Supplementary Material (ESI) for Soft Matter

Switching of Friction by Binary Polymer Brushes

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Supporting Information

Force measurements using AFM

Adhesion force measurements. A typical force curve obtained using AFM is given in Figure 1S.

Friction force measurements. When the tip moved on the surface, torsion of the cantilever was proportional to the frictional force between two surfaces in the contact. A typical friction loop obtained with an AFM is shown in Figure 2S. Slow scan axis was disabled during the capture of friction loops. In this loop, left to right (forward) direction is defined as Trace (T) and the right to left (backward) direction as Retrace (R). The larger the separation between the friction trace and retrace (TMR), the larger the friction force.[1] From Figure 2S, it can be noticed that the sign of the friction signal is reversed for the Retrace scan compared to that of the Trace scan, which is due to the reversal of the torque applied to the end of the tip when the scanning direction is reversed. Hysteresis is observed in the friction loop because AFM tip tilts in opposite directions during Trace and Retrace scanning. The noise signal observed in the friction loop is mostly due to the stick-slip behaviour of the tip.

The friction voltage signal (half of the difference between Trace and Retrace scans) is converted to units of force using a conversion factor based on the Ruan and Bhushan's method.[2,3] Based on this method, the AFM tip is traced and retraced across the single-crystal silicon (rms roughness < 0.1 nm) in parallel direction. The plot of ''Trace minus Retrace (TMR)'' value versus average piezo centre position results in a linear fit. Slope (δ) of this line is related to the coefficient of friction between the tip and sample surface by $\mu' = \delta\,(L/2h)$,[4] where μ' is the coefficient of friction, L is the length of the cantilever, and h is the height of the cantilever. After the determination of coefficient of friction, tip is scanned perpendicular to the cantilever axis, for different normal loads. A graph is plotted between lateral deflection signals obtained versus normal load. A conversion factor k_f (in nN/V) of the cantilever can be obtained by equating the slope of this plot with the coefficient of friction (μ') obtained previously. This conversion factor k_f can be used to convert the friction voltage signal to force units. Different values of conversion factor k_f were obtained for different type of cantilevers.

The coefficient of friction of materials (μ) is defined by the Amonton's law,[5] according to which μ is equal to the ratio of friction force applied to a probe, to the normal force applied to a probe. Slope of the plot between friction force and normal force gives the coefficient of friction.

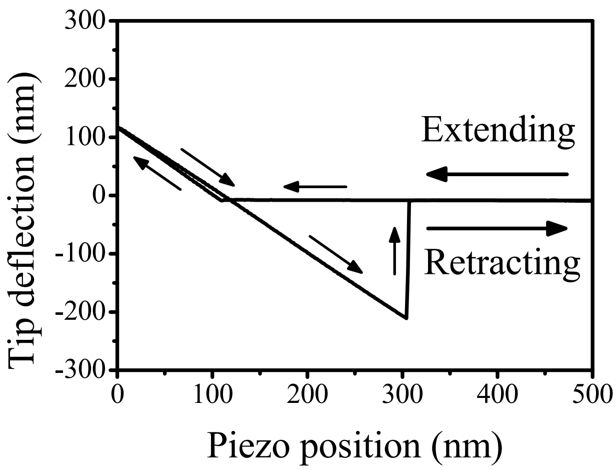


Figure 1S. Typical force curve obtained using AFM, the horizontal axis represents the tip position and the vertical axis represents the cantilever deflection.

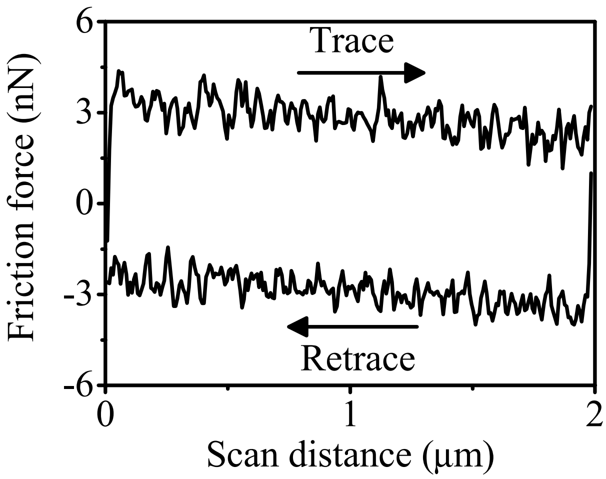


Figure 2S. Typical friction trace and retrace, determined by AFM.

Control experiments

Control experiments were carried out using ellipsometry to investigate the effect of humidity present in the environment on the polymer film thickness. For this purpose, thickness of the PS and P2VP brush layers was measured before solvent treatment, after solvent treatment followed by drying, and after keeping the dried sample at 21 °C and 40 % relative humidity for 12 h. From Table 1S, no significant change in the effective thickness values was observed. Ellipsometric measurements were also performed for the thick spin coated films of PS and P2VP (Table 1S). No significant change in the effective thickness was observed for these thicker films also. This suggested that the adsorption of water, if any, was not significant enough to bring about any detectable change in the effective thickness of the polymer films under our experimental conditions.

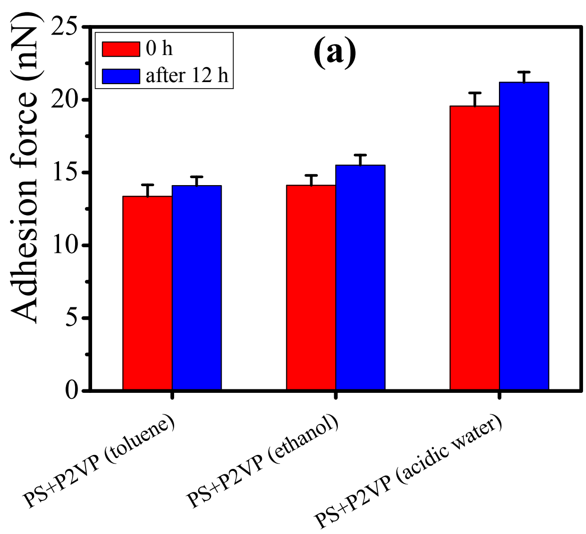
Control experiments were also carried out using Si_3N_4 tip to investigate the effect of humidity present in the environment on the adhesion and friction forces between the sample and the tip surfaces. For this purpose, adhesion and friction force measurements were carried out on the binary brush surfaces treated with selective solvents immediately after drying with nitrogen as well as after keeping the samples in same environment (21 °C and 40 % relative humidity) for 12 h. The results obtained are presented in Figure 3S. As could be observed from Figure 3S (a), there was an increase in the adhesion force for the brush samples exposed to the 40 % relative humidity for 12 h as compared to the samples for which force measurement was carried out immediately after the drying with nitrogen. Similar trend was also observed for the friction coefficient values (Figure 3S (b)). These results suggested that very thin water layer was deposited on the brush samples when they were kept for 12 h in the environment with humidity. This resulted in the increase in the meniscus force contribution due to the water meniscus formed between this thin water layer and the tip. Hence, increase in the adhesion force and friction coefficient values was observed for binary brush samples treated with different solvents. Moreover, higher increase in the adhesion and friction was observed for the binary brushes when hydrophilic P2VP chains were on the top (binary brushes treated with ethanol and acidic water) as compared to that for the binary brushes with hydrophobic PS chains on the top (binary brushes treated with toluene).

Table 1S. Ellipsometric data.

Sample	**Effective thickness, n.d (Initial, N_2 dried) (nm)**	**Effective thickness, n.d (after solvent treatment, N_2 dried) (nm)**	**Effective thickness, n.d (after 12h) (nm)**
PS brush (Toluene)	7.85 ± 0.04	7.86 ± 0.026	7.86 ± 0.042
P2VP brush (Ethanol)	7.97 ± 0.03	7.97 ± 0.030	7.99± 0.031

Spin coated PS	98.31 ± 0.93	--	98.32 ± 1.05
Spin coated P2VP	104.24 ± 1.09	--	104.26 ± 1.04

* n = refractive index of the film, d = thickness of the film.



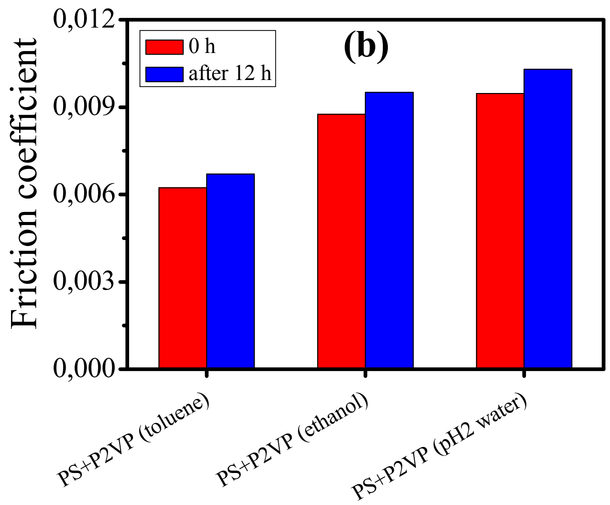


Figure 3S. Variation of the adhesion force (a) and friction coefficient (b) for different polymer brushes measured (using Si_3N_4 tip) immediately after drying with nitrogen as well as after keeping the samples at 21 °C and 40 % relative humidity for 12 h.

On the basis of control experiments, we expected some meniscus force contribution to total adhesion and friction forces on all the brush samples measured using different probes immediately after solvent treatment and drying with nitrogen. Furthermore, meniscus forces were higher for the hydrophilic brushes (when P2VP chains were on the top) and tips than that for the hydrophobic brushes (when PS chains were on the top) and tips.

References

[1] *AFM/LFM Instruction Manual*, Digital Instruments, Santa Barbara, **1999**.

[2] Ruan, J ; Bhushan, B. *ASME J. Tribo.* **1994**, 116, 378-388.

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