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Kobayashi, Motoyasu
Japan Science and Technology Agency, ERATO, Takahara Soft Interfaces Project, Kyushu University

Terada, Masami
Japan Science and Technology Agency, ERATO, Takahara Soft Interfaces Project, Kyushu University

Takahara, Atsushi
Institute for Materials Chemistry and Engineering, Kyushu University | Japan Science and Technology Agency, ERATO, Takahara Soft Interfaces Project, Kyushu University

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PAPER

Reversible adhesive-free nanoscale adhesion utilizing oppositely charged polyelectrolyte brushes†

Motoyasu Kobayashi,*[a] Masami Terada[a] and Atsushi Takahara*[ab]

Two prepared silicon wafers bearing cationic and anionic polyelectrolyte brushes were joined with 2 μL of water under 0.098 MPa of pressure at room temperature. The bonded area was fixed at 5×10 mm^2. A lap shear strength of 1.52 MPa was achieved through the adhesion of poly[2-(methacryloyloxy)ethyl trimethylammonium chloride] and poly(3-sulfopropyl methacrylate potassium salt) brush substrates due to electrostatic attractive interactions between the positively and negatively charged polymers. In contrast, the lap shear strength of bonded polymer brushes with like charges was only 0.027–0.072 MPa. The polyelectrolyte brushes remained on the substrates even after their separation in the lap shear test; and the brush substrates readhered in the presence of a small amount of water. Furthermore, the adhering substrates were smoothly debonded in aqueous NaCl solution due to the electrostatic interaction of the hydrated salt ions. However, the substrates did not separate in deionized water. In summary, reversible nanoscale adhesion was achieved using oppositely charged polyelectrolyte brushes combined with aqueous solution.

Introduction

Adhesion techniques using a simple, clean, nontoxic, and environmentally benign process at a nanoscale thickness are necessary for the advancement of nanodevices, nano- to microanalysis systems, and microfluidic devices. Alternatives to conventional adhesives or glues include biomaterial-based adhesives or micropatterned elastomeric surfaces with pillars utilizing van der Waals forces. For example, Messersmith *et al.* proposed a bioadhesive inspired by the composition of adhesive proteins in mussels, 3,4-dihydroxyphenyl-L-alanine (L-DOPA).[1,2] Micro-sized pillars or micropatterned surfaces with higher aspect ratios inspired by the toe pads of geckos have been investigated to understand the adhesion mechanism, which is based on van der Waals and capillary forces.[3–5] Self-welding or interdiffusion between miscible polymer/polymer interfaces at temperatures below the bulk-glass transition temperature has also been examined because these processes are chemically stable, low-cost, and simple nanoscale adhesion methods for soft materials.[6–9]

Ionic interactions between oppositely charged polyelectrolytes also present an attractive and promising adhesion force.

Polyelectrolyte complexes[10] formed between positively and negatively charged polymers have already be utilized in layer-by-layer assembly[11] as a novel adhesive layer.[12,13] Neoh and coworkers prepared surface-grafted polyelectrolytes on ozone- or argon-plasma-pretreated polymer films, such as polyaniline emeraldine base,[14] polytetrafluoroethylene,[15] low-density polyethylene,[16,17] and polycarbonate,[18,19] by photolytically or thermally induced graft copolymerization of 1-vinylimidazole[20] or methacrylate monomers, such as acrylic acid, styrenesulfonic acid sodium salt, 3-(N-2-methacryloyloxyethyl-N,N-dimethyl) ammonium propane sulfonate (MAPS), N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)ammonium betaine, and 3-sulfopropyl methacrylate potassium salt (SPMK).[21] Two polyelectrolyte-grafted films were joined by direct contact in the presence of water and subsequent drying. A lap shear adhesion strength as high as 3.40 MPa (=N mm^{-2}) was achieved between two polyaniline films grafted with poly(MAPS)[22] due to the strong interchain electrostatic interaction arising from the amphoteric side chains of the ammonium cation species and the sulfonate anion species. Photolytically or thermally induced graft polymerization is a conventional technique for fabricating surface-grafted polymers on a film or substrate. However, it is difficult to control the molecular weight, the graft density, and the thickness of the grafted polymer layer.

Over the last decade, well-defined surface-grafted polymers with sufficiently high graft density, called polymer brushes,[23,24] have been prepared *via* surface-initiated polymerization combined with controlled/living radical polymerization, such as atom transfer radical polymerization (ATRP).[25] Generally, polymer brushes are grown from surface initiating sites that are

[a]*Japan Science and Technology Agency, ERATO, Takahara Soft Interfaces Project, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan. E-mail: motokoba@cstf.kyushu-u.ac.jp*

[b]*Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan. E-mail: takahara@cstf.kyushu-u.ac.jp; Fax: +81-92-802-2518; Tel: +81-92-802-2517*

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immobilized on solid surfaces or substrates through covalent bonding. Therefore, the brush chains cannot be released from the substrate, even in a good solvent solution. The thickness of the brush layer is also controllable through the molecular weight of the polymer when surface-initiated polymerization proceeds in a living manner. LaSpina and Geoghegan *et al.* investigated the pH-sensitive adhesion of poly(*N*,*N*-dimethylaminoethyl methacrylate) brushes on poly(methacrylic acid) gel,[26] which was analyzed by Johnson–Kendall–Roberts experiment and neutron reflectivity measurement.

In this study, positively and negatively charged polyelectrolyte brushes approximately 100 nm thick were prepared by surface-initiated ATRP of 2-(methacryloyloxy)ethyltrimethylammonium chloride (MTAC), sodium methacrylate (MANa), and SPMK on silicon wafer bearing immobilized alkylbromides. The oppositely charged polyelectrolyte brush substrates were expected to bond strongly to each other in the presence of a small amount of water, as previously reported by Neoh.[14] In addition, we demonstrated debonding of the brush substrates in aqueous salt solution as well as readhesion with water. This is the first report of a reversible adhesive-free nanoscale adhesion with oppositely charged high-density polyelectrolyte brushes that employed environmentally benign aqueous solutions as triggers.

Experimental

Materials

Copper(I) bromide (CuBr, Wako Pure Chemicals, 99.9%) was purified through successive washes with acetic acid and ethanol then dried under vacuum. Ethyl 2-bromoisobutylate (EB, Tokyo Chemical Inc. (TCI), 98%) was dried and distilled over CaH_2 before use. Commercially available copper(II) bromide (CuBr$_2$, Wako Pure Chemicals, 99%), 2,2′-bipyridyl (bpy, Wako, 99.5%), 4,4′-dimethyl-2,2′-bipyridyl (Me$_2$bpy), 2,2,2-trifluoroethanol (TFE, Acros, 99.9%), 2-propanol (TCI, 99.5%), ascorbic acid (Aldrich), SPMK (Polysciences Inc., 98%), and MANa (Wako, 98%) were used without additional purification. Commercially available MTAC aqueous solution (Aldrich, 80%) was concentrated using a vacuum pump to remove water, and then dissolved in TFE. The MTAC/TFE solution was purified by alumina column chromatography and membrane filtration. The surface initiator, (2-bromo-2-methyl)propionyloxy hexyltrimethoxysilane (BHM), was synthesized by hydrosilylation of 5′-hexenyl 2-bromoisobutylate treated with trimethoxysilane in the presence of a Karstedt catalyst. The BHM monolayer was immobilized on silicon wafers or glass plates (10 × 40 × 0.5 mm^3) in dry toluene at 298 K for 4 h. Deionized water was purified using the Arium 611 UV system (Sartorius Stedim Biotech). The chemical structure of the polyelectrolyte brushes is illustrated in Fig. 1.
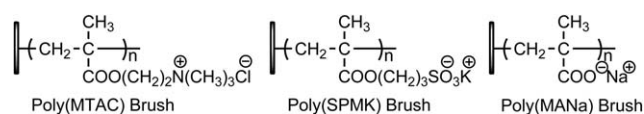

Fig. 1 Chemical structures of the polyelectrolyte brushes.

Brush preparation

The typical protocol was followed for surface-initiated ATRP on MTAC in TFE.[27] Briefly, a few sheets of the BHM-immobilized silicon wafers, 4.0 mL of MTAC/TFE solution (2.0 M), and 0.30 mL of 2-propanol were charged in a well-dried glass tube with a stopcock then degassed using a freeze–thaw process repeated three times. A catalyst solution containing CuBr (0.020 mmol), bpy (0.040 mmol), and EB (0.020 mmol) diluted with TFE was injected into the monomer solution. The resulting reaction mixture was degassed again by repeated freeze–thaw cycles to remove the oxygen and then stirred in an oil bath at 333 K for 16 h under argon, which simultaneously generated poly(MTAC) brushes from the substrate and free (unbound) poly(MTAC) from EB. The reaction was stopped by opening the glass vessel to air at 293 K. The reaction mixture was poured into THF to precipitate the free polymer and unreacted MTAC. The silicon wafers were washed with TFE using a Soxhlet apparatus for 12 h to remove the free polymer adsorbed on the surface. The wafers were then dried under reduced pressure. The poly(SPMK)[28] brushes were prepared by surface-initiated ATRP of SPMK (36.5 mmol) from a BHM-immobilized silicon wafer in a water (6.0 mL) and methanol (15.0 mL) mixture with CuBr$_2$ (0.050 mmol), Me$_2$bpy (0.010 mmol), and ascorbic acid (0.050 mmol) under argon atmosphere at 298 K for 16 h. The resulting substrates were washed with water for 12 h using a Soxhlet apparatus and ethylene glycol. The synthesis procedure for the PMANa brushes was similar to that reported by Huck[29] and Klok *et al.*[30] CuBr (0.020 mmol), Me$_2$bpy (0.040 mmol), and BHM-functionalized silicon wafers were introduced into a glass tube, which was then degassed by seven cycles of vacuum pumping and flushing with argon. MANa (70 mmol) was dissolved in water (17.5 mL) to obtain 2.20 M aqueous solution and the pH was adjusted to 8.4 by the addition of a 0.1 M aqueous sodium hydroxide solution. The monomer solution was degassed by applying three freeze–pump–thaw cycles. A portion of the MANa aqueous solution (7.0 mL) was transferred to the argon-purged copper catalyst, and degassing continued for three additional freeze–pump–thaw cycles. Surface-initiated polymerization was performed at 298 K for 3 h under an argon atmosphere. The substrates were washed with hot water for 12 h using a Soxhlet apparatus.

Characterization

Size-exclusion chromatography (SEC) of the free soluble poly(MTAC) was performed to determine the number-average molecular weight (M_n) and molecular weight distribution (MWD) with a Shimadzu HPLC system connected to three Tosho polystyrene gel columns (1 × G3000PW$_{XL}$-CP + 2 × G5000PW$_{XL}$-CP) and equipped with a multi-angle light-scattering detector (MALS; Wyatt Technology DAWN-EOS, wavelength: $\lambda = 690$ nm), and an acetic acid (500 mM) aqueous solution containing sodium nitrate (200 mM) was used as an eluent at a rate of 0.6 mL min^{-1}. The thickness of the brush layers was determined with a MASS-102 spectroscopic ellipsometer (Five Lab Co.) equipped with a Xenon arc lamp (wavelength 380–890 nm) at a fixed incident angle of 70°. XPS measurement was performed with an XPS-APEX (Physical Electronics Co.

Ltd.) using a monochromatic Al-Kα X-ray source at a power of 150 W and a pressure of 1×10^{-6} Pa. All XPS data were collected at a takeoff angle of 45°, and a low-energy (25 eV) electron flood gun was used to minimize sample charging. The survey spectra (0–1000 eV) and the high-resolution spectra of the C_{1s}, O_{1s}, N_{1s}, S_{2p}, K_{2p}, Cl_{2p}, and Si_{2p} regions were acquired at analyzer pass energies of 100.0 and 25.0 eV, respectively. The X-ray beam was focused on an area with a diameter of approximately 0.2 mm.

During the adhesion process, 2 μL of deionized water was injected onto a brush-immobilized rectangular silicon substrate and then another substrate was pressed onto it under a constant load of 4.9 N at 298 K and 55% relative humidity. The contact area of the substrates was maintained at 5×10 mm^2, unless otherwise specified. After 2 h of drying time, a supporting aluminium plate ($10 \times 30 \times 0.3$ mm^3) was bonded to both ends of the lapping substrates using a cyanoacrylate-type instant glue to prepare an easy-to-clip sample for the lap shear test. The adhesion strength was determined by measuring the lap shear adhesion force with a tensile tester (Shimadzu EZ-Graph) at 298 K in an ambient atmosphere. As shown in Fig. 2(b), the sample was held at both ends of the aluminium plates with two mechanical chucks connected to a load cell and a tester base anchor. The crosshead speed was set to 1 mm min^{-1} in tensile mode. The lap shear strength was defined as the force corresponding to the breaking point divided by an adhesion area of 50 mm^2. To measure the adhesion holding time, a specimen prepared as previously described was attached to a hanging weight of 100 g (3.0 cm^3 in volume) and slowly immersed in a 0.5 M aqueous NaCl solution at 298 K, as shown in Fig. 2(c). We measured the time until the bonded brush substrates debonded and separated from each other in a graduated cylinder filled with an aqueous salt solution.

Results and discussion

Three types of polyelectrolyte brushes, poly(MTAC),[27] poly(SPMK),[28] and poly(MANa),[29,30] were prepared with surface-initiated ATRP on alkylbromide-immobilized silicon wafers, as shown in Fig. 1. The M_n and MWD of free poly(MTAC) were 383 000 and $M_w/M_n = 1.18$, respectively. The M_n of the surface-grafted poly(MTAC) was also measured by SEC after the isolation of grafted polymer cleaved from the substrate surface. We confirmed both ATRP from the surface-immobilized

initiator and sacrificial free initiator in a solution proceeded in a controlled manner to give polymers with almost same M_n.[27,31] The thickness of the poly(MTAC) brush was approximately 115 nm, and the thickness of the poly(SPMK) and poly(MANa) brushes was approximately 150 nm. Based on the thickness and M_n, the graft density of the poly(MTAC) brush was estimated at 0.20 chains nm^{-2}.

Two silicon wafers, one prepared with cationic and one with anionic polyelectrolyte brushes, were joined in a 5×10 mm^2 contact area using 2 μL of water and pressed under a pressure of 0.098 MPa. Polymer brushes with anionic or cationic side chains show expanded chain conformations in pure water due to the electrostatic repulsions among the ionic side chains. After 2 h of adhesion time, followed by drying at 298 K in ambient air, the adhesion strengths of the samples were determined by measuring the lap shear adhesion force with a tensile tester at 298 K, as shown in Fig. 2(b). Fig. 3 represents the lap shear adhesion strength between two silicon substrates immobilized with polymer brushes after 2 h of adhesion with 2 μL of water. For the combination of poly(SPMK) and poly(MTAC) brushes, the average adhesion strength reached 1.52 ± 0.43 MPa. This value was weaker than typical adhesion strength of commercially available adhesives (10–30 MPa), however, it would be sufficiently useful adhesion strength for many applications because the adhered brush substrates with 1 cm^2 adhesion area could lift up a weight of ca. 15 kg. The right side Y axis in Fig. 3 stands for the tensile load (kg) per 1 cm^2 adhesion area calculated from the
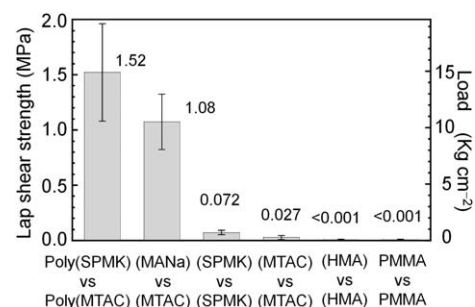

Fig. 3 Lap shear adhesion strengths of pairs of polyelectrolyte brushes—immobilized on silicon substrates at 298 K in an ambient atmosphere and 55% relative humidity.
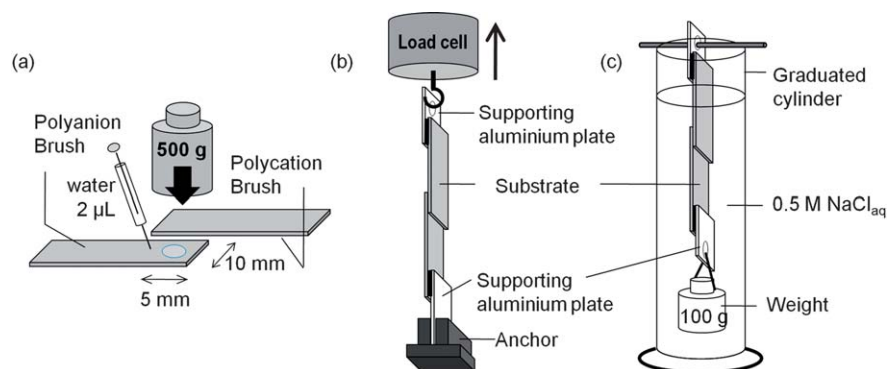

Fig. 2 Schematic view of (a) the adhesion process of the polyelectrolyte brushes, (b) the lap shear test setup using a tensile tester, and (c) the holding adhesion test in 0.5 M aqueous NaCl solution.

lap shear strength (MPa). The lap shear adhesion strength between the poly(MANa) brush and poly(MTAC) brush substrates was 1.08 ± 0.25 MPa. The sulfonate anion group of SPMK apparently interacted more strongly with the ammonium cation group in MTAC than with the carboxylic acid in MANa. The adhesion between two polymer brushes bearing the same polarity, such as combination of poly(SPMK)/poly(SPMK) brushes and poly(MTAC)/poly(MTAC) brushes, was also shown in Fig. 3. However, the lap shear strength of bonded polymer brushes with the same charges was only 0.027–0.072 MPa, which was far below that observed between opposite charged brushes. The lower adhesion strength between two identical poly(SPMK) brush substrates is due to the lack of electrostatic attractive interaction.

As a control experiment, we prepared PMMA[32] and poly (hexyl methacrylate) (HMA) brush substrates. The dry thickness of these polymer brushes was 100–120 nm. The PMMA brushes were joined in the presence of a small amount of water and dried at 298 K for 2 h in air. However, the adhesion of the PMMA brush sample was too weak for the lap shear adhesion strength to be measured. The sample for the poly(HMA) brush also easily debonded before we began the lap shear test. Tanaka et al. previously reported that PMMA spin cast films (not brushes) adhered with 5 μL of water with 0.1–0.2 MPa lap shear adhesion strength due to the swelling of the polymer segments at the surface as well as successive entanglement of the surface–polymer chains during the drying step. In contrast, the interdiffusion of opposing PMMA brush chains was restricted due to the high graft density. The adhesion of poly(HMA) brushes wetted with toluene instead of water was also attempted to enhance the interdiffusion or entanglement between opposite brush chains, but the adhesion strength was lower than 0.01 MPa.

On the other hand, poly(MTAC) and poly(SPMK) brushes 10–20 nm thick hardly adhered; i.e., the adhesion strength was lower than 0.01 MPa. Due to the high graft density, the substrate surface must be sufficiently covered with ionic functional groups even though the brush thickness was less than 10 nm. These results suggested that the adhesion was affected not only by electrostatic interactions, but also by the molecular weight or chain length of the brushes. We predicted that the electrostatic interactions contributed greatly to the adhesion process of the polyelectrolyte brushes. However, the opposite brush chains might also interdiffuse at the interface, leading to enhanced adhesion strength.

The delaminated surface of the polyelectrolyte brushes after the lap shear test was analyzed with XPS. Fig. 4 shows the wide-scan XPS spectra of the poly(MTAC) brush and poly(SPMK) brush surfaces before and after the lap shear test. The XPS spectrum of the poly(MTAC) brush surface after the lap shear separation had peaks at C_{1s}, N_{1s}, O_{1s}, and Cl_{2p}. The atomic ratio after the lap shear test was consistent with the MTAC component, except for the K_{2s} peak. For the poly(SPMK) brush, Cl_{2p} and N_{1s} peaks appeared after the lap shear test along with the original SPMK components carbon, oxygen, sulfur, and potassium, which probably appeared because a trace amount of the poly(MTAC) chain was transferred to the poly(SPMK) brush surface when the substrates were separated. No significant changes in the thickness of poly(MTAC) and poly(SPMK) brushes were observed by an ellipsometer after the lap shear test.
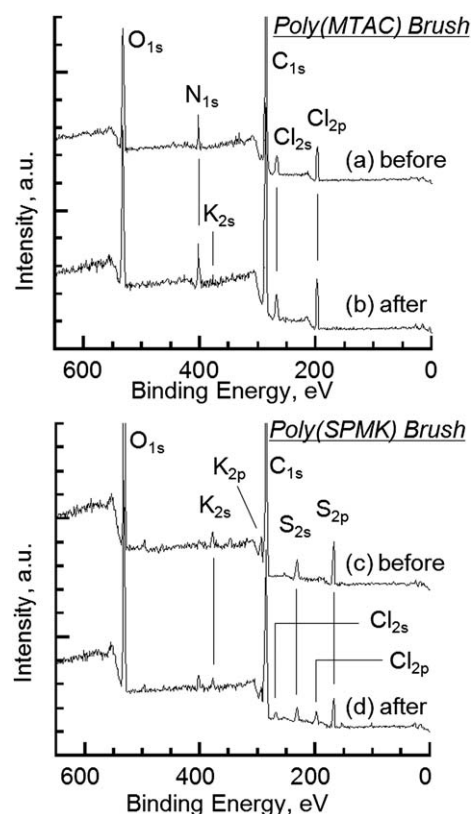

Fig. 4 XPS spectra of the poly(MTAC) brush surface (a) before and (b) after the lap shear test, and the poly(SPMK) brush surface (c) before and (d) after the lap shear test.

Therefore, most of the polyelectrolyte brushes were retained on each substrate after the lapped junction was delaminated, and adhesion failure occurred predominantly at the interface of the polyanion brush and the polycation brush.

The lap shear adhesion strength of the bond between poly (MTAC) and poly(SPMK) brushes, 1.52 MPa, was lower than the adhesion strength of 2–3 MPa reported by Neoh et al. We believe that the surface-grafted polyelectrolytes used by Neoh's group, which were prepared by thermally induced free radical polymerization on argon-plasma pretreated poly(aniline) films, sufficiently migrated or diffused from one surface side to another and became entangled due to the relatively low graft density as well as the annealing above 373 K during the adhesion process. In contrast, the graft density of our polymer brushes, prepared by ATRP, was relatively high. Interdigitation of oppositely charged polymer brushes would occur to some extent in an aqueous environment. However, the interdiffusion might not be extensive enough for entanglement. In addition, the XPS spectra of the brush surfaces after the lap shear test revealed that potassium and chloride counter ions remained in the brush layers. These free counter ions could have led to interactions between the ammonium cations and sulfonate anions attached to the polymer chains, reducing the adhesion strength.

Because the polymer brushes remained on the substrate after the lap shear test, we predicted that the brush substrates would be able to rebond with a small amount of water. Fig. 5 shows the follow-up records on the lap shear adhesion strength of a joint
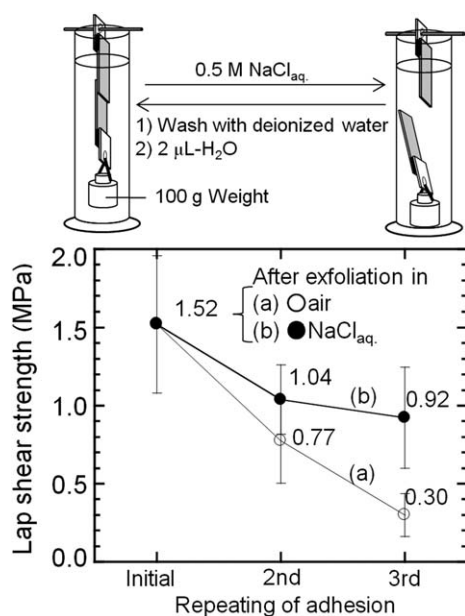
Fig. 5 The lap shear adhesion strength of rebonded substrates with poly(SPMK) and poly(MTAC) brushes after (a) the lap shear test in air and (b) exfoliation in a 0.5 M aqueous NaCl solution. The brush substrates were bonded with 2 μL of water and dried at 298 K for 2 h in air. For (b), one adhesion cycle included adhesion with water, exfoliation in a 0.5 M aqueous NaCl solution, a wash with deionized water, and a drying period.

consisting of samples of poly(MTAC) and poly(SPMK) brushes through repeated cycles of bonding by interfacial contact with water and separation in the lap shear test in air. The adhesive strength decreased in a stepwise manner from 1.52 MPa to 0.77 ± 0.27 and 0.30 ± 0.13 MPa with each rebonding process. However, the brushes were still present on each substrate. Although the reason for the reduction in adhesive strength

remains unclear, the formation of potassium chloride salts at the brush interface, the nanoscale decomposition of the brushes, and the adsorption of minute amount of contamination from the atmosphere are possible causes.

The retention of adhesion in water was examined by hanging a 100 g weight at the bottom of a sample, as shown in Fig. 2(c). Interestingly, once two substrates bearing oppositely charged polymer brushes were bonded, debonding did not occur despite the fact that the bonded substrates were immersed in deionized water for over 24 h. Self-delamination was also observed within 10–60 min when the brush substrates were immersed in a 0.5 M aqueous NaCl solution, because the hydrated salt ions permeated the adhesion interface and disrupted the electrostatic interactions between the brushes accompanying swelling of the interface. Reduction of the interaction between oppositely charged PMTAC and PSPMK brushes in aqueous salt solution was reported by Spruijt et al. using dynamic force spectroscopy.[33] After the debonded substrates were washed with deionized water to remove salts, they readily rebonded. As shown in Fig. 5, the lap shear adhesion strength of the rebonded substrates was 1.04 ± 0.22 MPa, relatively close to the initial bond strength. Even after repeated bonding with deionized water and debonding in salt aqueous solution three times, the lap shear adhesion strength was still 0.92 ± 0.32 MPa. The polymer brushes were likely cleaned by the water and salt aqueous solution during the debonding and readhesion process. Therefore, we concluded that the potassium chloride salt formed by MTAC and SPMK, as well as possible impurities adsorbed from the atmosphere, were washed out, maintaining the strong adhesion strength at the brush interface. Fig. 6 shows the AFM images of both brush layers before and after the adhesion and debonding process in salt aqueous solution. Surface morphologies of polymer brush surface can be seen in Fig. 6(a), (b), (e) and (f). The root mean square (rms) of the surface roughness of the polymer brushes slightly increased after adhesion and debonding. For example, the rms values of the poly(MTAC) brush surface in a 10 × 10
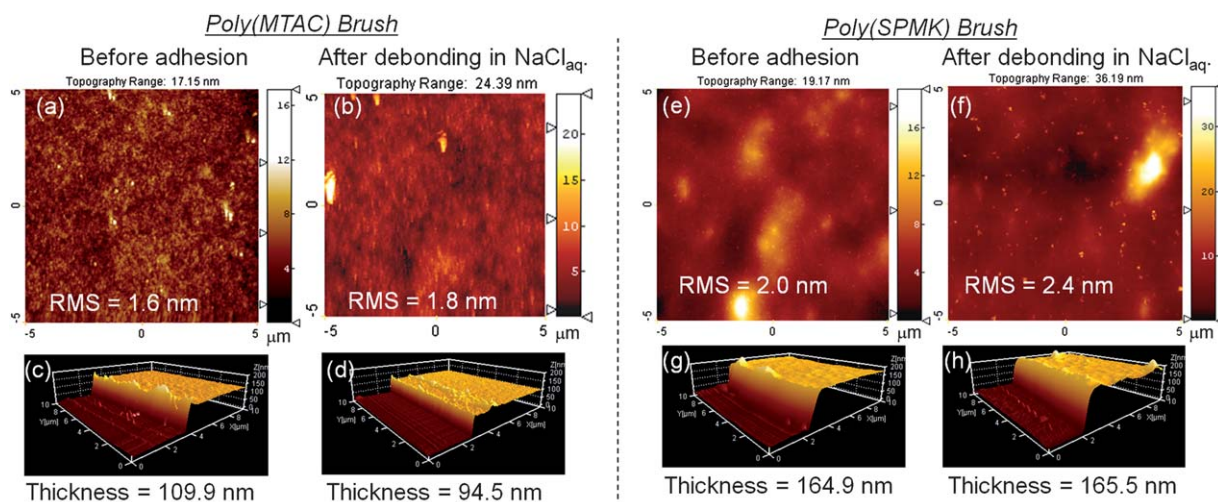

Fig. 6 AFM images of (a–d) poly(MTAC) brush and (e–h) poly(SPMK) brush surfaces before adhesion and after adhesion and debonding in 0.5 M NaCl aqueous solution. The rms values were measured in 10 × 10 μm² area. The brush layers were partially scratched in advance to estimate the brush thickness. (c and d) and (g and h) are 3-D images at the boundary of brush and scratched area (silicon surface). AFM was carried out in air (35% relative humidity).

Table 1 Lap shear adhesion strength of various substrates bearing poly (SPMK) and poly(MTAC) brushes

Substrates with polymer brushes		Lap shear adhesion strength/MPa
Poly(MTAC)	Poly(SPMK)	
Glass	Glass	0.99 ± 0.50
Glass	Silicon	1.07 ± 0.48
Silicon	Glass	0.86 ± 0.51
Stainless steel[a]	Silicon	0.11 ± 0.08

[a] SUS304 plate (thickness = 0.5 mm).

μm^2 scanning area before and after adhesion were 1.6 and 1.8 nm, respectively. Fig. 6(c), (d), (g) and (h) show 3D images of the brush layers that were partially scratched in advance with a needle to estimate the brush thickness. Although the thickness of the poly(MTAC) brush was decreased slightly after the debonding from 106 nm to 94 nm, no significant change was observed in the thickness of the poly(SPMK) brush throughout the adhesion and debonding process. These results suggested that adhesion and debonding with deionized water and an aqueous salt solution are alternately reversible processes that do not result in any damage to the brushes.

Because polymer brushes can be immobilized on various substrates, we explored the adhesion of heterogeneous materials using oppositely charged brushes. Polyelectrolyte brushes were prepared on glass, stainless steel, and silicon wafers through surface-initiated ATRP. Table 1 shows the lap shear adhesion strengths of the poly(SPMK) and poly(MTAC) brushes on the various substrates. The adhesion strength between the poly (SPMK)-grafted glass substrate and the poly(MTAC)-grafted silicon wafer was 1.07 ± 0.48 MPa. The reverse combination of these brushes led to an adhesion strength of 0.86 ± 0.51 MPa, which was lower than the adhesion strength between two silicon wafers. This reduction was likely due to the surface roughness of the glass used, which was approximately 1–50 nm in a 10×10 μm^2 area. The stainless steel surface also had a large degree of roughness. Therefore, the polyelectrolyte brushes on the glass and stainless steel substrates could not efficiently make contact with the opposite brushes, resulting in a lower adhesion strength.

In conclusion, we demonstrated reversible nanoscale adhesion based on electrostatic interactions between oppositely charged polyelectrolyte brushes combined with deionized water or an aqueous salt solution. Positively and negatively charged polyelectrolyte brushes approximately 100 nm thick were prepared by the surface-initiated ATRP of MTAC and SPMK on silicon wafers, glass and stainless steel substrates. Two substrates with oppositely charged polyelectrolyte brushes bonded strongly to each other with a small amount of deionized water to yield a lap shear adhesion strength of 1.52 MPa. The brushes also smoothly debonded in aqueous NaCl solution and each brush layer was maintained on the substrate after separation. These reversible adhesion and debonding processes can be developed into novel adhesive using environmentally friendly aqueous solvents.

References

1 H. Lee, B. P. Lee and P. B. Messersmith, *Nature*, 2007, **142**, 338–344.
2 H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426–430.
3 G. Huber, H. Mantz, R. Spolenak, K. Mecke, K. Jacobs, S. N. Gorb and E. Arzt, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 16293–16296.
4 C. Greiner, A. del Campo and E. Arzt, *Langmuir*, 2007, **23**, 3495–3502.
5 A. Mahdavi, L. Ferreira, C. Sundback, J. W. Nichol, E. P. Chan, D. J. D. Carter, C. J. Bettinger, S. Patanavanich, L. Chignozha, E. Ben-Joseph, A. Galakatos, H. Pryor, I. Pomerantseva, P. T. Masiakos, W. Faquin, A. Zumbuehl, S. Hong, J. Borenstein, J. Vacanti, R. Langer and J. M. Karp, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 2307.
6 Y. Yang, C. Zeng and L. J. Lee, *Adv. Mater.*, 2004, **16**, 560–564.
7 X. Zhang, S. Tasaka and N. Inagaki, *J. Polym. Sci., Part B: Polym. Phys.*, 2000, **38**, 654–658.
8 K. Akabori, D. Baba, K. Koguchi, K. Tanaka and T. Nagamura, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 3598–3604.
9 T. Date, T. M. Ishikawa, K. Hori, K. Tanaka, T. Nagamura, M. Iwahashi and T. Serizawa, *Chem. Lett.*, 2009, 660–661.
10 A. F. Thünemann, M. Müller, H. Dautzenberg, J.-F. Joanny and H. Löwen, *Adv. Polym. Sci.*, 2004, **166**, 113–171.
11 Y. Lvov, G. Decher and H. Möhwald, *Langmuir*, 1993, **9**, 481–486.
12 D. Matsukuma, T. Aoyagi and T. Serizawa, *Langmuir*, 2009, **25**, 9824–9830.
13 T. Fujie, Y. Okamura and S. Takeoka, *Adv. Mater.*, 2007, **19**, 3549–3553.
14 Z. F. Li, E. T. Kang, K. G. Neoh, K. L. Tan, C. C. Huang and D. J. Liaw, *Macromolecules*, 1997, **30**, 3354–3362.
15 E. T. Kang, J. L. Shi, K. G. Neoh, K. L. Tan and D. J. Liaw, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 3107–3114.
16 H. S. Han, K. L. Tan, E. T. Kang and K. G. Neoh, *J. Appl. Polym. Sci.*, 1998, **70**, 1977–1983.
17 T. Wang, E. T. Kang, K. G. Neoh, K. L. Tan and D. J. Liaw, *Langmuir*, 1998, **14**, 921–927.
18 W. Chen, K. G. Neoh, E. T. Kang, K. L. Tan, D. J. Liaw and C. C. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 357–366.
19 E. T. Kang, K. G. Neoh, Z. F. Li, K. L. Tan and D. J. Liaw, *Polymer*, 1998, **39**, 2429–2436.
20 Z. H. Ma, H. S. Han, K. L. Tan, E. T. Kang and K. G. Neoh, *Eur. Polym. J.*, 1999, **35**, 1279–1288.
21 Y. X. Liu, E. T. Kang, K. G. Neoh, K. L. Tan, C. C. Huang and D. J. Liaw, *J. Appl. Polym. Sci.*, 1999, **74**, 816–824.
22 Z. H. Ma, H. S. Han, K. L. S. Tan, E. T. Kang and K. G. Neoh, *Int. J. Adhes. Adhes.*, 1999, **19**, 359–365.
23 A. M. Granville and W. J. Brittain, *Polymer Brushes: Synthesis, Characterization, Applications*, ed. R. C. Advincula, W. J. Brittain, K. C. Caster and J. Rühe, Wiley-VCH, Weinheim, Germany, 2004, pp. 35–50.
24 Y. Tsujii, K. Ohno, S. Yamamoto, A. Goto and T. Fukuda, *Adv. Polym. Sci.*, 2006, **197**, 1–46.
25 K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921–2990.
26 R. LaSpina, M. R. Tomlinson, L. Ruiz-Pérez, A. Chiche, S. Langridge and M. Geoghegan, *Angew. Chem., Int. Ed.*, 2007, **46**, 6460–6463.
27 M. Kobayashi, M. Terada, Y. Terayama, M. Kikuchi and A. Takahara, *Macromolecules*, 2010, **43**, 8408–8415.
28 M. Ramstedt, N. Cheng, O. Azzaroni, D. Mossialos, H. J. Mathieu and W. T. S. Huck, *Langmuir*, 2007, **23**, 3314–3321.
29 V. L. Osborne, D. M. Jones and W. T. S. Huck, *Chem. Commun.*, 2002, 1838–1839.
30 S. Tugulu, R. Barbey, M. Harms, M. Fricke, D. Volkmer, A. Rossi and H.-A. Klok, *Macromolecules*, 2007, **40**, 168–177.
31 Y. Terayama, M. Kikuchi, M. Kobayashi and A. Takahara, *Macromolecules*, 2011, **44**, 104–111.
32 H. Sakata, M. Kobayashi, H. Otsuka and A. Takahara, *Polym. J.*, 2005, **37**, 767–775.
33 E. Spruijt, M. A. Cohen Stuart and J. van der Gucht, *Macromolecules*, 2010, **43**, 1543–1550.