

Correlation between Conformation Change of Polyelectrolyte Brushes and Lubrication^{*}

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Abstract We directly monitor the absolute separation profiles that function as film thickness between a single glass disk and the charged polyelectrolyte brushes decorated steel slider in water using a home-made slider-on-disk apparatus, which reflects the structural conformation variations and interactions of polymer brushes under externally applied pressure, in addition to probing the relative variation of friction forces under different applied loads and sliding velocities. We find that the polyelectrolyte brushes modified surfaces can sustain high pressure and have extremely low friction coefficients (around 0.006 at pressures of 0.13 MPa; 0.5–0.6 without brushes). The water-lubrication characteristics are correlated to the structural conformation changes of the polyelectrolyte brushes that are mainly governed by electrostatic interactions and the osmotic pressure of counterions inside the polymer chains, which can be used to support and distribute the normal pressure. The apparent thickness of the brush decreases with the increase of loading forces, an increase in the ionic strength causes the polymer chains collapse, and the friction forces increase. This fundamental research is of great importance to understand the mechanical and structural properties of polyelectrolyte brushes and their influences on the tribological behaviors, and helps to design friction/lubrication-controlled surface/interface by taking advantage of polyelectrolyte brushes.

Keywords: Polyelectrolyte brush; Lubrication; Conformation; Electrolyte.

INTRODUCTION

Lubricious surfaces are widely found in biological systems in aqueous media in nature, such as cartilage surfaces in human hips or knees, which have extremely low friction coefficients. The excellent lubrication property is mainly attributed to the ultrastructure network of cartilage and the synergistic combination of bio-macromolecules in synovial fluid for water lubrication^[1–4]. The intrinsic mechanical properties of the cartilage such as tensile strength and viscoelasticity, enable the cartilage to absorb and distribute loads at the interface in aqueous media when it contacts and rubs a surface, and it allows the fixation of a large number of water molecules within the contact region and provides a lubricating fluid layer to reduce the friction forces between two surfaces. However, the water itself cannot perform alone as a stable boundary lubricant not only due to its low viscosity but due to negligible viscoelastic component at frequencies concerned and linearity of its squeeze flow behavior, this can be overcome by lubricant additives such as biomacromolecules, improving the lubrication performance of water at high pressures^[1]. Surface-bonded charged polymers are widely used to

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precisely control the surface tribological performances because of their chemical diversity and hydration properties^[5–7]. Moreover, these surface attached polymers can form brush-like structure and are known to impart interesting physicochemical behaviors due to their excellent performances in terms of lubrication, responsiveness, wettability and antifouling at surfaces^[8–14].

Polymer brushes are highly stretched in good solvents and have been reported as promising candidates for ultralow friction surfaces^[15–18]. The highly hydrated polymer chains maintain a lubricating fluid layer at the shearing interface and allow a continuous rapid exchange of hydration water molecules with other hydrated ions and free water molecules, as well as the steric repulsion between the polymer chains, allowing the brush/counter-surface tribopair to separate and maintain fluid under externally applied pressure, the resulting fluid-like layer aids in reducing shear forces by several orders of magnitude when slide past each other^[19, 20]. Several theoretical and experimental studies have investigated the origin of lubrication properties of polymer brushes^[10, 15, 21, 22]. Water lubrication is of particular interest because water is the natural lubrication medium and it is believed that understanding of biological lubrication can be applied to systems of technological importance. “Grafting from” methods are widely used for the design of robust brush-like surfaces with high grafting densities and homogeneous morphology which have good lubrication and wear properties even at high pressure, particularly the widely employed surface-initiated atom transfer radical polymerization (SI-ATRP)^[23–25].

Polyelectrolyte brushes in aqueous state are of great interest in understanding frictional processes in biological systems and yet some of the most fundamental questions in this area are not fully resolved, such as how the structural conformation or the mechanical property of a polymer affects a lubricating process. Furthermore, a translation of the experimental results to practical applications is still a challenge at present. Most tribological studies concerned with nano-scale friction behavior with a very low-loaded contact or between two symmetric polyelectrolyte brushes coated surfaces, which made it possible to detect surface/interface tribological characteristics at the atomic level^[26–30]. Extending this aqueous brush-assisted lubrication to macroscopic scale or other systems (*e.g.*, asymmetric systems composed of polymer brushes versus bare surfaces) is of importance for specialized applications. Of particular significance in macroscopic systems, there is a need to understand and control the effect of the applied normal pressure on the structural conformation of brushes with respect to their tribological performance. In this paper, the separation profiles of the two surfaces were measured as a function of the chain conformation changes, as well as the interaction between polyelectrolyte brushes by using a home-made slider-on-disk apparatus, which allows quantitative analysis of the variation of the brush thickness under compression and shear forces. By choosing the “strong” polyelectrolyte brushes poly(3-sulfopropyl methacrylate potassium salt) (PSPMA), it is possible to regulate the surface tribological properties in aqueous media by changing the solvent conditions. These findings provide a new way to study the correlation between the conformation change and friction force and help design synthetic polymers based lubricants for practical applications.

EXPERIMENTAL

Materials

3-Sulfopropyl methacrylate potassium salt (SPMA, 95%, TCI), 2,2'-bipyridyl (bipy, AR, Shanghai, China), Copper(I) bromide (CuBr, AR, Beijing, China), NaNO₃ (AR, Beijing, China). Chromium (Cr) films were prepared *via* thermo evaporation of 100 nm Cr on stainless steel sliders (4 mm × 9 mm).

ATRP Initiator Immobilization

Catecholic initiator was synthesized following a published procedure^[31]. The Cr coated steel slider was immersed in a 1.5 mg/mL solution (ultrapure water: ethanol = 4:1, *V/V*) of catecholic initiator for 24 h at room temperature and then washed with ultrapure water and ethanol thoroughly to yield an ATRP initiator modified surface.

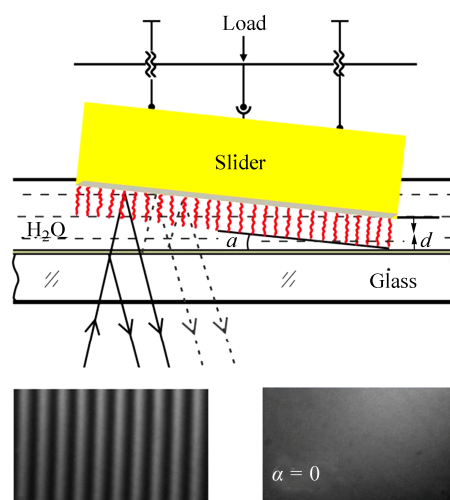
Polymer Brushes Synthesis

PSPMA brushes were prepared through surface-initiated atom transfer radical polymerization (SI-ATRP). The

general polymerization procedure involved dissolving the SPMA monomer (3.25 mol/L) into a Schlenk tube containing 7.5 mL H₂O/MeOH (2:1, *V/V*) and degassing by dry N₂ for 20 min, then bipy and CuBr were added successively, [SPMA]:[bipy]:[CuBr] = 100:2:1. The initiator modified substrates were placed in the polymerization bath for a certain time at room temperature to yield PSPMA decorated Cr surfaces.

Characterization

The distance (d) and friction force measurement protocols are described in detail in our previous work^[32]. Interferometry is used to monitor the distance of the two parallel surfaces, one is the Cr-PSPMA surface and the other one is that of a glass disk. In this experiment, the Cr-PSPMA surface slides in parallel with the glass disk (when the number of the fringe is 0, $\alpha = 0$, Scheme 1). Once the fringe was identified, the experiment was performed under different loads and electrolyte solutions. The surface roughness of the steel slider $R_a = 8$ nm, and that of the glass disk, $R_a = 4$ nm. The experiments were carried out at room temperature ((25 ± 1) °C, humidity, $(50 \pm 5)\%$ RH).



Scheme 1 Schematic view of the experimental setup

RESULTS AND DISCUSSION

In this study we measured the absolute gap distance as a function of structural conformation changes of the brushes and the friction forces between two surfaces, where one surface is coated with PSPMA brushes and another one is the surface of bare glass substrate in aqueous media. The charged polyelectrolyte brushes PSPMA were grown from catecholic initiator modified Cr-coated steel slider through surface-initiated atom transfer radical polymerization, a powerful tool to prepare well-defined polymer films which has been reported previously^[33, 34]. We have estimated the grafting densities by measuring the ratio between the swollen height and dry height of the PSPMA brushes^[35, 36]. The average dry thickness of the PSPMA brushes was about 80 nm, and the swollen thickness in water was about 210 nm and the grafting densities were found to be ~ 0.2 – 0.5 chains/nm². First, for the loading and unloading processes, measurements were carried out to get the gap distance d versus the normal load F_n between the surfaces of the slider and the glass disc, brush-modified slider and bare slider were used for comparison, the data are shown in Fig. 1. The distance d (defined as the variation of film thickness h) profiles between the Cr-PSPMA surface and the glass disk are calculated from the variation of the intensity of the interference light which is described in detail in the published work^[32]. The absolute distance d obtained from the slider-on-disk apparatus can be regarded as a function of hydrated brushes thickness changes which reflects changes of the chain conformation. The “zero” point of d in Fig. 1 corresponds to the thickness of the incompressible part of the PSPMA brushes. The film thickness is difficult to measure by any of the present techniques when the brushes are subjected to an external compression, but the the variation of the the brush

thickness and the structural conformation of the attached polymers can be estimated by the separation d . Experimental results indicated that the charged brush is compressed and slides across the solid surface, very low friction coefficient is maintained in aqueous media.

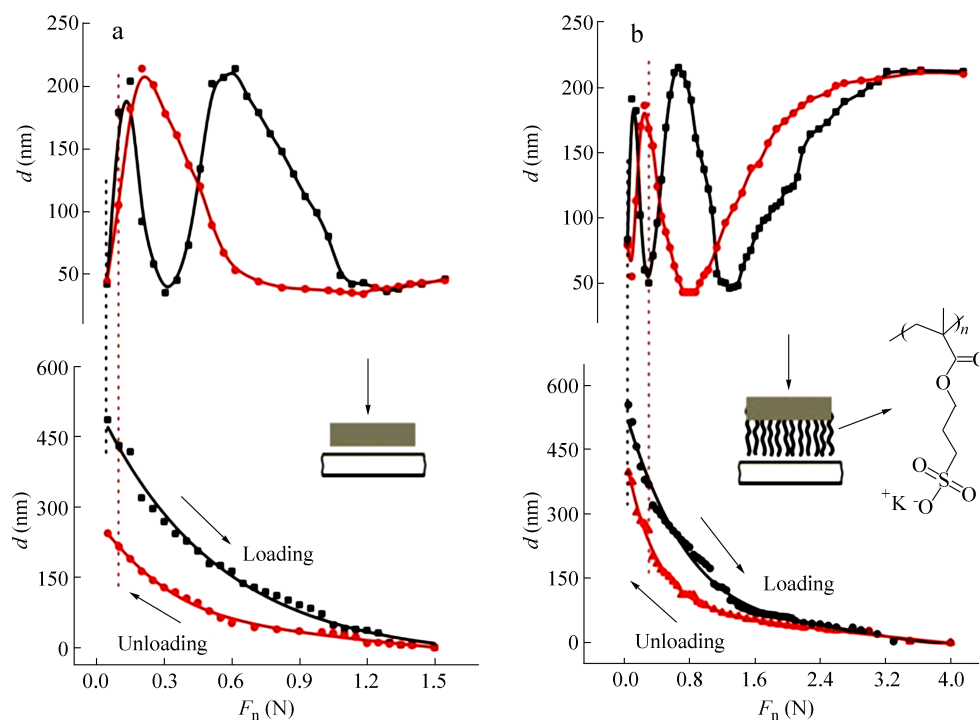


Fig. 1 The profiles of the interference intensity I and the distance d between the slider and the glass disk calculated from the intensity I versus normal force F_n for (a) bare Cr surface and glass disk and (b) PSPMA brushes coated Cr-PSPMA surface and glass disk in water (Lines were added to guide the eyes.)

In general, the apparent thickness of the brush decreases with the increase of the applied load. Without the brushes (bare slider surface), free water molecules in the gap can be easily squeezed out at extremely low compression of 1.2 N due to its low viscosity (Fig. 1a), and cannot either support higher normal pressure or recover when decreasing the normal load (unloading procedure). In the case of the PSPMA modified surfaces (Fig. 1b). The stretched brush is a result of electrostatic interactions and the osmotic pressure of the counterions, which are counterbalanced by the elastic free energy of the chains. At a relatively lower load (< 0.4 N), the free water molecules around the polymer chains are easily lost, indicating that the highly stretched polyelectrolyte brushes are “soft”. When the normal load is higher than 0.4 N, the distance d in the moderate compression regime decreases slowly with increasing the normal load, the presence of bound water associated to the hydrated polymer chains can help to support the load. The profiles of both on loading (approaching) and unloading (separating) processes are almost overlapped at the high load due to the compression induced “enlarged” osmotic pressure and electrostatic interactions (> 1.6 N, Fig. 1b). In this case, at the brush interface where forms a tightly bound and structured water layer in the proximity of hydrophilic polymer chains, and can interact preferentially with the free water molecules in the surrounding due to the hydration effect when the loads decrease (the separation d increases). PSPMA brushes in aqueous solution improve the water lubrication performance at high contact pressure, the highest normal load applied to the PSPMA bearing slider is nearly 3 orders of the magnitude higher than that of the bare slider, indicating that the robust hydrated brushes can resist high external compression (Fig. 1b). At lower loads (< 1.6 N), the free/fluid water molecules in the gap are easily lost and cannot restore to its original state, such hysteresis phenomenon observed in the compression/decompression curves between the two surfaces across water can be attributed to the energy dissipation of polymers during the

compression, which is the difference between energy gain when they are compressed together and the energy cost to separate the two surfaces. By comparison, more detailed information on the brushes characteristics is provided.

It has been demonstrated that factors like ionic strength of the solvent and the external applied forces have strong effect on the conformation of the polymer brushes and hence the frictional forces^[8]. Increase in ionic strength triggers conformational changes of the brush and results in a reduction of the average thickness. Interestingly, besides the conformational changes, an increase in the compressibility of the PSPMA brushes upon increasing the concentration of NaNO_3 was observed. The correlation between the structural conformation of PSPMA brushes upon the normal compression and the ionic strength of the solvent is given in Fig. 2. The measured normal forces versus d profiles show that the compressibility or stiffness of the PSPMA brush is greatly influenced by the solvent conditions. In good solvents, chains tend to stretch perpendicular to the surface, however, when such brushes are immersed in electrolyte solutions, the charges of the pendant groups in the polymer chains are screened, and the minimization of the intrinsic electrostatic repulsions of the charged groups in the polymer chains with increasing the ionic strength results in a reduction of the entire brush thickness and will also lead to a collapsed and less lubricious film^[37–40]. At low ionic strength the PSPMA brush height is almost independent of the external salt concentration, PSPMA brushes both in 0.1 mol/L NaNO_3 and pure water give nearly the same resistance to compression in the normal direction, this is because at low NaNO_3 concentrations, screening effect only occurs at the outer edge of the brushes, leaving the overall chains unaffected^[41]. Once the concentration of external ions reaches to the concentration of the free counterions inside the brushes, PSPMA brushes show strong conformational changes in high concentration NaNO_3 solutions (1 mol/L, Fig. 2b), the counterion osmotic pressure inside the PSPMA brushes reduces due to the screening effect. In such situation, the brushes energetically favor less swollen conformation, the mechanical properties of the brush change from viscoelastic toward more rigid^[42–44]. As demonstrated in Fig. 2(b), in the high compressed

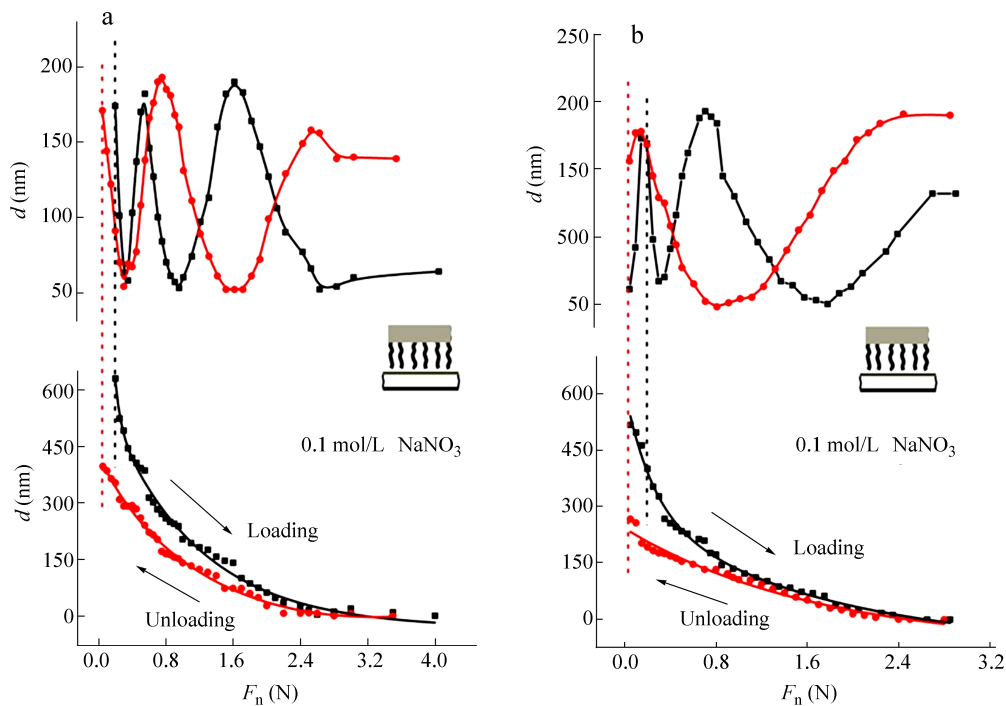


Fig. 2 The curves of the interference intensity I and the distance d between Cr-PSPMA surface and glass disk versus normal load F_n in aqueous NaNO_3 solutions of different concentrations: (a) 0.1 mol/L NaNO_3 and (b) 1 mol/L NaNO_3

region (0.8–1.2 N), the thickness variation is smaller than that in the same region in water media, indicating the brushes are harder to compress. Meanwhile, perhaps these tightly trapped counterions in the hydrated chains in turn result in the repulsion force surrounding the brushes and prevent further compression of the polymer layer. And hence the variation of d is smaller in NaNO_3 solutions than that in pure water and it would become increasingly difficult to further compress an already collapsed brush.

When nominally flat surfaces slide against each other, unavoidable asperity-asperity contact between the surfaces results in a high friction coefficient ($\mu = 0.5\text{--}0.6$) at the interface (Fig. 3a, inset). While the presence of the brushes layer greatly reduce the friction coefficient at the interface, such a thin coating of hydrated polyelectrolyte brushes can serve as an effective boundary lubricant by impeding the direct asperity-asperity contact at the interface, and reduce the interfacial friction by several orders of magnitude (Fig. 3). The lowest friction coefficient observed is around 0.006 at a pressure of 0.13 MPa in water, this is probably because of water lubrication, and combined with the electrostatic repulsive interactions among the anionic sulfonic groups. In contrast, the friction coefficient of PSPMA brushes in 1 mol/L NaNO_3 is higher than that in water (Fig. 3b). Upon increasing the NaNO_3 concentrations, the PSPMA brushes shrink strongly and become rigid and an increase in friction force is expected under similar compressive load at a given speed. The polyelectrolyte brushes in a high ionic strength solution behave as overall electrically neutral chains because the electrostatic interactions are screened. At higher loads the adsorbed water molecules are squeezed out and the brushes dehydrate, leading to an increase of the friction. Further increase in load (> 5 N, Fig. 3), the friction forces increase rapidly, most possibly, the attached charged brushes are sheared off or detached from the interface, resulting in wear of the brushes^[21], or the inevitable asperity-asperity contacts are expected. So an appropriate selection of polymer brush and solvent mixture can be used to tune the conformational properties of the polymer brushes at the interface, as well as the consequent frictional forces.

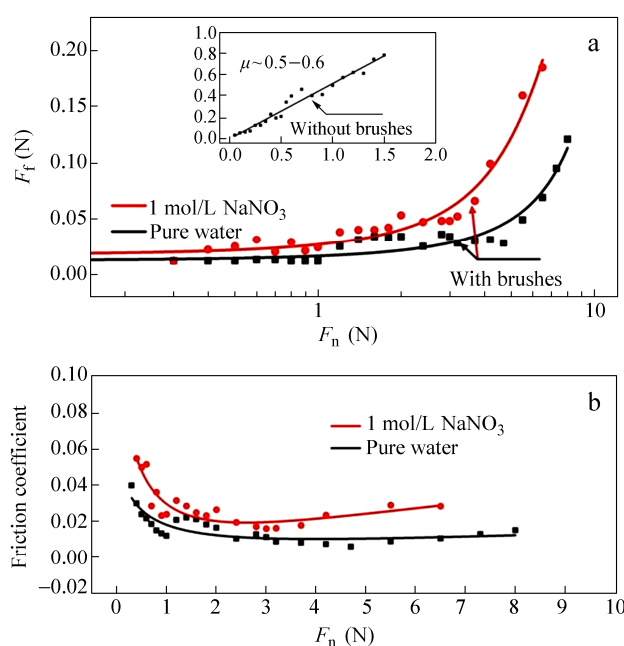


Fig. 3 Friction force F_f (a) and friction coefficient (b) as a function of normal load F_n measured using PSPMA coated Cr surface against bare glass (inset in Fig. 3a, bare Cr surface against bare glass) in pure water and 1 mol/L NaNO_3 at a shear rate of 6.75 mm/s. The data points are average values from separated measurements.

An interfacial lubricious polyelectrolyte film is formed owing to the strong electrostatically induced hydration between the hydrated chains and the counter-surface, the extent of hydration of charged polymer

chains can differ greatly depending on the conformation of the polymer chains or the surrounding salt concentration^[45, 46]. In general, the polyelectrolyte chains in aqueous solutions of low ionic strength favor an expanded conformation due to the intramolecular repulsion forces. In pure water, the brush height is balanced by the osmotic pressure of the counterions and the elastic energy of the stretched chains. The thickness of the brush can be written as^[34, 40, 47]:

$$h \approx Naa^{1/2} \quad (2)$$

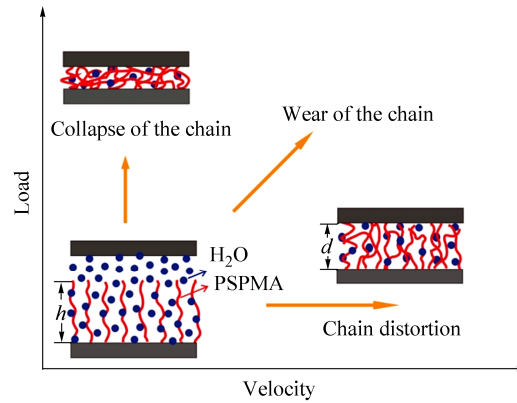


Fig. 4 Schematic representation of influence of applied load and speed or both on the conformation and the tribological properties of the polymer brushes

where N is the polymerization index, a is the monomer size, and α is the fraction of charged monomers. The polymer chains in a brush are strongly stretched. It is also observed that the polymer brushes adopt completely different conformations depending on the solvent conditions. A decrease in swelling thickness with an increase in the concentration of NaNO_3 solution was observed due to the screening of the charges of the chains, and the osmotic pressure of the counterions inside the brush reduces. In this case, the height depends strongly on the interaction of the polymer with the aqueous conditions, giving a brush height which is mainly balanced between the elastic and the electrostatic interactions^[40]:

$$h \approx Na \left(\frac{a}{D} \right)^{2/3} a^{2/3} \varphi_s^{-1/3} \quad (3)$$

where φ_s is the added salt volume fraction and a is the size of the counterion, D is the distance between two anchoring points. The structural conformation changes of the polymer brushes are correlated with their tribological performances, it is shown that highly hydrated PSPMA brushes improve the lubricating properties at the interface. Next, we consider the case of the compressed brushes between two surfaces in the case of the separation $d < h$, according to self-consistent field theory, the free energy per chain, F , as a function of brush height h , is described as follows^[48]:

$$F = k_B T N (\pi^2 \delta^2 \omega^2 / 12)^{1/3} (1/2 d_h + d_h^2 / 2 - d_h^5 / 10) \quad (4)$$

where, polymerization index, N ; grafting density, σ , $d_h = h/h_0$, h is the height of the compressed brush and h_0 is the height of the free brush. k_B , T , and ω , refer to the Boltzmann constant, temperature and the excluded volume parameter, respectively. It gives an estimation of the brush properties in the case of the height and the energy profile, the compressed height of the brushes between two confined surfaces is obtained by balancing the free energy at the grafting surface, which is a result of the change in conformational entropy when the brushes are compressed. For cases of weak compression, the measured decrease of the brush height is obtained by balancing the stretch energies and gives rise to an increase in the free energy, *i.e.*, the repulsive force. In the region of strong compression ($h < h_0$), repulsive forces can be estimated by the osmotic pressure, the repulsive force at the surface increases upon compression^[48]. The force (or the applied pressure p) that is needed to compress a brush

to a height $h < h_0$ is denoted as follows^[48]:

$$h = f(p/\Pi_0)\sigma^{(1-\nu)/((d-1)\nu)} \quad (5)$$

where Π_0 is the osmotic pressure at an equilibrium brush of coverage σ , with d dimension, ν is the swelling exponent, f is the sum of a stretch contribution and an excluded-volume contribution. As illustrated in Fig. 4, the brush-like hydrated layer provides high load bearing capacity and a fluid interface, thereby lowering the friction forces. At a very low normal pressure, the collapse of the brushes maybe suppressed by the osmotic pressure, the presence of water keeps the charged polymers hydrated and reduces the friction forces in the boundary/interfacial lubrication regime. At a moderate compression, water molecules were partially squeezed out around the brushes, resulting in a less swollen conformation. This hydration layer reduces the friction forces between the compressed chains as they rub past each other under compression in aqueous conditions. On further compression, more water was squeezed out of the hydrated chains, the counterion osmotic pressure of the polymer segments helps to support external pressure (Fig. 4). Thus, it is proposed that the essential feature of the lubricious polyelectrolyte is that the polymer layers should be sufficiently hydrated and stretched, as well as a high fluidity of the hydration layer surrounding the charged brushes between the brush-counter surface. This is more easily achieved with hydrophilic polyelectrolyte brushes than neutral polymers due to the electrostatic repulsion and the osmotic pressure.

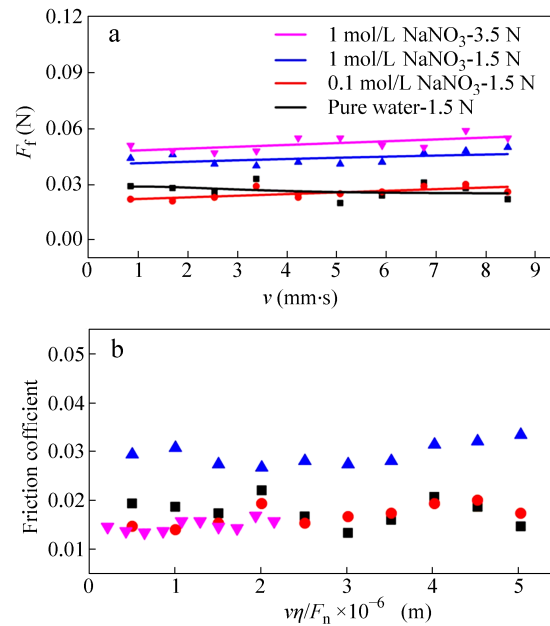


Fig. 5 (a) Variation of friction forces F_f with respect to the sliding velocity v and applied load F_n between the PSPMA-coated Cr surface and the bare glass disk; (b) Macro-scale *Stribeck* curve obtained for polymer brushes

Figure 5(a) shows the dependence of frictional forces on speed and load. The friction forces of the PSPMA brushes in aqueous solutions are affected by the salt concentration. The PSPMA brushes in 0.1 mol/L NaNO_3 solution shows almost the same friction coefficient (~ 0.026) as that in pure water at the sliding velocity between 1–10 mm/s, the presence of water keeps the hydrophilic polymer hydrated and reduces the friction between two surfaces. However, an increase in frictional force with increase in percentage of NaNO_3 in the solvent as the brushes collapse, the friction coefficient increases to 0.044 in a higher NaNO_3 concentration of 1.0 mol/L. Figure 5(b) shows the Stribeck curves obtained for PSPMA brushes versus glass contact, the interfacial friction coefficient does not vary significantly as a function of sliding velocity. Collapsing and stretching of the brushes

in the different solvent conditions are correlated with the frictional properties, which are different in the pure water and salt solutions. Generally, friction forces were found to be greater under high concentration of NaNO_3 solutions than in pure water at the same normal pressure. A small separation equals to a high compression, and great shear force was observed (Fig. 2). In pure water, the repulsion forces induced highly stretched and hydrated polymer layer serves as an efficient lubricant, which can sustain higher load and has lower friction coefficient. When the polyelectrolyte brushes are immersed in the salt solutions, at low external salt concentrations the overall brush height is unaffected, which give nearly the same resistance to compression in the normal direction and nearly the same friction forces. Only at a very high degree of collapse, the influence of the salt concentration on the friction forces can be observed. Then the concentration of the NaNO_3 is increased to 1 mol/L, the slight increase in the friction forces with the addition of the NaNO_3 can be attributed to the less hydrated but swollen chains at high salt concentration, which may be understood in terms of the conformation and hydration of the polymer chains. Furthermore, the increase in rigidity or stiffness of the compressed brushes may explain the increase in friction. The effect of NaNO_3 concentration on friction is observed only when the ionic concentration is sufficient high and the brushes are strongly collapsed (Fig. 5).

CONCLUSIONS

In conclusion, the gap distance between a single glass disk and a charged polyelectrolyte brushes decorated steel slider has been investigated under loading/unloading process in aqueous solutions, and the friction forces were measured under different applied loads and velocities. The results show that the effective lubrication by the highly charged anionic PSPMA brushes in water are able to reduce friction coefficient from 0.5–0.6 to below 0.01 at low sliding velocities, the great friction reduction is attributed to the swollen polyelectrolyte brushes which form a diffuse and dynamic interface in an aqueous medium, thus, the sliding between two surfaces can be accommodated by shearing of a thin hydrated polymer films generated in the contact area, such a fluid layer is able to effectively separate the two tribological surfaces during the sliding contact. This fundamental research presents a new and powerful platform for studying the relationship between the structural conformation of the polymer brushes and their tribological performance. Moreover, experiments on brush coated surfaces could potentially provide a deep understanding of the mechanisms that are crucial for the designing of surfaces/interfaces and devices with tailored tribological properties by using synthetic polymers under biologically relevant conditions.

REFERENCES

- 1 Lee, S. and Spencer, N.D., *Science*, 2008, 319: 575
- 2 Klein, J., *Science*, 2009, 323: 47
- 3 Klein, J., *Proc Inst. Mech. Eng., Part J*, 2006, 220: 691
- 4 Dédinaite, A., *Soft Matter*, 2012, 8: 273
- 5 Raviv, U., Tadmor, R. and Klein, J., *J. Phys. Chem. B*, 2001, 105: 8125
- 6 Müller, M.T., Yan, X., Lee, S., Perry, S.S. and Spencer, N.D., *Macromolecules*, 2005, 38: 3861
- 7 Zappone, B., Ruths, M., Greene, G.W., Jay, G.D. and Israelachvili, J.N., *Biophys. J.*, 2007, 92: 1693
- 8 Wei, Q., Cai, M., Zhou, F. and Liu, W., *Macromolecules*, 2013, 46: 9368
- 9 Wu, Y., Xue, Y., Pei, X., Cai, M., Duan, H., Huck, W.T.S., Zhou, F. and Xue, Q., *J. Phys. Chem. C*, 2014, 118: 2564
- 10 Chen, M., Briscoe, W.H., Armes, S.P. and Klein, J., *Science*, 2009, 323: 1698
- 11 Barbey, R., Lavanant, L., Paripovic, D., Schüwer, N., Sugnaux, C., Tugulu, S. and Klok, H.-A., *Chem. Rev.*, 2009, 109: 5437
- 12 Stuart, M.A.C., Huck, W.T.S., Genzer, J., Müller, M., Ober, C., Stamm, M., Sukhorukov, G.B., Szleifer, I., Tsukruk, V.V., Urban, M., Winnik, F., Zauscher, S., Luzinov, I. and Minko, S., *Nat. Mater.*, 2010, 9: 101

- 13 Senaratne, W., Andruzzi, L. and Ober, C.K., *Biomacromolecules*, 2005, 6: 2427
- 14 Galvin, C.J. and Genzer, J., *Prog. Polym. Sci.*, 2012, 37: 871
- 15 Kobayashi, M., Terada, M. and Takahara, A., *Faraday Discuss.*, 2012, 156: 403
- 16 Raviv, U., Giasson, S., Kampf, N., Gohy, J.-F., Jérôme, R. and Klein, J., *Langmuir*, 2008, 24: 8678
- 17 Dedinaite, A., Thormann, E., Olanya, G., Claesson, P. M., Nyström, B., Kjøniksen, A.-L. and Zhu, K., *Soft Matter*, 2010, 6: 2489
- 18 Kumar Vyas, M., Schneider, K., Nandan, B. and Stamm, M., *Soft Matter*, 2008, 4: 1024
- 19 Dunér, G., Thormann, E., Ramström, O. and Dédinaite, A., *J. Dispersion Sci. Technol.*, 2010, 31: 1285
- 20 Nalam, P.C., Ramakrishna, S.N., Espinosa-Marzal, R.M. and Spencer, N.D., *Langmuir*, 2013, 29: 10149
- 21 Raviv, U., Giasson, S., Kampf, N., Gohy, J.-F., Jérôme, R. and Klein, J., *Nature*, 2003, 425: 163
- 22 Dhinojwala, A., Cai, L. and Granick, S., *Langmuir*, 1996, 12: 4537
- 23 Edmondson, S., Osborne, V.L. and Huck, W.T.S., *Chem. Soc. Rev.*, 2004, 33: 14
- 24 Li, B., Yu, B., Huck, W.T.S., Zhou, F. and Liu, W., *Angew. Chem. Int. Ed.*, 2012, 51: 5092
- 25 Yan, J., Li, B., Yu, B., Huck, W.T.S., Liu, W. and Zhou, F., *Angew. Chem. Int. Ed.*, 2013, 52: 9125
- 26 Liu, J., Li, J., Yu, B., Ma, B., Zhu, Y., Song, X., Cao, X., Yang, W. and Zhou, F., *Langmuir*, 2011, 27: 11324
- 27 Loveless, D.M., Abu-Lail, N.I., Kaholek, M., Zauscher, S. and Craig, S.L., *Angew. Chem., Int. Ed.*, 2006, 45: 7812
- 28 Dedinaite, A., Pettersson, T., Mohanty, B. and Claesson, P. M., *Soft Matter*, 2010, 6: 1520
- 29 Israelachvili, J., Min, Y., Akbulut, M., Alig, A., Carver, G., Greene, W., Kristiansen, K., Meyer, E., Pesika, N., Rosenberg, K. and Zeng, H., *Rep. Prog. Phys.*, 2010, 73: 036601
- 30 Bhushan, B., Israelachvili, J.N. and Landman, U., *Nature*, 1995, 374: 607
- 31 Fan, X., Lin, L., Dalsin, J.L. and Messersmith, P.B., *J. Am. Chem. Soc.*, 2005, 127: 15843
- 32 Guo, F., Wong, P. L., Fu, Z. and Ma, C., *Tribol. Lett.*, 2010, 39: 71
- 33 Ramstedt, M., Cheng, N., Azzaroni, O., Mossialos, D., Mathieu, H. J. and Huck, W.T.S., *Langmuir*, 2007, 23: 3314
- 34 Li, B., Yu, B., Huck, W.T.S., Liu, W. and Zhou, F., *J. Am. Chem. Soc.*, 2013, 135: 1708
- 35 Harris, B.P. and Metters, A.T., *Macromolecules*, 2006, 39: 2764
- 36 Jordan, R., Ulman, A., Kang, J.F., Rafailovich, M.H. and Sokolov, J., *J. Am. Chem. Soc.*, 1999, 121: 1016
- 37 Moya, S., Azzaroni, O., Farhan, T., Osborne, V.L. and Huck, W.T.S., *Angew. Chem., Int. Ed.*, 2005, 44: 4578
- 38 Zhang, H. and Rühe, J., *Macromolecules*, 2005, 38: 4855
- 39 Kumar, N.A. and Seidel, C., *Macromolecules*, 2005, 38: 9341
- 40 Tran, Y., Auroy, P. and Lee, L.-T., *Macromolecules*, 1999, 32: 8952
- 41 Rühe, J., Ballauff, M., Biesalski, M., Dziezok, P., Gröhn, F., Johannsmann, D., Houbenov, N., Hugenberg, N., Konradi, R., Minko, S., Motornov, M., Netz, R.R., Schmidt, M., Seidel, C., Stamm, M., Stephan, T., Usov, D. and Zhang, H., *Adv. Polym. Sci.*, 2004, 165: 79
- 42 Habicht, J., Schmidt, M., Rühe, J. and Johannsmann, D., *Langmuir*, 1999, 15: 2460
- 43 Ramos, J.J.I. and Moya, S.E., *Macromol. Rapid Commun.*, 2011, 32: 1972
- 44 Cuellar, J.L., Llarena, I., Moya, S.E. and Donath, E., *Macromolecules*, 2013, 46: 2323
- 45 Nomura, A., Okayasu, K., Ohno, K., Fukuda, T. and Tsujii, Y., *Macromolecules*, 2011, 44: 5013
- 46 Liao, W.P., Elliott, I.G., Faller, R. and Kuhl, T.L., *Soft Matter*, 2013, 9: 5753
- 47 Zhao, X.j. and Zhang, G.l., *Chinese J. Polym. Sci.*, 2014, 32(5): 568
- 48 Milner, S.T. and Witten, T.A., *Macromolecules*, 1988, 21: 2610