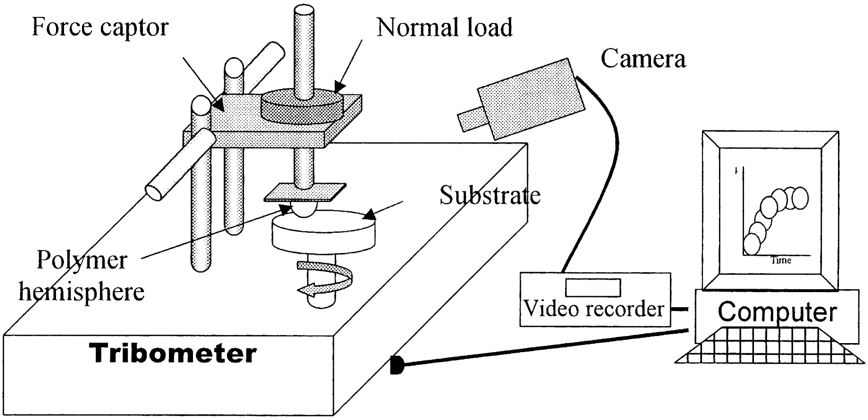

FIGURE 3 Pin-on-disk tribometer.

area, using a mirror placed under the transparent glass substrate and a video camera for recording the contact area images.

Surface energy of PDMS films was determined by wettability measurement. Equilibrium contact angle of different liquid drops (water, polar liquid and diiodomethane, nonpolar liquid) was measured with a model G2 automated Kruss contact angle apparatus (Kruss, Charlotte, NC, USA). Contact angle hysteresis (difference between receding and advancing angles) was measured with water and diodomethane using a tensiometry technique (speed equal to 10 mm/min, immersion length equal to 7 mm).

RESULTS AND DISCUSSION

It is important to note that increasing the initial molecular weight of PDMS induces two global consequences: a lower crosslinking density (higher chain length between chemical nodes) and also a greater quantity of free chains (nonlinked to the network) and pendant chains (linked to the network by only one extremity). Even if they are chemically identical, PDMSs differ by their molecular structure.

Surface Properties

Surface energy and contact angle hysteresis of PDMSs (before extraction) are presented in Table 2. Substantially identical low values of surface energy (determined from equilibrium contact angles) are observed for the three samples, with a nondispersive (or polar) component equal to zero, which shows that the ability of PDMS to exchange polar or specific interactions (hydrogen) can be considered negligible. This low surface energy is mainly due to the orientation of CH_3 groups (moreover, PDMS are initially vinyl terminated and do not contain any OH function).

TABLE 2 Surface Energy Values and Contact Angle Hysteresis (Determined with Water by Tensiometry) of PDMS

	Surface energy			Hysteresis (°) with water
	$\gamma_s{}^D$ ($\pm 1\,mJ/m^2$)	$\gamma_s{}^{ND}$ ($\pm 1\,mJ/m^2$)	γ_s ($\pm 2\,mJ/m^2$)	
PDMS 6	27	0	27	12
PDMS 17	26	0	26	17
PDMS 28	26	0	26	24

Contact angle hysteresis measurements (performed with water), however, indicate significant differences between PDMSs, with an increase of hysteresis for higher Mw PDMSs. Contact angle hysteresis can be induced by a chemical or topological heterogeneity. However, chemical composition of PDMS is identical (same functionality), and surface roughness is low and also identical for all samples (close to 10 nm, determined by atomic force microscopy; results not shown). The third origin of hysteresis is linked to energy dissipation phenomena associated with interfacial chain movements under the liquid flow. The longer and more numerous free and pendant chains of PDMS 17 and 28 can constitute greater "molecular obstacles" for liquid molecules, and their movements will require and dissipate more energy, which could explain the higher value of hysteresis.

Moreover, if longer free and pendant chains are present (for PDMS 17 and 28), the real number of water/chain interactions can be higher. The surface of PDMS 17 and 28 could then be considered, at a molecular scale, as a more "three-dimensional" layer, compared with PDMS 6, with the merging of more numerous and longer chains. For PDMS 17 and 28, the number of interactions can, consequently, vary during the wetting and dewetting processes, which will induce hysteresis. The origin is, in that case, not directly a chemical heterogeneity, but a variation in the number of water/chain interactions during the wetting/dewetting process, coupled with some relaxation phenomena.

Contact angle hysteresis has also been measured for PDMS after extraction of free chains. Higher values are obtained after extraction for both polymers. However, extraction of free chains by immersion in good solvent induces a residual surface deformation of the polymer film. This topological change is able to partially explain the higher hysteresis. Perhaps pendant chains (which are not extracted) could also dissipate more energy during wetting and dewetting processes.

Adherence Study

Tack experiments were performed in ambient air, at room temperature (20°C), and for two separation speeds (1 and 100 mm/min), two contact times (0 and 300 s), and one normal force (1 N). Adherence energy was calculated by dividing the integral of the separation force *versus* distance by the contact area corresponding to the maximum force. Table 3 presents the adherence energy values obtained for PDMS 6, 17, and 28 before extraction.

It is important to note that the failure is not purely "adhesive" or interfacial, but occurs inside the polymer, very close to the interface with the glass substrate. Atomic force microscopy images and infrared

TABLE 3 Adherence Energy Values (in J/m^2) of PDMS 6, 17, and 28 Measured for a Normal Force Equal to 1N and for Two Contact Times, t (0 and 300 s), and Separation Speeds, V (1 and 100 mm/min)

Adherence energy (J/m^2)	t = 0 s V = 1 mm/min	t = 0 s V = 100 mm/min	t = 300 s V = 1 mm/min	t = 300 s V = 100 mm/min
PDMS 6	0.38	0.46	0.51	1.04
PDMS 17	0.49	3.14	1.79	3.69
PDMS 28	3.71	10.09	7.09	16.37

spectroscopy (reflection mode) have confirmed the presence of a thin residual polymer layer (thickness = some tens of nanometers) on the glass plate after tack and friction experiments.

The analysis of tack results will be focused on the influence of structural parameters, especially free chains and degree of crosslinking. The effect of experimental parameters (speed and contact time) will be briefly discussed.

Experimental results show a great influence of degree of crosslinking on adherence. Table 3 indicates a significant increase of adherence energy when Mw is increased. To explain this behavior, it is important to understand well what is happening during a tack test.

PDMS and glass are initially in static contact, under a given load and during a given time. During this contact step, polymer chains develop and exchange physical interactions with the glass surface. The number and strength of these interactions will directly determine the interfacial or adhesion strength. PDMS 17 and 28 contain more numerous and longer free and pendant chains. The higher mobility of these chains allows better substrate wetting at a molecular scale (more numerous contact points or interactions).

After this contact step, the PDMS hemisphere and glass substrate are separated at a given speed. However, the energy measured during this separation step is not only a function of the adhesion energy (*i.e.,* interfacial interactions) but also of the dissipative properties of the PDMS. A part of the energy will indeed be dissipated during chain movements (chains extension and then pull-out and reptation, and perhaps chain breaking).

The longer chains of PDMS 17 and 28 require more energy for extension and reptation (and chains can be more constrained during separation due to the greater number of interactions). Both effects (better adsorption and greater dissipation) are able to explain the increase of adherence value for the higher Mw.

Moreover, a good correlation between tack results and contact angle hysteresis evolution can be observed: hysteresis and adherence values increase with the molecular weight. Both experiments involve interfacial chain movements. Surface energy value (identical for all PDMSs) is not, in that case, a pertinent or sufficient parameter. Contact angle hysteresis is more appropriate because it reflects both interactions and dissipation.

The effect of extraction of free chains can be discussed. Tables 4 to 6 present adherence values before and after extraction for PDMS 6, 17,

TABLE 4 Adherence Energy Values (in J/m^2) of PDMS 6 Before and After Extraction of Free Chains (Normal Force = 1N)

	t = 0 s		t = 300 s	
Adherence energy (J/m^2)	V = 1 mm/min	V = 100 mm/min	V = 1 mm/min	V = 100 mm/min
PDMS 6				
before extraction	0.38	0.46	0.51	1.04
after extraction	0.22	1.43	1.21	2.04

TABLE 5 Adherence Energy Values (in J/m^2) of PDMS 17 Before and After Extraction of Free Chains (Normal Force = 1N)

	t = 0 s		t = 300 s	
Adherence energy (J/m^2)	V = 1 mm/min	V = 100 mm/min	V = 1 mm/min	V = 100 mm/min
PDMS 17				
before extraction	0.49	3.14	1.79	3.69
after extraction	0.41	2.05	1.70	7.00

TABLE 6 Adherence Energy Values (in J/m^2) of PDMS 28 Before and After Extraction of Free Chains (Normal Force = 1N)

	t = 0 s		t = 300 s	
Adherence energy (J/m^2)	V = 1 mm/min	V = 100 mm/min	V = 1 mm/min	V = 100 mm/min
PDMS 28				
before extraction	3.71	10.09	7.09	16.37
after extraction	3.26	57.80	15.00	85.08

and 28, respectively. Results show globally an increase of adherence after extraction. This result can be initially quite surprising, because free chains are sometimes able to favour adherence, due to their greater mobility and adsorption capacities (especially when they are functionalized in order to develop stronger interactions with the substrate). In our case, elimination of free chains induces a greater adherence. This effect is more pronounced for PDMS 28, which presents (before extraction) the highest quantity of free chains. Two explanations can be proposed. Firstly, free chains are not chemically connected to the network. They can, therefore, constitute a "low cohesion layer" (or weak boundary layer), and reduce the stress transfer from the interface to the network. Secondly, pendant chains are chemically bonded to the network and therefore cannot be eliminated. However, they possess a greater mobility (one free end) compared with perfectly crosslinked chains. Adsorption of pendant chains will be then important, and stress transmission to the network will be efficient. Moreover, extension and movements of pendant chains during separation will be more difficult compared with free chains (more dissipative), and total reptation is impossible. Both effects are, consequently, able to explain the adherence increase after extraction.

But we must also note that extraction of free chains induces a stiffness decrease. A lower modulus is measured after extraction, especially for PDMS 6 (from 1.4 MPa before extraction to 1.2 MPa after), for which the swelling effect of free chains is greater, due to the lower distance between nodes (more internal tensions induced by swelling). This change of mechanical properties is also able to influence adherence behaviour. However, the modulus difference before and after extraction is quite similar for PDMS 17 and 28, but the adherence increase after extraction is much greater for PDMS 28. Effect of modulus seems, therefore, to be minor.

PDMS 28 exhibits the greatest adherence increase after extraction. Two reasons can be advanced. Firstly, the sol fraction is higher (greater structural change for this PDMS before and after extraction) and, secondly, pendant chains are more numerous and longer, which will be very favourable for adherence (better adsorption and more dissipative chain extension).

A longer contact time leads to higher adherence. An increase of contact time allows the development of a more intimate molecular contact due to the relative viscous flow of the polymer near the surface [18], as a "molecular creep" associated with chain motions and rearrangements at the interface (macroscopic creep is negligible, due to the crosslinked nature of PDMS).

Separation speed has a significant influence, with an increase of adherence with speed. This time or speed dependence is a direct consequence of dissipation phenomena, due to the viscoelastic nature of polymers [19, 20].

Bulk mechanical properties of PDMS are not significantly dependent on the tensile rate (very low glass temperature, −123°C). However, the separation process during the tack test induces irreversible chain movements of great amplitude; such as chain reptation and pull-out. These large scale movements, which, in an adhesion problem, preferentially affect adsorbed chains (especially free and pendant), are rate sensitive. The separation energy is then greater for higher speed because the viscous resistance to chain slippage becomes more important (greater frictional resistance to motion). Moreover, PDMS 28 is more sensitive to speed, mainly because extension and reptation of longer chains are more difficult.

Also, it can be noted that the greater influence of free chain extraction is obtained for the higher contact time and speed. This proves that pendant chains require time to develop better adsorption and probably also that their movements and breaking are more dissipative (more speed dependent).

Tack experiments indicate an increase of adherence energy with the molecular weight. The following role of chain length is proposed: more numerous and longer free chains, present for the higher molecular weight, favour the substrate wetting, and their extension dissipates more energy during separation. Free chain extraction induces an adherence increase, particularly for the higher Mw. These results underline the major role in adhesion of pendant chains, which present both advantages of greater mobility and an efficient stress transmission.

Friction Properties

Friction of PDMS hemispheres in contact with glass substrate was studied with a pin-on-disk tribometer which simultaneously determines the friction force and the contact area. Typical curves are presented in Figure 4. Two steps can be identified: A first step (zone 1) corresponding to the PDMS/glass separation (“static” friction) and a second one (zone 2) corresponding to a dynamic sliding regime. During the first step, the contact area, initially circular, is simultaneously decreased and deformed, and is then still constant during the sliding step. Friction stress is determined by dividing the friction force by the corresponding contact area. This allows one to compare polymers of different stiffness. This first step of the friction process (zone 1) is particularly analyzed, because it is *a priori* more directly linked to

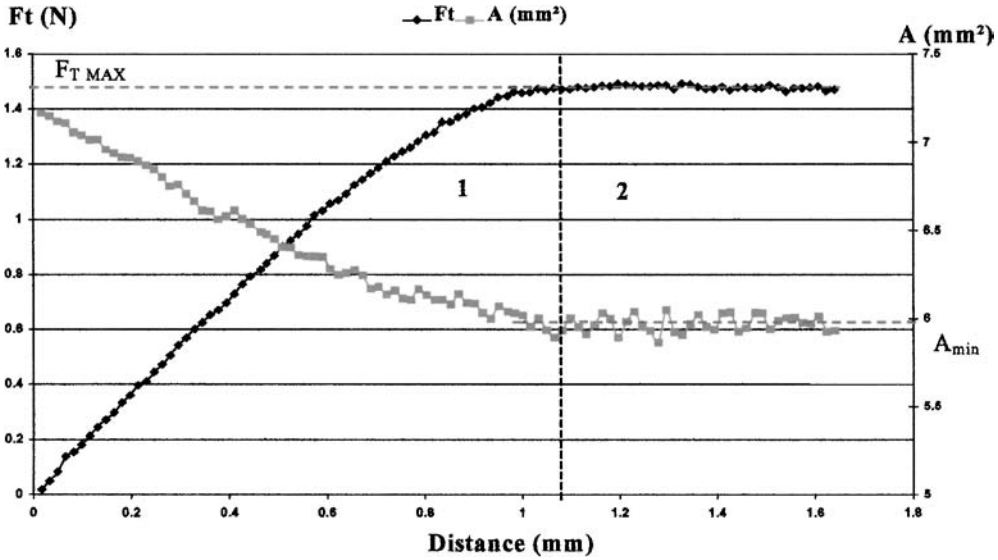

FIGURE 4 Evolution of friction force, F, and contact area, A, as a function of sliding distance during a friction test.

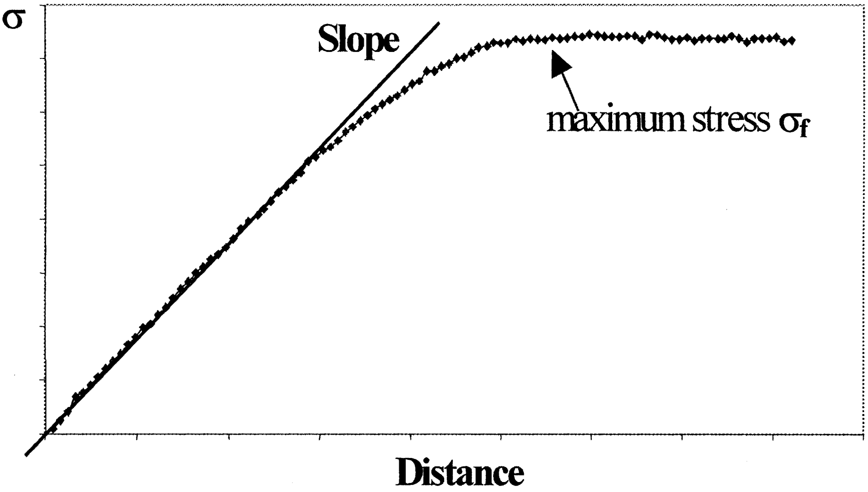

FIGURE 5 Friction stress, σ, *versus* sliding distance: determination of maximum friction stress, σ_f, and slope.

adhesion properties. Figure 5 presents the shape of the friction stress *versus* distance curve. Maximum friction stress, σ_f, corresponding to the polymer friction resistance, is determined. The initial slope of the curve is also calculated. Friction tests have been performed for PDMS 6 and 17, before and after extraction of free chains, under a normal force equal to 1 N and for various speeds. The initial contact time is equal to zero.

Table 7 presents the friction stress values obtained for both polymers before and after extraction. We can first discuss the influence of molecular weight or degree of crosslinking before extraction.

TABLE 7 Friction Stress Values σ_f (in N/mm^2) for PDMS 6 and 17 Before and After Extraction of Free Chains, Measured at Different Friction Speeds, V

Friction stress σ_f (N/mm^2)	V = 0.41 mm/s	V = 0.82 mm/s	V = 2.09 mm/s	V = 4.73 mm/s
PDMS 6				
before extraction	0.220	0.215	0.185	0.175
after extraction	0.220	0.220	0.210	0.210
PDMS 17				
before extraction	0.074	0.073	0.065	0.065
after extraction	0.074	0.074	0.072	0.072

Table 7 indicates a higher friction stress for PDMS 6 (σ_f close to $0.2\,\mathrm{N/mm^2}$) compared with PDMS 17 (σ_f close to $0.07\,\mathrm{N/mm^2}$). Friction resistance of PDMS 6 is then significantly higher, despite a lower adherence as indicated by tack results.

This unexpected difference between tack and friction results can be partially explained by the role of elastic contact, continuously present during the friction test (and absent during the separation step of tack). This elastic contact (induced by the normal load) acts for PDMS 6 (which exhibits low adhesive capacities) like a forced wetting, allowing good stress transmission (directly to the network). This effect of elastic contact is able to balance the lower adhesive contact of PDMS 6. For PDMS 17, both adhesive and elastic contact are present during friction. However, free chains do not allow a correct stress transmission to the crosslinked network, and are able to constitute a "sliding" layer, with a lower shear resistance. Pendant chains, more numerous and longer for PDMS 17, can also favor the sliding.

What is the effect of free chain extraction now? Table 7 indicates a minor effect with substantially identical values before and after extraction for low friction speeds and a slight increase of friction resistance after extraction for higher speeds. These results are surprising, taking into account the significant effect of extraction on adherence values of both polymers.

Elimination of free chains allows a greater adherence, especially for PDMS 17. Absence of free chains does not, however, induce a significant friction increase. We can then suppose that more numerous and longer pendant chains of PDMS 17 exhibit a sliding behavior, doubtless due to chain alignment along the friction direction. PDMS 6 possess a lower quantity of pendant chains (and they are shorter). The crosslinked network can then be more directly in contact with the glass substrate. Long pendant chains of PDMS 17 act as a "barrier layer," preventing direct contact between crosslinked network and glass substrate. And they can be oriented under shear, decreasing the friction resistance.

Influence of Friction Speed

We can analyse the influence of friction speed on both maximum friction stress, σ_f, and the slope of the friction stress *versus* distance curve.

Friction speed has a slight effect on the maximum friction stress. However, before extraction of free chains, a global decrease of σ_f is observed when the friction speed is increased, and that for both polymers. This effect could be compared with a pseudoplastic behavior of the interfacial layer. This low influence of speed is surprising compared with tack results for which a great rate dependence was observed, with an increase of adherence energy with separation speed. A viscous pseudoplastic behavior of the confined interfacial layer could, therefore, be advanced: free and pendant chains can be more oriented and "disentangled" under a higher speed, inducing a lower friction resistance. A microsliding phenomena, favored by the presence of free chains, could also lead to a slight decrease of σ_f. After extraction of free chains, speed dependence is negligible.

The influence of friction speed on the slope of the friction stress *versus* distance curve slope has also been analysed. Figure 6 indicates a negligible effect for PDMS 17, both before and after extraction, with a quite constant slope. However, a significant speed dependence of the slope can be observed for PDMS 6 before extraction. This behavior is surprising, because this slope (in the case of a nonlubricated system) is generally linked to the material stiffness. Two behaviors can be envisaged for PDMS 17: the absence of a speed-dependence of the slope, due to the fact that mechanical properties are not rate sensitive in that speed range, or an increase of the slope with speed, indicating

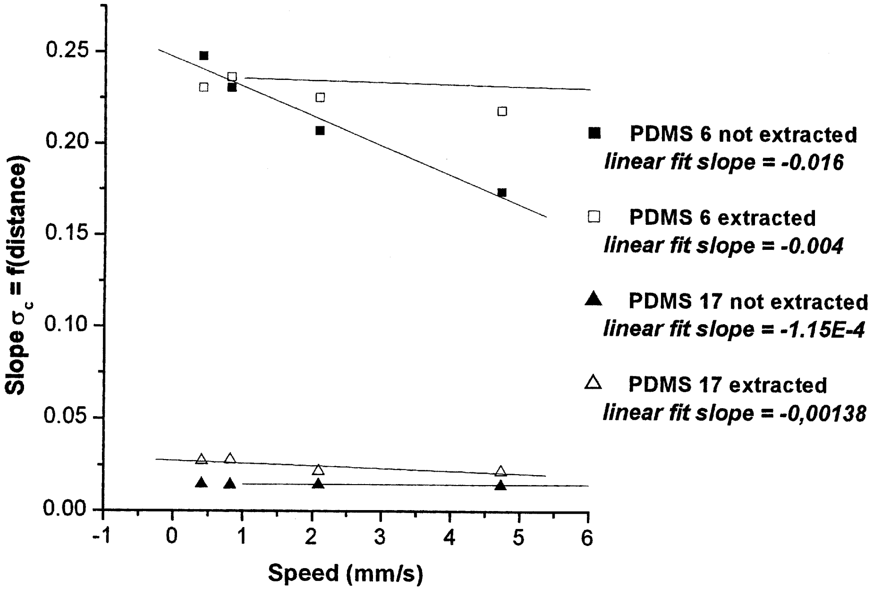

FIGURE 6 Evolution of the slope of the friction stress *versus* distance curve (see Figure 5) as a function of friction speed for PDMS 6 and 17 before and after extraction of free chains.

that chain movements are more difficult (as was observed in tack). But a decrease of the slope is unexpected. Some microsliding mechanisms, activated by a great friction resistance, are probably responsible for this behavior. Short free chains of PDMS 6, present before extraction, are able, under the high shear stress, to partially and locally slide inside the contact area. These microslidings cannot be detected with the video camera, which only measures an apparent contact area. After extraction of free chains, PDMS 6 presents a lower speed dependence, showing that free chains are mainly responsible for these probable microslidings.

Friction behaviors can be surprising when compared with adherence results. A higher friction stress is indeed measured for the lower molecular weight PDMS, which shows poor adhesive properties. Explanations based both on the elastic contact contribution (continuously present during friction) and on interfacial sliding properties of free and pendant chains can be proposed. For PDMS 6, a direct contact between the crosslinked network will generate an efficient stress transfer. For PDMS 17, numerous and long pendant chains avoid a direct contact between network and substrate and favor sliding (alignment). Figure 7 illustrates schematically PDMS surfaces before and

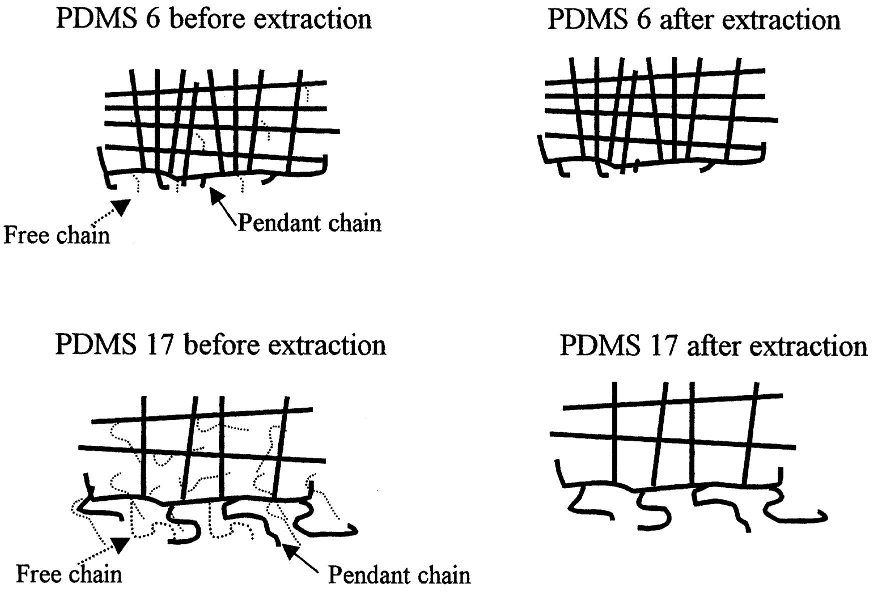

FIGURE 7 Schematic representation of PDMS 6 and 17 surfaces before and after extraction of free chains.

after extraction. Extraction of free chains has a slight effect on friction compared with adherence, for which a great influence was observed. For PDMS 17, which possesses more numerous free chains, this low effect can be explained by a quite similar sliding behavior of free and pendant chains: both can be oriented and aligned during friction, under shear.

CONCLUSIONS

This work has shown that complex molecular mechanisms are able to govern adhesion and friction. Some fine and subtle structural parameters, such as chain length or number of free and pendant chains, can greatly affect what is happening inside the polymer/substrate contact. A relationship between adhesion and friction is not, in that case, evident. Long and numerous pendant chains induce a greater adherence when they are submitted to a tensile stress, but a low friction resistance when they are submitted to a shear stress. Moreover, the contribution of elastic contact in friction, which can compensate a low adhesive contact, has also been evidenced. However, the problem seems to be more complex. Size effects must also be taken into account. Future work will be focused on the nanoscale study of adhesion and friction. Recent results (unpublished) obtained on the same PDMSs by atomic force microscopy show that, at a smaller scale (less bulk or volume contribution), behaviors are completely different, with a coherent relation between adhesion and friction, which are both higher for PDMS 17.

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