

CONTROL OF INTERFACIAL ADHESION BY POLYMER BRUSHES*

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Introduction

Polymer brushes present a versatile and facile route to constructing well-defined interface structures critical to many applications, including precise control over interfacial adhesion. For instance, adhesion of polydimethylsiloxane (PDMS), widely used in microfluidic devices and medical implants, to a majority of solid substrates is weak due to the low surface energy of PDMS. As a result, much attention has been paid to enhance adhesion via generic methods such as oxidization and silanization, whereas limited methods are available to fine-tune the adhesion between contacting surfaces of PDMS and a solid. For example, studies have demonstrated moderate adhesion enhancement between PDMS and a solid substrate by attaching end-functionalized PDMS chains [1]; however, a full understanding of the role of polymer brushes in adhesion is lacking, particularly when the brush chemistry is different from that of the opposite contacting surface.

At the NIST Combinatorial Methods Center, a high-throughput methodology for fabricating polymer brush libraries would be extremely valuable. These brush libraries having well-defined and spatially varying structures were then integrated with our combinatorial adhesion measurement platforms to unravel the complexity of adhesion between two surfaces. In this report, we demonstrated several examples in which specific polymer brush architectures were able to control and enhance adhesion; conversely, some brush architectures were able to diminish unwanted adhesion hysteresis.

Experimental [2]

Fabrication of polymer brush libraries. Surface-initiated atom transfer radical polymerization (ATRP) was performed to graft step-wise gradients of brushes of poly(hydroxyethyl methacrylate) (HEMA) varying in thickness. Two samples were prepared in parallel (i.e., in the same reaction flask): one sample was prepared on the surface of a quartz slide, which was used as a transparent substrate in adhesion measurements, and the other was prepared on the surface of a silicon wafer, which served as a reference sample for brush characterization via ellipsometry [3, 4].

Homopolymer brush libraries can be used directly to study interfacial adhesion, or these brushes can be chain-extended to form block copolymer brushes. Two forms of block copolymer brushes of HEMA and *n*-butylmethacrylate (BMA) were synthesized to form poly(HEMA) (PHEMA) and poly(BMA) (PBMA) block copolymers on the surface. In one case, the thickness of the bottom block of PHEMA was held fixed at a constant thickness, while the top block of PBMA was varied step-wise. In the other case, the thickness of the bottom PHEMA block was varied while the PBMA thickness was fixed at a constant. PHEMA brushes were also grafted from the surface of PDMS following a procedure similar to that on the rigid substrates. PDMS grafted with PHEMA was subject to different solvent treatments prior to each adhesion test in order to study the change in adhesion induced by solvent exposure. In addition, a uniform comb-shaped brush of PDMS was synthesized by ATRP in an aqueous environment to study the effect of polymer chain architecture on adhesion.

Adhesion measurements. Adhesion of PDMS to a solid substrate was measured on a custom-built axisymmetric adhesion test apparatus, which consisted of an inverted microscope (Leica DMIRE2) equipped with a programmable *x*-*y* stage, a CCD camera (Hamamatsu Photonics), an IW-812 piezoelectric nanopositioner (Burleigh Instruments), a load sensor (Sensotec) attached in-line between the lens and actuator shaft to monitor the overall system load, and a fiber optic displacement sensor (Phltech) mounted above the translation stage holding the contacting lens [5, 6]. LabView (National Instruments) software was used to build an interface directly between the computer, image software and instrumentation. The LabView program controlled the actuator and data acquisition, while indirectly coordinating image collection and microscope stage movement through Image Pro (Media Cybernetics) software. During each adhesion test, a PDMS lens having a radius of 5 mm was stepped into contact with the polymer grafted substrate with an increment of 1.0 μm per step at an interval of 30 s. When a maximum load of 1.5 g was reached, the PDMS lens was released from the surface at the same rate. The displacement of PDMS lens, the contact area between the lens and substrate, and the load were measured. These measured values were used to calculate the strain energy release rate, *G*, as a function of contact area [7].

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Results and Discussion

The variation of adhesion between PDMS and the quartz surface grafted with homogeneous PHEMA brushes with different thickness was insignificant, indicating that such adhesion is independent of the thickness of the polymer brush. The adhesion of PDMS to the PHEMA brush, however, was substantially stronger than that of other polymer brushes such as PMMA and PBMA that lack potential hydrogen-bonding sites in the backbone, implying that hydrogen bonding between PDMS and PHEMA is the main contributor to the observed strong adhesion. Based upon this observation, we chose to introduce a second block of PBMA, whose adhesion to PDMS is much weaker than that of PHEMA, to effectively screen the hydrogen-bonding sites of the PHEMA. In addition, because PHEMA and PBMA preferentially interact with different solvents, it was expected that the adhesion could be further tuned by treating the diblock polymer brush with different solvents in sequence [4, 8], leaving the preferred segments on the top of the surface to directly contact with the PDMS lens during the adhesion test.

Our results show that the presence of a small fraction of PBMA on the top of the PHEMA block was sufficient enough to regulate the adhesion, which decreased with the increase in PBMA thickness. When the thickness of with respect to that of PHEMA exceeded a particular threshold, PBMA dominated the surface composition, thus causing the surface to lose its ability to adjust the adhesion. Meanwhile, at an optimum thickness ratio of PBMA to PHEMA, the adhesion strength was switched from strong PHEMA/PDMS adhesion to the weak PBMA/PDMS adhesion by treating the substrate with N, N-dimethylformamide (DMF) and toluene, respectively. Such switchability in adhesion can be understood by the fact that DMF prefers PHEMA thereby bringing PHEMA segments up to the top surface of the brush, whereas toluene prefers PBMA thus keeping PBMA segments dominant at the interface. At present, we are investigating the correlation between adhesion strength and block copolymer composition, i.e., the thickness of each block and the ratio of two.

Furthermore, we examined the adhesion between untreated PDMS and PDMS grafted with PHEMA brushes. A reversible change in adhesion was observed in response to a cyclic sequence of solvent treatments of the PHEMA-grafted PDMS substrate with water, acetone, toluene, and water. The reversibility of adhesion was attributed to the relocation of flexible PDMS chains under exposure to different solvent, allowing more PDMS chains to move towards the utmost outer layer of the surface when a preferred solvent was used.

Besides the fine-tuning of adhesion via block copolymer brushes, we find a substantial diminishment in adhesion hysteresis of PDMS to a quartz surface after a comb-shaped PDMS brush was grafted from the surface of quartz. Currently, we are fabricating libraries of comb-shaped PDMS brushes with variations in arm length of

PDMS for a better understanding of the effect of brush architecture on adhesion hysteresis.

Conclusions

Three polymer brush architectures were discussed which impart a wide range of control over the adhesion of PDMS to a substrate. First, regulation of strong adhesion of PDMS to HEMA-grafted rigid substrates was achieved by the chain-extension of PBMA block of various thickness on the top of PHEMA along with the proper solvent treatment of the brush-grafted substrate. Secondly, control over adhesion between PDMS and PDMS was realized by solvent treatment of PDMS on which a PHEMA brush was grafted. Thirdly, the adhesion hysteresis of PDMS to a solid substrate was diminished by grafting a comb-shaped PDMS brush to the surface.

References

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