

# Precise Design of Antifouling, Intelligent Adhesion Surfaces through Polyelectrolyte Brush Immobilization

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Since surfaces and interfaces of soft materials play an important role in various technological applications, precise control of soft interfaces would greatly promote the innovation of materials science and technology. Hydrophilic polymers show unique functionality at various soft interfaces. In this study, high-density hydrophilic polymer brushes nano-coatings were prepared on Si-wafer and various substrates by surface-initiated controlled radical polymerization.<sup>1-3</sup> Chain conformation at liquid/solid liquid/solid interface was characterized by neutron reflectivity.<sup>4</sup> Applications of polymer brushes as structural nano-coatings such as super hydrophilicity,<sup>5-6</sup> antifouling behavior,<sup>7</sup> and repeatable adhesion<sup>8</sup> are presented.

Various high-density polymer brushes were prepared by surface-initiated controlled radical polymerization from immobilized initiator.<sup>1</sup> Surface wettability of polymer brushes was discussed based on the conventional static and dynamic contact angles measurements of water, diiodomethane, hexadecane in air, and captive bubble measurement in water. Surface free energy was estimated by Owens & Wendt equation. Polyacrylate brush with perfluoroalkyl chain gave a hydrophobic surface, whereas poly(vinyl alcohol), poly(2,3-dihydroxypropyl methacrylate), and poly(oligo ethylene glycol methacrylate) brushes showed lower contact angle of water. Further hydrophilic surface was obtained by polyelectrolyte brushes, such as poly(sodium methacrylic acid) (PMANa), poly(2-methacryloyloxy ethyltrimethylammonium chloride) (PMTAC), poly(3-sulfopropyl methacrylate potassium salt) (PSPMK), poly[4-{dimethyl(2'-methacryloyloxy ethyl)ammonio}butanoate], poly[3-{dimethyl(2'-methacryloyloxyethyl)ammonio}propanesulf

onate] (PMAPS), poly(2-methacryloyloxyethyl phosphorylcholine) brushes. Polyelectrolyte brushes repelled both of air bubble and hexadecane droplet in water indicating excellent antifouling property.

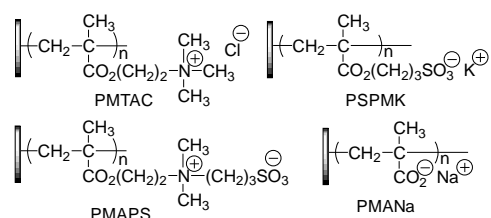


Figure 1. Chemical structures of polyelectrolyte brushes

The ionic interaction between oppositely charged polyelectrolytes is an attractive and promising adhesion force. Repeatable adhesion and debonding between cationic and anionic polymer brush substrates were demonstrated using an aqueous salt solution and deionized water. As shown in Figure 2(a), 2  $\mu\text{L}$  of deionized water was placed on a brush-immobilized silicon substrate and then another substrate was pressed onto it under a constant load of 4.9 N at 298 K. The contact area of the substrates was maintained at 5

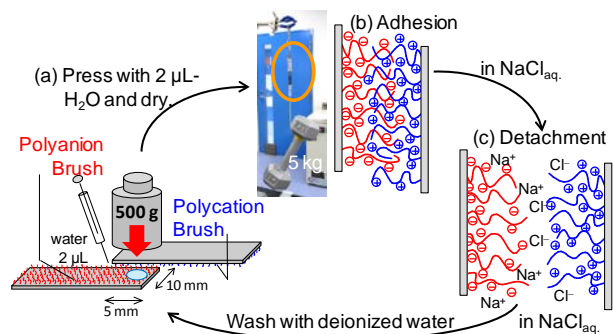


Figure 2. Schematic view of (a) adhesion process of cationic PMTAC and anionic PSPMK brushes, (b) the bonded substrate hanging a 5 kg dumbbell, and (c) detachment of oppositely charged polyelectrolyte brushes in 0.5 M NaCl aqueous solution.

$\times 10 \text{ mm}^2$ . After 2 h of dry, the adhesion strength was evaluated by measuring the lap shear adhesion force with a tensile tester at 298K in an ambient atmosphere.

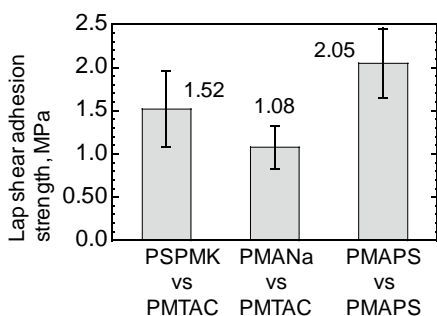


Figure 3. Lap shear adhesion strengths of pairs of Si-wafers bearing polyelectrolyte brushes at 298 K in ambient atmosphere and 50% relative humidity. The PSPMK-PMTAC and PMANa-PMTAC brushes were joined with 2- $\mu\text{L}$  water at 298 K and air dried. PMAPS brushes were joined in hot water at 333 K and air dried.

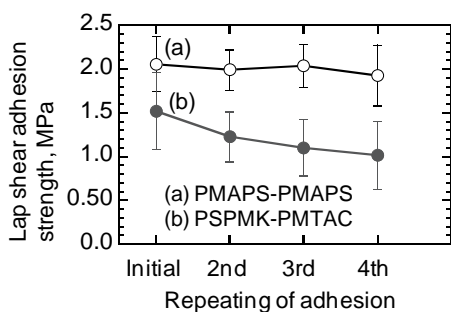


Figure 4. (a) The lap shear adhesion strength of rebonded Si-wafers with PMAPS brush after the debonding in water at 333 K. One adhesion cycle included adhesion in water at 333 K and air dried at 298 K for 3 h, and debonding by hanging a 100 g weight in water at 333 K. (b) The Lap shear adhesion strength of rebonded substrates bearing PSPMK and PMTAC brushes after the debonding in a 0.5 M aqueous NaCl solution. For (b), one adhesion cycle included adhesion, debonding in a 0.5 M aqueous NaCl solution, a wash with deionized water, and a drying period.

The PSPMK and PMTAC brushes adhered strongly with the average adhesion strength of 1.52 MPa. Figure 3 represents the lap shear adhesion strength of Si wafers bearing PSPMK, PMTAC, and PMANa brushes. Interestingly, the bonded substrates did not separate even in deionized water hanging a 100-g weight for over 24 h. On the other hand, spontaneous detachment took place within 60 min in 0.5 M NaCl salt

aqueous solution, because the hydrated salt ions permeated the polymer chain layer at adhesion interface to screen the electrostatic interaction between brushes. After the debonded substrates were washed with deionized water to remove the salt, they readily adhered each other again, as shown in Figure 4(b).

Repeatable adhesion system was also demonstrated by zwitterionic PMAPS brush. Two prepared silicon wafers bearing poly(MAPS) brushes were joined in a hot water at 333 K under 0.098 MPa of pressure for 1 min and dried under air atmosphere for 3 h. A lap shear strength of 2.05 MPa was observed through the adhesion of brush substrates due to dipole-dipole attractive interactions between sulfobetaine units. (Figure 3) The adhering substrates were smoothly debonded in hot water at 333 K within 1 h due to swelling of PMAPS brush above an upper critical solution temperature (UCST). Figure 4(a) shows that repeatable adhesion and debonding was successfully achieved by the PMAPS brush on the substrates.

## References

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