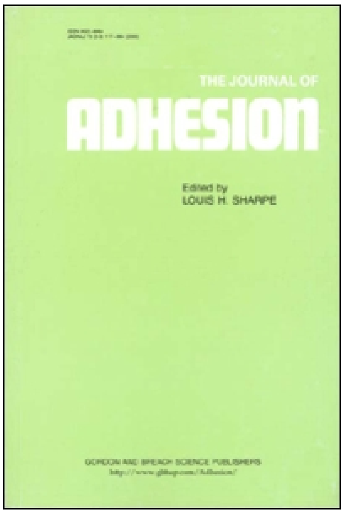

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Triblock Copolymer Lubricant Films under Shear: Effect of Molecular Cross-Linking

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Triblock Copolymer Lubricant Films under Shear: Effect of Molecular Cross-Linking

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The normal interaction and the behavior under shear of mica surfaces covered by a triblock copolymer of poly(L-lysine)-b-polydimethysiloxane-b-poly(L-lysine) (Plys$_{40}$-b-PDMS$_{40}$-b-Plys$_{40}$) before and after cross-linking reaction with two dicarboxylic acids were studied, combining the capabilities of the surface forces apparatus and atomic force microscopy (AFM). At low pH values, this copolymer spontaneously adsorbed on the negatively charged mica surfaces from aqueous solutions as a consequence of the positive charge of the polylysine moieties, forming an extremely smooth boundary layer.

This smooth layer displays a very small resistance to shear under small loads, exhibiting outstanding lubrication properties. Nevertheless, the fusion of two contacting layers can be induced by compression at a certain pressure, a process that causes a marked increase in the friction forces. Cross-linking of the adsorbed polymer molecules by covalent bond formation with dicarboxylic acids increases the mechanical stability of the adsorbed layers and hinders the fusion of the boundary layers under pressure but impairs its lubrication properties to a certain extent.

Keywords: Friction; Lubrication; Nanotribology; Surface forces apparatus; Wear

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1. INTRODUCTION

Significant advances in the description of surfaces in contact under shear have been achieved in the past three decades as a result of the emergence of new techniques, both experimental and theoretical. The behavior of a single asperity contact under shear has been extensively investigated using experimental tools as the surface forces apparatus (SFA) nanotribometer and atomic force microscopy (AFM) as well as different tools of computational modeling. Systems with very different mechanical and chemical properties have been investigated. Adhesive and nonadhesive surfaces have been studied.

The understanding of the features governing the performance of rubbing surfaces should lead to strategies of surface modification that ultimately would allow the control of this performance, *e.g.*, allowing the reduction of frictional losses. In this direction, several research groups have shown in the past how exceptional lubrication properties can be achieved by coating smooth surfaces with charged surfactant and/or polymer layers [1–3]. Friction coefficients at least 10 times smaller than the friction coefficient of ice have been reported. Nevertheless, it has also often observed that the adsorbed layers are often modified by the combined effect of shear and compression [1,2]. Under stress, the cohesion of the layer is reduced, eventually leading to wear, which is a detriment to their potential use as boundary lubricant layers. Increasing the strength and the resistance of the adsorbed layer should improve its performance in a particular application.

Recently, we reported that triblock copolymers of poly(L-lysine)-polydimethysiloxane-poly(L-lysine) adsorb on smooth mica surfaces, forming layers whose morphology is determined by the molecular structure of the copolymer [4]. In particular, by choosing the proper molecular architecture, extremely smooth adsorbed layers with exceptional lubrication abilities can be obtained. In this article, we explore the possibility of improving the cohesion of the adsorbed layer by covalently bridging the adsorbed copolymer molecules. Previous studies with this type of copolymer have shown that molecular cross-linking can be achieved in bulk solution by introducing covalently bonded bridges between the amine groups along the soluble peptide block, using a cross-linking agent that contains aldehyde functions [5]. This approach could expand the range of stability of the boundary layer. In this article, we show that it is possible to use an analogous strategy to preserve the structure of the adsorbed polypeptide-based layers and to improve their resistance to normal and shear stress.

2. EXPERIMENTAL SECTION

2.1. Materials

We investigated self-assembled layers of the triblock copolymer poly-(L-lysine)-*b*-polydimethysiloxane-*b*-poly(L-lysine) ($Plys_{40}$-*b*-$PDMS_{40}$-*b*-$Plys_{40}$) (TB40). In aqueous solution, the Plys moieties of this copolymer are sensitive to pH. They become positively charged at neutral or acidic pH values. On the opposite side, at basic pH values they tend to lose their electrical charge, typically becoming neutral at pH values greater than 9. Depending upon the length of the polylysine chain, this change may trigger a coil-to-rod transition [6]. Indeed, it is well known that polypeptides may adopt an α-helix conformation in the uncharged state, driven by intramolecular hydrogen bonds, and a coil-like conformation when they are charged, behaving as a polyelectrolyte. This behavior has also been observed when the Plys chains are attached to another segment, forming block copolymer micelles [7].

In acidic conditions, spontaneous adsorption of the copolymers onto negatively charged surfaces may occur, driven by electrostatic interaction. As has been observed in the past for many surface active species, different supramolecular structures can be formed on the surfaces [8]. The morphology of the adsorbed layers depends on the molecular structure of the adsorbate and on the size of the hydrophobic and hydrophilic moieties [9].

2.1.1. Synthesis of Triblock Copolymers Plys-b-PDMS-b-Plys

The preparation of the block copolymer used in this study is based on the procedure previously reported by Kumaki and coworkers [10]. Briefly, a thoroughly dried Schlenk flask was charged with of N^{ε}-trifluoroacetyl-L-lysine NCA (Sigma-Aldrich, Lyon, France, 99.7%) dissolved in a mixture of DMF (Sigma-Aldrich, France, 99.8%)/THF (Sigma-Aldrich, France, 99.9%) 20:80. Then, a commercially available α,ω-diamino end-functionalized polydimethylsiloxane (Sigma-Aldrich, France, PD:1.4) previously dissolved in the same solvent mixture was added to the solution. Several cycles of vacuum/N_2 were performed to purge the Schlenk flask and to avoid the presence of humidity in the reaction media. After 5 days at room temperature, the reaction product was precipitated in water and extensively washed with diethyl ether (Sigma-Aldrich, France, 99.7%) to eventually eliminate residues of decomposed monomer and unreacted macro initiator.

2.1.2. Deprotection of the Trifluoroacetyl Protective Groups

To remove the trifluoroacetyl (TFA) protective groups, the polymer was dissolved in the minimum amount of THF required. Then, 1.5 equivalents (related to the number of TFA groups to be deprotected) of KOH (Sigma-Aldrich, Lyon, France, $>85\%$ pellets) were added to the solution and allowed to react for 3 days. During the reaction, the unprotected copolymer precipitated and was then purified by centrifugation.

2.1.3. Cross-Linking Reaction of Adsorbed Copolymer Layers

To strengthen the adsorbed copolymer layer, a cross-linking reaction between the TB40 molecules adsorbed on the mica surfaces was performed, inspired by a previously described procedure [5]. Two different dicarboxylic acids of different molecular weight were used here as possible cross-linking agents: malonic ($HOOC\text{-}CH_2\text{-}COOH$; Prolabo, Paris, France, 99%) and pimelic acid ($HOOC\text{-}(CH_2)_7\text{-}COOH$; Sigma-Aldrich, Lyon France, 99.5%). After adsorption of the TB40 layer and removal of the excess (nonadsorbed) copolymer by rinsing with water at pH 4, the adsorbed layer was allowed to react for 12 h with a 1-mg/ml solution of the dicarboxylic acid and the carboxylic activating agent 1-(3-dimethylaminopropyl-3-ethyl-carbodiimide methiodide) (Sigma-Aldrich, Lyon, France). The excess of diacid and activator were then rinsed with water at pH 4. The cross-linking reaction was performed in situ in the SFA chamber or in the liquid cell of the AFM, in such a way that the modified mica surfaces were *never dried* during a particular experiment.

2.2. Methods

2.2.1. Atomic Force Microscopy (AFM)

The structure of the adsorbed layers at the mica/water interface was examined using a Digital Instruments NanoScope IIIa Multimode atomic force microscope in soft-contact and tapping modes. In the soft-contact mode, the electrostatic interaction between the tip and the substrate allows imaging using electrical double-layer forces, minimizing the scanning-induced deformation of the substrate. Standard cantilevers were used with sharpened Si_3N_4 tips (Digital Instruments, Santa Barbara, CA). These were irradiated with ultraviolet light for 20 min prior to use. The solution was held in a fluid cell and sealed by a silicone O-ring. Both were previously rinsed with ethanol and then dried using filtered nitrogen gas. The solid substrate used in all experiments was muscovite mica (METAFIX, Montdidier, France), which was cleaved using adhesive tape immediately before use. The polymer layer adsorption, subsequent rinsing, and cross-linking reaction were performed inside the fluid cell; the modified surfaces were never exposed to air after the initial adsorption. Experiments were performed in Millipore water with a conductivity of 18 $M\Omega cm^{-1}$. The pH of the aqueous phase was adjusted by adding small amounts of NaOH (Prolabo, France) or nitric acid (Sigma-Aldrich, Lyon, France) as necessary.

2.2.2. Surface Forces Apparatus (SFA)

An SFA modified for nanotribological studies was used to measure the interaction between polymer-coated mica surfaces. This technique has been extensively described in the past [11]. With the SFA, it is possible to study a single asperity contact between the surfaces, owing to the molecular smoothness of cleaved mica surfaces and the crossed-cylinder configuration used. The separation between the surfaces can be controlled with an accuracy of a fraction of a nanometer by using a piezoelectric nanopositioner, and the geometry of the contact region can be determined with great accuracy by using multiple beam interferometry (MBI) [12].

We are able to induce a lateral relative motion between the surfaces by using piezoelectric bimorphs [13]. Shearing cycles are carried out by moving one surface at constant velocity V over a certain distance, after which the driving direction is reversed. The other surface is attached to a vertical double-cantilever spring whose deflection is monitored using strain gauges (SurForce Inc, Santa Barbara, CA, USA) [14]. The friction force F_f induced by the relative displacement between the surfaces in contact can then be calculated from the experimentally measured spring force F_s obtained from the deflection of this double-cantilever spring, with an accuracy of $\pm 5\,\mu N$.

3. RESULTS

3.1. Adsorbed Copolymer Layers

3.1.1. Adsorption: AFM Images of the Adsorbed Layer

Figure 1 shows height and phase AFM images and a typical height profile of self-assembled layers of the copolymer investigated, measured in tapping mode after the mica surfaces were in contact with the copolymer solution at pH 3 for a few hours and then rinsed with water at pH 4.5. No change on the adsorbed structure was observed after longer periods of adsorption, from a few hours to 2 days. We also observed that the layers were irreversibly adsorbed: no substantial modification of the density of

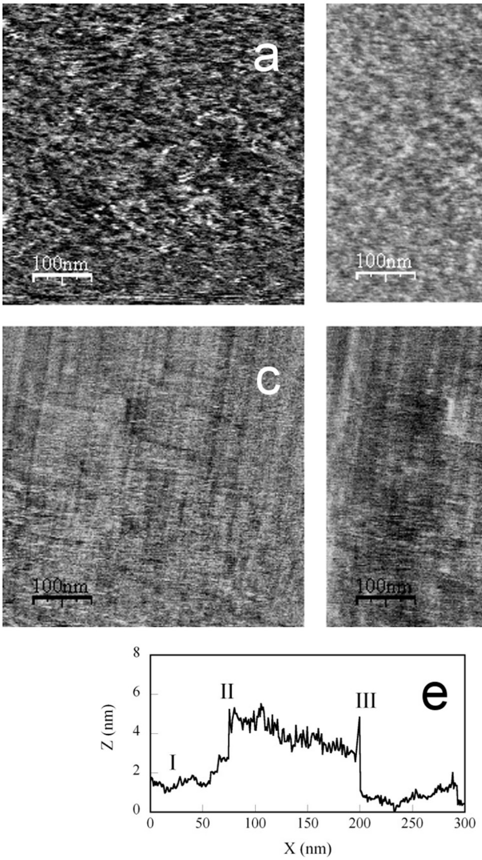

FIGURE 1 Tapping mode AFM height (left column, height scale 1 nm) and phase (right column, phase scale 15°) images of TB40 adsorbed layers on mica from a solution at pH 3, after rinsing with an aqueous solution at pH 4.5. Micrographs (a) and (b) were measured at a larger amplitude setpoint than (c) and (d). Varying the amplitude setpoint during scanning may induce the transition between the two states. The height profile (e) was measured after the transition between the two observed structures was induced by this procedure, slightly increasing the setpoint between I and II (while a texture similar to (c) was observed) and then decreasing it between II and III (while a texture similar to (a) was observed).

the adsorbed layers was detected after rinsing several times with aqueous solutions at pH values between 2 and 11.

TB40 adsorbs in the form of an extremely smooth molecular layer, although the observed morphology seems to depend on the amplitude setpoint required while imaging. If the interaction between the tip and the sample is reduced by adjusting the amplitude of vibration (setpoint), the film appears isotropic and homogeneous, with a typical RMS roughness of 0.2 nm (*c.f.* Fig. 1a, b). In this case, we are probably scanning on top of the water-soluble polylysine moieties exposed to the aqueous phase. In contrast, after increasing the interaction force between the tip and the substrate by slightly decreasing the amplitude setpoint, a smoother layer can be identified, with a typical RMS roughness of 0.1 nm (*c.f.* Fig. 1c, d). In this case, the tip is probably touching the inner part of the adsorbed layer for a fraction of the tapping cycle while scanning. As can be observed in Fig. 1e, there is a difference of height of around 2 nm between both (stable) conditions of imaging. During the measurement of this height profile, the required amplitude of vibration (setpoint) was progressively modified to trigger the change between the two conditions of imaging.

3.1.2. Surface Forces Apparatus: Normal Interaction Forces

Interaction force curves between mica surfaces coated with layers of TB40 were measured with the SFA. In these experiments, the interaction force between identical macroscopic mica surfaces is measured and normalized by their local radii of curvature. The position $D = 0$ was determined with the mica surfaces in contact immersed in distilled water before the adsorption of the copolymer layer.

The interaction force profiles between mica surfaces immersed in a 1-mg/ml solution of TB40 at pH 3 for 16 h and then rinsed with water at pH 3 is presented in Fig. 2. Several distinctive features can be identified: first, a long-range exponential repulsion typical of the interaction between charged surfaces is observed. Second, an adhesive interaction is observed even though the polylysine moieties are electrically charged at this pH value. This adhesive interaction appears only after a strong repulsive barrier between the surfaces is overcome and a discontinuity in the force profile (jump-in) is observed. If the surfaces are separated before the jump-in, the measured force profile is completely reversible and no adhesive interaction is detected. In contrast, after the jump-in is observed, a tensile pull-off force is necessary to separate the adhering surfaces. The energy of adhesion between the surfaces, γ, can be determined from the pull-off force [9]. We determined a value of γ of the order of 15 mN/m, which was not affected either by time under compression or by the normal force applied before separating the surfaces. The observed force profile is similar to the one measured with bilayer forming surfactants [1,15].

The force profile, $F(D)$, measured between two cross-cylinders of radii R, can be related to the interaction energy per unit area of two flat surfaces, $W(D)$, using the Derjaguin approximation [9],

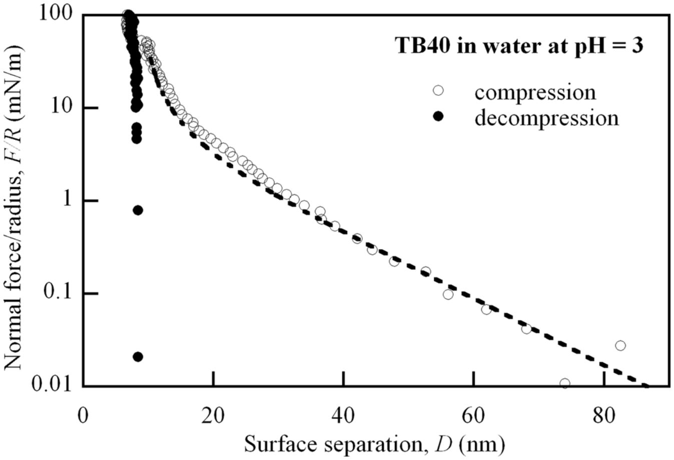

FIGURE 2 SFA normal force profile between self-assembled TB40 layers after rinsing with water at low pH. TB40 concentration in original solution is 1 mg/ml; pH 3. Adsorption time is 12 h. The broken curve represents a theoretically calculated DLVO fit of the measured data, assuming constant charge boundary conditions ($\sigma = 0.13\,\mathrm{C/m^2}$) and a Debye length of 11.6 nm, as described in the text.

$F(D) = 2\pi R\ W(D)$. In the present study, the energy of interaction at separations larger than 30 nm can be described using the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory, which combines the electrostatic repulsion and the van der Walls attraction between the surfaces [9]. A satisfactory fit of the data to the DLVO model could be obtained assuming boundary conditions of constant surface charge, as illustrated in Fig. 2. The fit was performed considering that the plane of charge is located at the position of the repulsive hard wall force *before the jump-in*. The best adjustment to the measured data was obtained considering a surface charge density for the polymer-coated surfaces of $0.13\,\mathrm{C/m^2}$ (corresponding to 0.8 elementary charges per square nanometer) and a decay length of the electrostatic repulsive force (Debye length, κ^{-1}) of 11.6 nm, which would be expected for an ionic strength corresponding to a pH of 3.15.

3.1.3. Surface Forces Apparatus: Behavior under Shear

In general, at low pH values we detect an exceedingly small frictional resistance between the coated mica surfaces as long as the boundary layer remains unharmed (before the adhesive jump-in) and the pH remains acid, independent of the presence of the copolymer in the solution. We have observed a similar response in the past in the

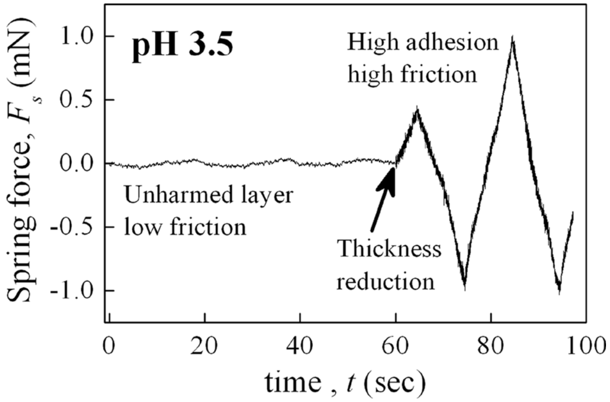

FIGURE 3 Friction signal recorded at the moment of the shear-induced fusion of adsorbed TB40 layers. Before the fusion, the friction force is below the detection limit of our setup. After the reduction of the film thickness from 7.5 nm to 5 nm of the adsorbed layers, there is a dramatic increase in adhesion energy and friction force. $L = 1.86\,\text{mN}$, $V = 0.15\,\mu\text{m/s}$.

study of several bilayer-forming cationic surfactants [1,2]. In contrast, after increasing the pH of the solution surrounding the modified surfaces more than 10, the cohesion of the adsorbed layer was drastically reduced. It was not possible to shear the adsorbed layers in any extension without causing their irreversible damage.

Analogous to the case of the surfactant bilayers, the excellent lubrication properties observed at acid pH are lost when the adsorbed polymer layers are disrupted—after the repulsive barrier is overcome—and the adhesive interaction emerges. A typical friction trace measured during the process of layer disruption is presented in Fig. 3. As can be observed in the figure, after the shear-induced reduction of film thickness takes place, the resistance to sliding increases tremendously. The reciprocating motion at constant speed of the lower surface causes a triangular response of the measured force: the surfaces remain stuck together. No sliding is observed because the maximum tangential force achievable with our experimental setup is not large enough to surmount the static friction force, certainly due to the adhesive interaction.

3.2. Modification of the Adsorbed TB40 Layer: Chemical Reaction with Dicarboxylic Acids

The chemical reaction of the adsorbed copolymer layer with dicarboxylic acids substantially modifies the properties of the adsorbed layer. As is described next, these changes depend strongly on the type of dicarboxylic acid used. Although the reaction with the shorter chain (malonic acid) reduces the cohesion of the adsorbed layer and its ability to sustain load and shear, the reaction with the longer pimelic acid seems to have the opposite effect to certain extent.

3.2.1. AFM Images of the Modified Layers

Figure 4 shows the morphology of the adsorbed TB40 layers before (Fig. 4a) and after (Fig. 4b, c) reaction with the dicarboxylic acids, as determined by AFM in soft-contact mode. The changes induced by the chemical reaction are different for each dicarboxylic acid tested. The reaction with malonic acid reduces the cohesion of the adsorbed layer, as evidenced by the frequent appearance of scanning-induced scratches during the AFM experiment even at the lightest interaction force between the tip and the adsorbed layer. This was never observed before the chemical reaction. The scanning-induced wear is probably related to a diminished electric charge density of the adsorbed layer, which reduces both the attractive interaction between the polymer molecules and the negatively charged mica surfaces, and the repulsive interaction between the AFM tip and the adsorbed polymer layer. On the contrary, the reaction with the longer pimelic acid seems to increase the roughness and the cohesion of the adsorbed layer. After the chemical reaction, the typical RMS roughness of the layer increased from 0.2 nm to 0.5 nm measured in images of 500 × 500 nm. In this case, no scanning-induced damage of the adsorbed layers was identified. These values can be compared with the typical roughness of 0.05 nm measured on molecularly smooth mica surfaces. The strengthening of the adsorbed layer after the reaction with this acid is also substantiated by the SFA results described next.

3.2.2. Surface Forces Apparatus: Normal Interaction Forces

The interaction forces between mica surfaces coated with TB40 layers after reaction with the dicarboxylic acids are presented in Figure 5. Here again the effect of the reaction with each of the diacids investigated is markedly different. Altough the interaction between the surfaces after the chemical reaction with the shorter diacid became much less repulsive, the opposite effect was observed for the case of the longer acid. The reaction with the shorter malonic acid made it possible to completely expel the adsorbed layer and to achieve intimate mica–mica contact by compression only. In contrast, the interaction force between the coated surfaces after reaction with the pimelic acid was almost reversible and purely repulsive. The long-range electrostatic repulsive interaction appears nearly unmodified

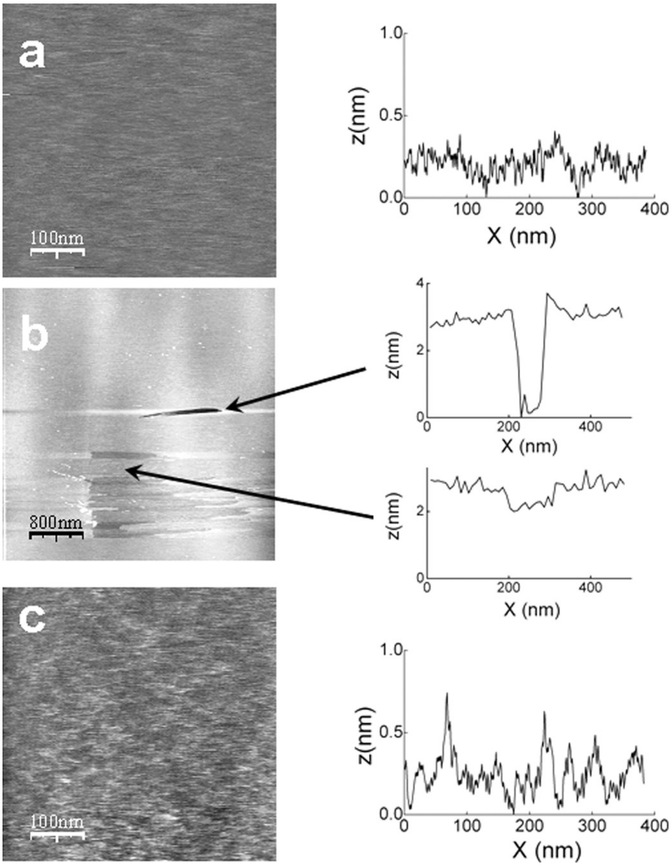

FIGURE 4 Chemical reaction with dicarboxylic acids. Contact AFM height images and height profiles of Plys$_{40}$-PDMS$_{40}$-Plys$_{40}$ adsorbed layers on mica (a) before and after reaction with (b) malonic and (c) pimelic acid. The reaction with pimelic acid increases the roughness of the adsorbed layer, whereas the reaction with malonic acid decreases the cohesion of the layer.

by the reaction at separations larger than 40 nm, but the polymer-related steric–entropic repulsion is clearly enhanced (*c.f.* Fig 2). This extra repulsive interaction was diminished to a certain extent by the combined effect of shear and compression, as can be also observed in Fig. 5. However, a repulsive hard wall was always observed at 10 nm, making it very difficult to attain fusion of the layers. Only occasionally was a reduction of the trapped layer thickness observed after shearing the modified surfaces under a high normal load. This reduction was accompanied by a subsequent modification of the

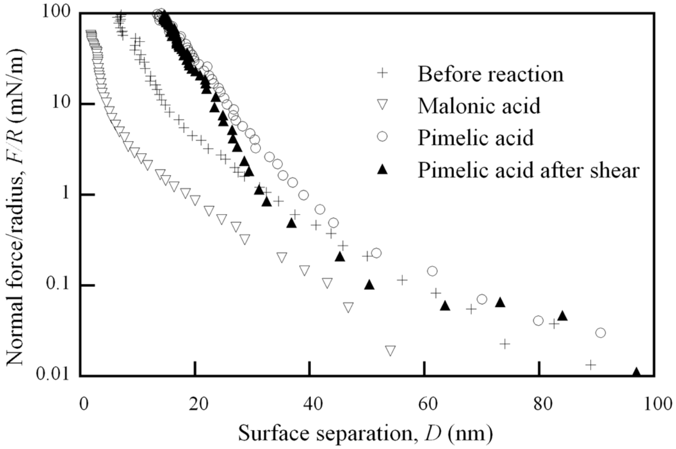

FIGURE 5 Normal interaction force profile between two adsorbed TB40 layers before and after reaction with pimelic and malonic dicarboxylic acids, at pH 3. A markedly different effect of each diacid investigated can be observed.

normal interaction force between the surfaces, with the re-emergence of a finite adhesion and high frictional forces.

3.2.3. Surface Forces Apparatus: Behavior under Shear

The chemical reaction with each diacid investigated also has a very different effect on the behavior of the surfaces under shear. After the reaction with the shorter acid, the surfaces lost the outstanding lubricative properties described in the previous section. Shearing under very small loads induced the removal and irreversible damage of the adsorbed layers evidencing a reduction in the cohesion of the adsorbed layer, in agreement with the behavior observed in the AFM experiments. In contrast, after the reaction with the longer diacid, the cohesion of the adsorbed polymer layer was enhanced. As mentioned before, the fusion of the cross-linked layers and the appearance of the high adhesion state were rarely observed by the combined effect of compression and shear. However, the exceptional lubrication properties of the adsorbed layers were also lost in this case. In the range of loads investigated, F_f remains small but measurable, increasing to some extent with the driving velocity. The dependence of F_f with driving velocity and applied load after this reaction is presented in Fig. 6. A sublinear and reversible variation of F_f with the applied normal load was observed: the same results were obtained by increasing or decreasing the applied normal load. This suggests that the layers

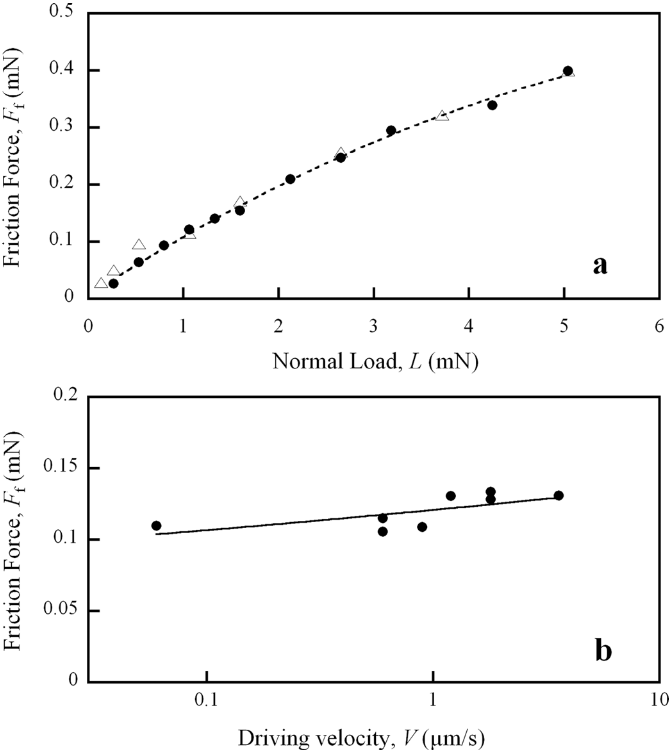

FIGURE 6 Friction force between two adsorbed layers of TB40 after cross-linking reaction with pimelic acid. (a) Load-dependence of the friction force at $V = 0.5\,\mu\text{m/s}$ while increasing (circles) and decreasing (triangles) the applied normal load. The continuous line was calculated assuming a Hertzian contact and a contact shear stress, as described in the discussion. (b) Driving-velocity dependence of the friction force at $L = 1.1\,\text{mN}$.

were not greatly modified by the applied shear, despite the shear-induced variation of the interaction force profile observed (Fig. 5).

4. DISCUSSION

The copolymer TB40 adsorbed in the form of a smooth molecular film on mica. From our results, we are not able to determine if the films consist of a molecular monolayer, with one polylysine group attached to the mica surfaces and the other exposed to the aqueous environment, or a bilayer, with the first layer having both polylysine moieties adsorbed on the mica surfaces and the second layer exposing the polylysine moieties to water. Most likely we have a combination of both, with molecules adsorbed in the form of loops and tails.

The measured interaction force profiles between the smooth TB40 layers (*c.f.* Fig. 2) resemble what have been reported in the past in other studies of adsorbed polyelectrolytes [3,16–20]. At separations greater than 30 nm, the normal interaction force can be described by the DLVO theory. The repulsive double-layer forces decay exponentially with the distance between the surfaces with a decay length very close to the expected Debye–Hückel screening length, as predicted by the Poisson–Boltzmann theory [9]. Closer in, the measured forces exceed the predictions of the DLVO theory: an additional repulsive interaction is observed. This force, of osmotic origin, is due to the decreasing entropy associated with the compression of the polymer layers and to the presence of the hydrated counter ions that remain trapped between the compressed layers as a result of electroneutrality limitations.

At even shorter separations, the behavior under shear and compression of the smooth TB40 layers displays strong similarities to the behavior of bilayer-forming surfactants. If two flat surfactant bilayers are compressed, eventually the hemifusion of the layers can be induced. In the hemifused region, the mica surfaces are covered by a monolayer of surfactant, and the surfaces are held together by the hydrophobic attraction between the chains of the surfactant molecules. This is the same behavior we observed with the TB40 layers, with the PDMS moieties playing the role of the hydrophobic tail of the surfactant molecules. In addition, we observed that before the adhesion instability, these smooth polymer-coated surfaces exhibit remarkably good lubrication properties and extremely low frictional forces. This also resembles closely what we have observed previously for charged flat bilayers under shear [1,2]. The friction forces under these conditions were smaller than the detection limit of our experimental setup; we can only estimate an upper limit for the corresponding coefficient of friction, $\mu = F_f/L$, of around 0.01, an extremely low value (as a reference, the kinetic friction coefficient of an ice–ice contact under similar load conditions is around 0.03 [21]).

Superior lubrication properties have also been reported in the past for other polyelectrolyte-coated smooth surfaces under shear. This spectacular performance has been attributed to the small interpenetration between the polymer adsorbed layers on both surfaces [3], due to the increasing osmotic pressure related to the presence of the hydrated counter ions in the confined thin film.

The reaction with the shorter dicarboxylic acid seems to reduce the cohesion of the adsorbed layer, as evidenced by the easy disruption of the layer by scanning with the AFM tip (Fig. 4b) and the inferior repulsive interaction (Fig. 5) between the coated surfaces. Similarly, the layer is rapidly damaged when two surfaces are sheared, even under very small normal loads. These results suggest that the malonic acid molecules are not long enough to form intermolecular bridges between the adsorbed molecules, rather forming covalent bonds with single triblock copolymer molecules. The chemical reaction probably reduces the effective electric charge on the adsorbed polylysine moiety in contact with the mica surface, decreasing the affinity for the negatively charged substrate and enabling the removal of the adsorbed molecules upon compression and/or shear.

In contrast, the reaction with the longer chain dicarboxylic acid appears to increase the cohesiveness of the adsorbed layer. After the cross-linking reaction, the adsorbed layer appears somehow rougher (Fig. 4c), and there is an enhanced repulsive interaction between the surfaces. The fusion of the adsorbed layers under compression is no longer observed, and the adhesion between the coated surfaces vanishes (Fig. 5). All of these effects are probably due to the reduced ability of the adsorbed molecules to be pushed apart when the surfaces approach, which suggests that this longer diacid is able to form intermolecular bridges to a certain extent.

The modification of the adsorbed layers also has implications on their performance under shear, as illustrated in Fig. 6. In a recent study, Maeda and coworkers studied the influence of cross-linking in the dry friction between adsorbed polymer layers [22]. They found that cross-linking the polymer molecules has profound implications on their behavior under shear, reducing the degree of interpenetration and the friction between the rubbing polymer layers. In contrast, in the present study the superior lubrication properties of the adsorbed layers are worsened by cross-linking the polymer molecules. This effect is also almost certainly related to the interpenetration of the polymer layers. As mentioned before, the unmodified layer owes its exceptional properties to the small intermolecular interpenetration upon compression. The cross-linking of the adsorbed polymer molecules diminishes the importance of the forces at the origin of this effect either by reducing the charge density of the layers, by its elastic reinforcement, or both, increasing the interpenetration of the compressed polymer layers. This deleterious effect could probably be avoided if the outer moiety of the adsorbed molecules—which seems to be responsible for the exceptional lubrication ability of the original layer—were not modified by the reaction.

Several aspects of the behavior under shear of the surfaces after the chemical reaction are noteworthy. The frictional resistance vanishes at the limit of small normal loads, indicating the absence of an adhesive contribution to the friction force, in agreement with the measured normal interaction force profile. The variation of the measured friction with the applied normal load can be suitably described by assuming a shear stress independent of the load and a Hertzian contact between the surfaces [9]. The result of this approximation is shown as a continuous trace in Fig. 6.

The dependence of the friction force on the driving velocity is also worth discussing. The nonzero frictional resistance observed at the slowest sliding velocities and the slowly increasing force with the logarithm of the applied velocity are both indications that a hydrodynamic description of the observed behavior would be inadequate. The friction between surfaces coated by neutral polymer brushes has been studied by several groups in the past. The results can usually be described by a power law of the form $F_f \sim V^{\alpha}$ [23,24]. This representation is clearly inappropriate for this gel-like coating. The relevant question to address, then, is by which mechanism energy is being dissipated after the cross-linking reaction. Models used to describe solid friction may provide an answer. The loss of the elastic energy stored in deformed regions of the adsorbed layer in the rubbing surfaces may be at the origin of the measured friction. This process brings about a nonvanishing friction force at the limit of zero velocity. In addition, considering it as a thermally activated process engenders naturally a linear dependence of the measured force with the logarithm of the applied driving velocity, as discussed by several authors in the past [25,26].

5. CONCLUSIONS

The behavior under shear and compression of layers of Plys_{40}-b-PDMS_{40}-b-Plys_{40} triblock copolymer adsorbed on mica has been studied before and after chemical reaction with two dicarboxylic acids. This copolymer self-assembles in the form of an extremely smooth layer on the mica surfaces, which opposes a very small resistance to sliding as long as the rubbing layers are intact.

The fusion of the layers adsorbed in opposite surfaces can be readily achieved by compression. After the fusion has taken place, the surfaces exhibit a strong adhesive interaction and very large frictional forces.

The endurance of the adsorbed layer to disruption by normal compression can be enhanced by cross-linking the adsorbed polymer molecules. The exceptional lubrication properties of the adsorbed layers disappear after this reaction has taken place. Nevertheless, it hinders the fusion of the adsorbed layers under normal compression, markedly enhancing its behavior under shear at intermediate and large normal loads.

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