Water Droplets for the Symmetric Adhesion of Two Poly(methyl methacrylate) Films

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Poly(methyl methacrylate) films were prepared by annealing below their glass-transition temperatures after spin-casting and were symmetrically pressed against each other with constant pressure in air. The films successfully adhered together with only water droplets. The interfacial adhesion strength was quantitatively examined by lap–shear tests. Polymer chains swollen with water molecules caused significant entanglement and resulted in strong adhesions.

Versatile and nontoxic adhesives of nanometer thickness, which are applicable to fine and complicated architectures, are desirable for current nanotechnologies due to the technical limitations of conventional polymeric adhesives. Recently, bio-inspired adhesives that mimic marine mussels[1] and gecko feet,[2] including their combinations,[3] have been widely studied. However, the synthesis of biomolecules or the fabrication of patterned surfaces is sometimes costly and time-consuming. More recently, two polymer films were successfully adhered together by simple physical contact when the mobility of the surface–polymer chains were enhanced either at the glass-transition temperature of the film surfaces[4] or in low-pressure carbon dioxide.[5]

Meanwhile, it has been reported that water-swollen layers of atactic (at) poly(methyl methacrylate) (PMMA) films, which were prepared by thermal annealing above the glass-transition temperature (T_g), were formed beneath the water/PMMA interface, possibly due to interfacial roughening and the partial dissolution of segments at the outermost region of the films, even though water is a typical nonsolvent for PMMA.[6] We hypothesized from this observation that water-swollen layers might be potentially applicable for adhesion. Here, we report on the symmetric adhesion of two PMMA films with different histories in the presence or absence of water droplets in air. Lap–shear tests then quantified the interfacial adhesion strength. To our knowledge, this is the first study to demonstrate that water droplets can be potentially utilized as unsubstantial adhesives for polymer films.

At-PMMA ($M_n = 294 \times 10^3$, $M_w/M_n = 1.3$, $mm{:}mr{:}rr = 5{:}37{:}58$) or isotactic (it) PMMA ($M_n = 290 \times 10^3$, $M_w/M_n = 1.1$, $mm > 98\%$) (Polymer Source) films of approximately 200-nm thickness, which was determined by atomic force microscopy (SPM-9600, Shimadzu) after scratching on silicon wafers, were spin-cast from chloroform solutions ($20\,\text{mg}\,\text{mL}^{-1}$) onto gold-coated poly(ethylene terephthalate) substrates ($10 \times 10 \times 0.25\,\text{mm}^3$, Tanaka Precious Metals). The films' mean roughness was less than 1 nm (see Table S1).[7] Two substrates were adhered together under controlled pressure using Tensilon RTG-1225 (A&D) for 1 h in air at room temperature. For adhesions with water, 5 µL of water droplets were mounted onto a single film, and then another film was pressed to it within 20 s (Figure 1, left). The adhered area was fixed at $50\,\text{mm}^2$ ($5 \times 10\,\text{mm}^2$). The adhered substrates were supported by easy-to-handle substrates ($10 \times 40\,\text{mm}^2$, Color Laser Transparencies TR-3, Canon) and were subjected to lap–shear tests at a rate of 50 $\mu\text{m}\,\text{min}^{-1}$ using the aforementioned apparatus (Figure 1, middle), following a previous report.[4] The G_L values were defined as the ultimate shear load divided by the adhered area. Surface plasmon resonance (SPR) measurements for the PMMA films contacting with water before adhesion were performed with a home-made apparatus in a Kretchmann configuration at room temperature (Figure 2, left and Supporting Information).[7] Static contact angles were measured with a commercial apparatus (CA-X, Kyowa Interface Science) just after mounting 3-µL water droplets in air at room temperature.

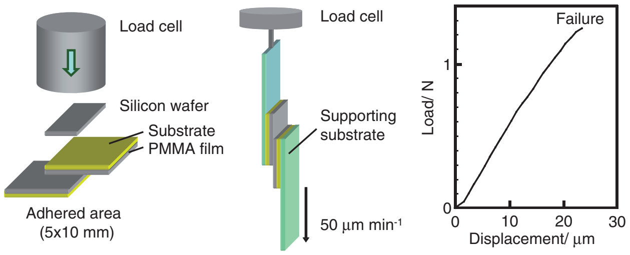

Figure 1. The adhesion method (left), the lap–shear test (middle), and a typical load-displacement curve for an at-PMMA film (right).

A typical load-displacement curve for at-PMMA films adhered with water under a pressure of 1 MPa is shown in Figure 1, right. The films were prepared under condition II (see below). The load increased monotonically with increasing displacement. The G_L values apparently increased with increasing pressure (data not shown), suggesting that the interfacial region between the two films failed when adhered under the aforementioned pressure. Therefore, the adhesions of the at-PMMA films were analyzed under the pressure. Similarly, the pressure for the it-PMMA films was determined to be 0.35 MPa.

Table 1 shows the G_L values for PMMA films adhered with or without water. The films were prepared under three different conditions. The spin-cast films were annealed in a desiccator for 1 h at room temperature (below the T_g) (condition I), under vacuum for 24 h at room temperature (condition II), and under vacu-

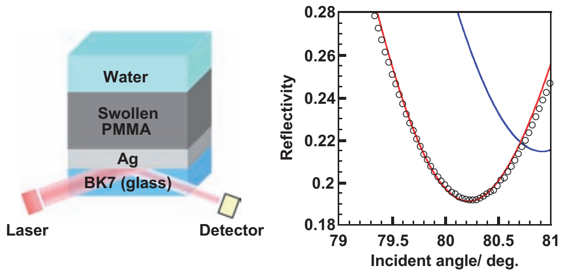

Figure 2. The SPR setup (left) and the reflectivity against incident angle for the at-PMMA film (condition II) (right). Experimental (open circles) and calculated results of a film containing no water (blue line) and 9 vol % water (red line).

Table 1. G_L values for adhered PMMA films

Polymer	Condition[a]	Water[b]	G_L/kPa[c]
At-PMMA	I	−	29 ± 4
		+	102 ± 3
	II	−	n.d.
		+	27 ± 3
It-PMMA	I	−	20 ± 16
		+	217 ± 27
	II	−	n.d.
		+	194 ± 40

[a] The details are shown in the text. [b] Minus and plus indicate adhesions without and with water droplets, respectively. [c] n.d. means that the substrates were not subjected to lap–shear test due to no or too weak adhesion.

um for 3 h at 423 K for at-PMMA or 353 K for it-PMMA (more than 20 K higher than each T_g) (condition III). Under condition I, the films adhered unexpectedly without water. As proposed in previous papers,[8] films prepared by spin-casting contain residual solvents, and the polymer chains should not be fully equilibrated. Due to one or both contributions, the films seemed to adhere together (see below). Interestingly, the G_L values increased with water under condition I, irrespective of the polymer species, indicating that the water droplets apparently promoted symmetrical adhesions of the PMMA films.

To minimize the contribution of residual solvents, the films were prepared under condition II. In fact, the films never adhered without water, suggesting that the adhesions under condition I without water could be attributed to residual solvents. Meanwhile, the films adhered strongly with water, thereby confirming that the water-swelling of the PMMA films undoubtedly promoted these adhesions. Furthermore, the films under condition III never adhered even with water, suggesting that the nonthermally annealed PMMA chains are essential for detectable adhesion. We, therefore, found that the PMMA films, possibly with highly mobile surface segments due to water-swelling, could be successfully adhered together by physical contact, thus effectively entangling the surface–polymer chains during water evaporation in air.

SPR measurements were performed for a 66.8-nm-thick at-PMMA film under condition II (Figure 2, right and Table S2[7]). The blue line depicts the reflectivity calculated using a model in which the water phase is simply on the film, and this far from our SPR results. Next, we used a different model in which the water molecules homogeneously penetrate into the film. The red curve denotes the best-fit reflectivity using a model with a 72.8 nm-thick PMMA film containing 9 vol % water. For the film under condition III, such an adsorption of water molecules into the film was not detected. These results make it clear that the water content of the PMMA film was much greater for condition II than for condition III. In addition, the static contact angle for at-PMMA films under condition II (71.8 ± 0.4°) was smaller than under condition III (77.6 ± 0.8°), suggesting that the former films were more hydrophilic. These observations are in good accordance with the findings obtained by the adhesion measurements.

It is important to discuss the difference in adhesion properties between at- and it-PMMA films. Regarding the promotion of adhesion strength, water was more effective on it-PMMA than at-PMMA, because the ratios of the G_L values for films prepared under condition I with/without water were 3.5 and 11 for at- and it-PMMA films, respectively. In addition, the G_L value for it-PMMA films prepared under condition II and adhered with water was apparently greater than that for at-PMMA films, even under lower pressures. Since it-PMMA films prepared under condition II (66.8 ± 0.6°) have a smaller contact angle than at-PMMA, the water-swollen layers in it-PMMA might be thicker than in at-PMMA. A detailed analysis of the it-PMMA surface structures is ongoing.

In conclusion, the adhesion between two PMMA films with different histories was quantitatively analyzed by lap–shear tests. It was first reported that films with thermally nontreated surface chains were successfully adhered together with water droplets at room temperature, although they did not adhere without water. This study revealed that water could be an unsubstantial adhesive for certain polymers with adequate surface structures. These adhesions could be attributed to the entanglement of water-swollen PMMA chains on the film surfaces. We believe that this novel and environmentally favorable adhesion strategy may be potentially applicable to other polymers.

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References and Notes

1 a) H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* **2007**, *318*, 426. b) G. Westwood, T. N. Horton, J. J. Wilker, *Macromolecules* **2007**, *40*, 3960.
2 a) S. Sethi, L. Ge, L. Ci, P. M. Ajayan, A. Dhinojwala, *Nano Lett.* **2008**, *8*, 822. b) L. Qu, L. Dai, M. Stone, Z. Xia, Z. L. Wang, *Science* **2008**, *322*, 238.
3 H. Lee, B. P. Lee, P. B. Messersmith, *Nature* **2007**, *448*, 338.
4 K.-I. Akabori, D. Baba, K. Koguchi, K. Tanaka, T. Nagamura, *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 3598.
5 Y. Yang, D. Liu, Y. Xie, L. J. Lee, D. L. Tomasko, *Adv. Mater.* **2007**, *19*, 251.
6 K. Tanaka, Y. Fujii, H. Atarashi, K. Akabori, M. Hino, T. Nagamura, *Langmuir* **2008**, *24*, 296.
7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
8 a) G. Reiter, P. G. de Gennes, *Eur. Phys. J. E* **2001**, *6*, 25. b) J. Perlich, V. Korstgens, E. Metwalli, L. Schulz, R. Georgii, P. Muller-Buschbaum, *Macromolecules* **2009**, *42*, 337.

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