

## Tailoring Adhesive Forces Between Poly(dimethylsiloxane) and Glass Substrates Using Poly(vinyl alcohol) Primers

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**ABSTRACT:** A thin poly(vinyl alcohol) (PVA) layer has been found to control adhesive forces between poly(dimethylsiloxane) (PDMS) and a glass substrate. Various PVAs were coated on glass substrates on top of which PDMS pre-polymer was cast. After thermal curing, the peel strength was tested. It was found that the fundamental adhesive forces are attributed to the degree of hydrolysis (or saponification value) of the PVAs. For a PVA modified with a silanol group, strong adhesive force resulted. The range of tailoring the force with the PVAs was 16 kgf/m. The production of thin interlaminated PVA layers as primers was demonstrated. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39927.

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### INTRODUCTION

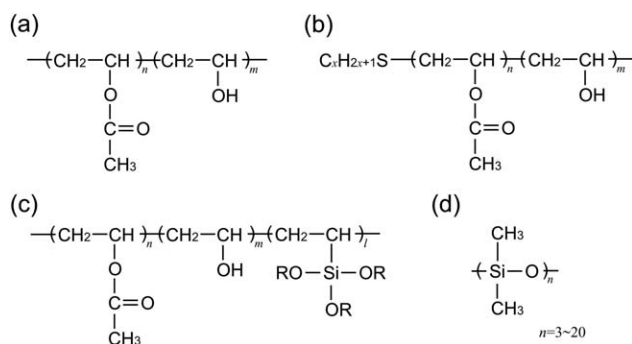
Silicone materials consisting of siloxane-bonded structures have been used in a wide array of applications such as silane coupling agents and silicone fluids, resins, and rubbers. Both organic and inorganic chemistry are responsible for the unique nature of silicone. In particular, poly(dimethylsiloxane) (PDMS) is especially useful in applied physics for flexible or stretchable electronics,<sup>1,2</sup> replication processes in nano and micro fabrication,<sup>3,4</sup> contact printing,<sup>5,6</sup> microelectromechanical systems,<sup>7</sup> and lab-on-a-chip fluidic cells.<sup>8,9</sup> When forming replication molds or temporal sealants, the cured PDMS parts are peeled or detached from various substrates. The adhesive force between the PDMS and the substrate is thus very important. Recently, we reported on a replication process<sup>10</sup> where the PDMS mold was made from a monolayer of close-packed, 500-nm diameter polystyrene spheres on a glass substrate. The PDMS pre-polymer was cast on the monolayer and infiltrated the interspatial regions between the spheres. After thermal curing, the PDMS mold was peeled away from the substrate. However, the lower half of the PDMS mold remained on the substrate because of the relatively strong adhesive force between the PDMS and the glass. As a result, the PDMS mold was an array of hemispheres. If the adhesive force between the PDMS and the substrate could be tailored, then the PDMS mold could be produced without damage or with “controlled damage,” such as what occurred with the hemisphere formation.

Various approaches to control adhesive forces by way of surface modification have been reported.<sup>11,12</sup> Plasma treatment improves surface wettability and chemical bondability, along with thermal treatments and ultraviolet light irradiation. In the plasma treatment, the chemical structure of the target surface is ablated and then crosslinked via oxidation. As a result, surface wettability is often improved. In addition, the ambient gas during the plasma treatment is important for the modification of bondability; the effect depends on what kind of inert gas is used. Recently, the application of the plasma treatment are expand to the tribology of polymer surfaces.<sup>13</sup> Steady-state friction of some polymer materials such as polycarbonate was reduced by O<sub>2</sub> plasma treatment. Chemical adsorption of primers, such as silane coupling agents, are also widely used for surface modification.<sup>14</sup> Silanol groups adsorb on oxidized inorganic surfaces via hydrogen bonding. The hydrogen bonding is then converted into strong siloxane bonds by dehydration. The surface repellency is improved by the adsorbed hydrophobic alkyl chains. However, these surface modifications need to be optimized for surface properties of desired substrates. It would be a great aid to many research and industrial applications if easier and more stable surface treatments are available to tailor wettability and bondability.

In this context, we examined poly(vinyl alcohol) (PVA) as a primer to tailor adhesive forces between PDMS and glass substrates. PVA is a water-soluble, semicrystalline polymer material

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**Figure 1.** Chemical structures of (a) normal PVA, (b) PVA modified with an alkyl group, (c) PVA modified with a silanol group, and (d) PDMS, respectively.

that is widely used in paper sizing, fiber or particle binders, adhesions, clear films, and emulsion stabilizers.<sup>15</sup> Fundamental characteristics of PVAs are determined by the degree of hydrolysis (DH) (i.e., the extent of hydroxyl groups in the polymer chain) resulting from saponification. Actually, the variation among commercial PVA materials is based on differences in the DH and in the degree of polymerization (DP). We focused on PVA saponification since the adhesive force between PDMS and PVA-coated glass substrates may be tailored by the number of PVA hydroxyl groups. Based on this concept, we tested the adhesion using various kinds of PVAs and found that it can be tailored by the DH and the preparation conditions. The range of tailored adhesive forces was up to 16 kgf/m, and both stronger and weaker adhesive forces relative to that of the bare glass substrate could be obtained. The results demonstrate that PVA is one useful primer for tailoring adhesion between PDMS and inorganic substrates.

## EXPERIMENTAL

Five commercial PVAs (PVA105, PVA205, PVA405, MP203, and R2105; Kuraray Co., Ltd., Tokyo, Japan) were used in this study. Their chemical structures are depicted in Figure 1(a–c), and their features are summarized in Table I. PVA105, PVA205, PVA405 are normal PVAs with the same DP (500) and differing DHs of 98.5 mol %, 88.0 mol % (partial segments were saponified), and ~80 mol %, respectively. The differences in DH can be evaluated by the three kinds of PVA. MP203 is a modified PVA with an alkyl chain at the end of the polymer chain.<sup>16</sup> The 350 DP is near that of other PVAs and the DH is 86.5–89.5 mol %. It is used as an emulsion stabilizer because the additional

**Table I.** Features of PVAs Used in this Study

PVA	DH <sup>a</sup> (mol %)	DP <sup>b</sup>
PVA105	98.5	500
PVA205	88.0	500
PVA405	~80	500
MP203	86.5–89.5	350
R2105	97.5–99.0	500

<sup>a</sup>Degree of hydrolysis.

<sup>b</sup>Degree of polymerization.

alkyl chain makes it a surfactant. The property of the alkyl part is not provided. R2105 is a modified PVA with silanol groups in the side chain, and was developed for use as a binder to inorganic materials.<sup>17</sup> The DH is 97.5–99.0 mol % and the DP is 500.

Water solutions of these PVAs were prepared at a concentration of 10 wt %. The solutions were spin-coated on bare glass substrates that were pre-cleaned with acetone in an ultrasonic bath. The films were 200 nm thick, as measured with a stylus profiler. PDMS pre-polymer [Figure 1(d)] was applied to the PVA-coated glass substrates to fabricate peel strength test pieces. It is a commercial product (SIM360, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) developed for fine pattern transfer. After application of the PDMS pre-polymer, the test pieces were thermally cured at 150°C for 30 min in an oven. Adhesion of PDMS to the PVA-coated glass substrates occurred simultaneously, thus forming the peel strength test pieces. More details are found in Supporting Information 1. Prior to thermal curing, test piece fabrication was normally carried out at room temperature (RT, 24–26°C) and 57–62% relative humidity (RH). In some cases, dry nitrogen was used to adjust the ambient conditions to ~27% RH at RT.

To evaluate the adhesive forces, we performed the 90° peel strength test<sup>18</sup> by being pulled by a variable weight connected to one end of each test pieces. Details of the experimental arrangement and a physical explanation are given in Supporting Information 2. We also performed contact angle measurements of water droplets on the PVA layers using a digital camera.<sup>19</sup> The contact angle of water was measured by sessile drop method by gently placing a droplet of 1- $\mu$ L of pure water (>10 M $\Omega$ ) onto the PVA-coated glass substrates. When the droplet is sufficiently small, the influence of gravity is negligible and the droplet is treated as a spherical cap. Therefore, the relationship between contact angle  $\theta$  and the spherical cap parameters (the spherical cap height  $h$  and the contact radius  $r$ ) is described by

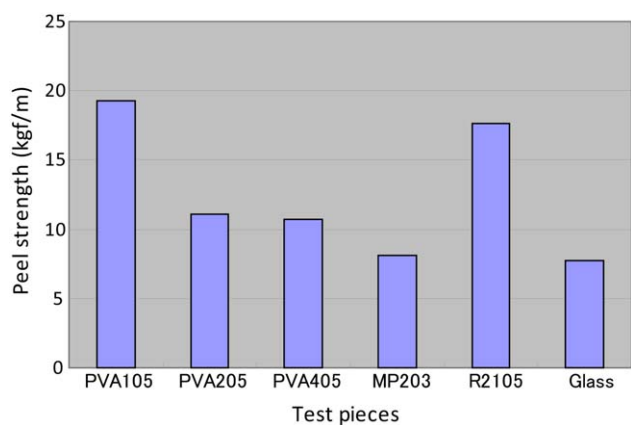
$$\tan\left(\frac{\theta}{2}\right) = \frac{h}{r} \quad (1)$$

The contact angle measurements of all samples were conducted at a laboratory condition of RT and 57–62% RH. The initial contact angle was measured within 100 ms of the initial droplet contact, followed by temporal changes in the contact angle every 15 s for 3 min. The initial contact angle indicates the surface wettability of the PVA layer before swelling, which can be used to assess the density of hydroxyl groups and the influence of modified functional groups. The temporal changes mainly indicate the effect of swelling that directly corresponds to the crystallinity.

## RESULTS AND DISCUSSION

### Evaluation of the Adhesive Forces

The results of the peel strength test are shown in Figure 2 and can be classified into two groups. One group consists of PVA105 and R2105, which exhibited relatively strong peel strengths of >15 kgf/m. The other group consists of PVA205, PVA405, MP203, and bare glass, which exhibited relatively weak

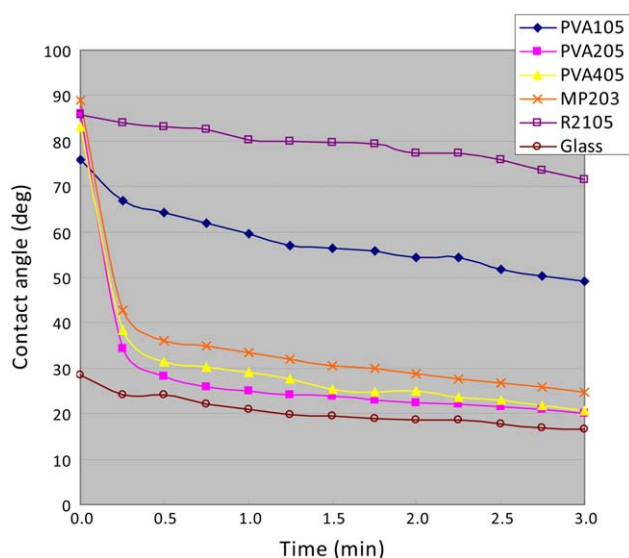


**Figure 2.** Peel strength tests of PDMS removed from PVA-coated glass substrates and bare glass substrate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

peel strengths of  $<15$  kgf/m. The PVA105 and R2105 had high DHs of  $>90$  mol %, whereas the others did not. To analyze the surface energy of each PVA-coated substrate, the initial contact angles were measured (Table II). PVA105, with high a DH, had a relatively low contact angle of  $75.7^\circ$ , which is attributed to the large number of hydrophilic hydroxyl groups. This is consistent with the fact that PVA405 had a relatively high contact angle, because of the higher number of hydrophobic acetate groups relative to that of PVA105. Although PVA205 had a slightly higher contact angle than that of PVA105, this is attributed to partial saponification, whereas PVA105 and PVA405 were normally saponified. The contact angle of PM203 was much higher than that of the others because of the alkyl end groups. As expected, the bare glass substrate had the lowest contact angle. The initial contact angles, however, do not directly correlate with the adhesive forces in Figure 2. When we investigated the temporal changes in the contact angles (Figure 3), the results could be classified into the two groups consistent with the adhesion (peel) strength. The contact angle of R2105 was sustained over  $70^\circ$  even after 3 min, decreasing almost linearly with a small negative slope. This time dependence indicates that the swelling on the R2105 surface was significantly inhibited by the high crystallinity. The time dependence of PVA105 is similar to that of R2105, with a slight change in the negative slope over the elapsed time of less than 0.5 min. For the bare glass substrate, the contact angle also decreased linearly because no swelling occurs. The contact angle was very low indicating a

**Table II.** Initial Contact Angles on Bare and PVA-Coated Glass Substrates

Test pieces	Annealing temperature		
	25°C (RT)	60°C	200°C
PVA105	75.7	73.8	51.3
PVA205	85.3	85.6	63.0
PVA405	82.1	80.6	66.7
Glass	28.2		
MP203	88.8	94.9	76.7
R2105	85.1	83.7	44.5

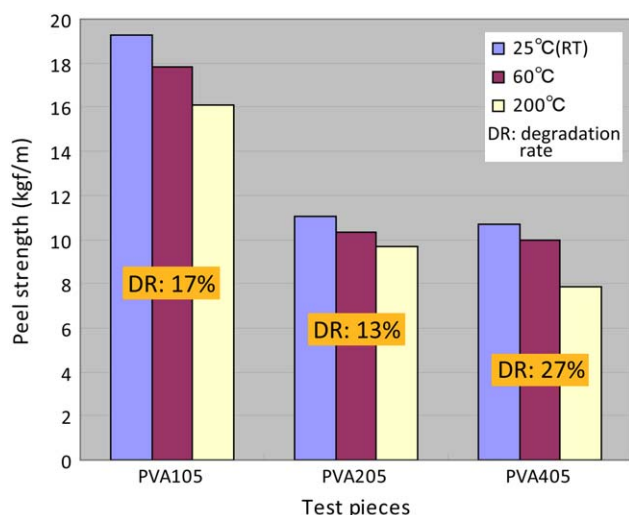


**Figure 3.** Time dependence of contact angles on bare and PVA-coated glass substrates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

relatively high hydrophilic surface from the pre-cleaning. On the other hand, the time dependences of the PVA205, PVA405, and MP203 contact angles displayed significant changes in the negative slopes. Initially ( $<0.5$  min), the contact angles rapidly decreased, and then the slopes became relatively small and constant. These results indicate that the PVA layers were swelling rapidly in the early period owing to the relatively low DH. The crystallization is enhanced by an increased concentration. Therefore, the crystallinity in PVA205, PVA405, and MP203 is relatively low and the swelling progressed quickly. Therefore, it was found that the adhesion between the PDMS and the PVA-coated glass substrates is strongly related to the amount of hydroxyl groups in the PVAs, as represented by the DH. The differences in the DH can be estimated by the contact angle time dependence that originates from the degree or the facility of crystallization.

#### Influence of Thermal Treatment

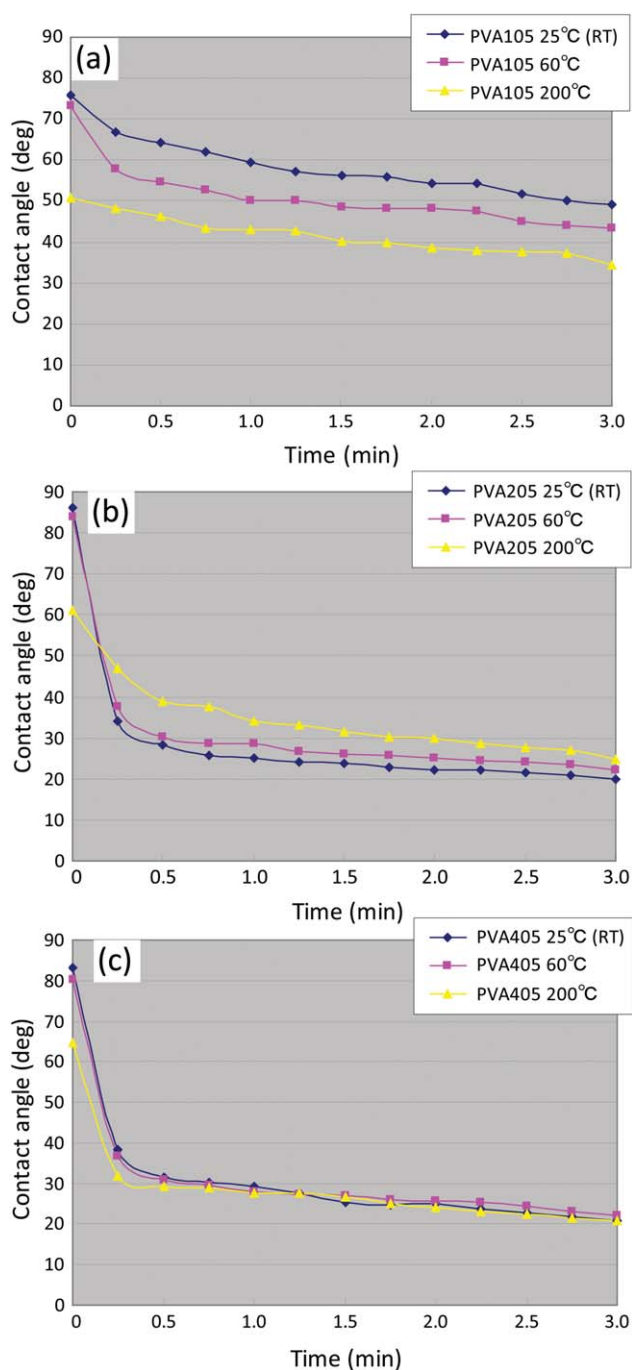
As revealed above, the fundamental factor in tailoring the strength of adhesion is the concentration of hydroxyl groups (i.e., the DH). In this section, the substantial range in adhesion for PVA105, PVA205, and PVA405 is evaluated by controlling the amount of free hydroxyl groups via thermally enhanced crystallization.<sup>20,21</sup> Figure 4 shows the peel strengths as a function of the temperature during the thermal treatment. The data for 25°C (RT) are the same as those in Figure 2. The graphs for 60°C and 200°C correspond to the results of peel strength tests with pieces fabricated by annealing the PVA-coated glass substrates at 60°C and 200°C for 10 min, respectively. The 60°C and 200°C conditions were intended to obtain crystallinity at the medium value of around 0.2, and a completely saturated value of 0.6, respectively.<sup>21</sup> The adhesion strength decreased with increasing annealing temperature for PVA105, PVA205, and PVA405, as expected. The extent of degradation was calculated from the minimum and maximum values of the peel strengths, and was found to be 17%, 13%, and 27%,



**Figure 4.** Influence of thermal treatment on peel strength of PDMS from PVA105-, PVA205-, and PVA405-coated glass substrates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

respectively, for PVA105, PVA205, and PVA405. We also investigated changes in the contact angle time dependence as a function of the thermal treatment. The results are shown in Figure 5. For PVA105, the contact angle decreased with increasing annealing temperature [Figure 5(a)]. The negative slopes were almost constant, reflecting the existence of a high crystallinity inhibiting the swelling. However, a discrepancy occurred, in that the contact angles decreased with increasing annealing temperature despite the fact that the amount of free hydrophilic hydroxyl group was reduced by crystallization. This is consistent with the results in Table II, in which the initial contact angles of all PVA surfaces decreased with increasing annealing temperature. This problem is attributed to the circumstance in interfacial activity where the hydrophilic and hydrophobic groups are balanced. In the case of PVA105, there are initially small concentrations of hydrophobic (acetate) groups because the DH is 98.5 mol %. Hence the balance between hydrophobic and hydrophilic groups to increase interfacial activity cannot occur. As a result of crystallization, the interfacial activity was lost. These considerations were supported by the characteristics of PVA205 and PVA405 shown in Figure 5(b,c), respectively. For PVA205, the contact angles increase with increasing annealing temperature, indicating an increase of interfacial activity by reducing hydrophilic groups and balancing with hydrophobic groups, as per the DH. For PVA405, the temporal changes in contact angles were almost independent of the annealing temperature. This means that the surface wettability is not influenced by the crystallization of hydroxyl groups because there is a relatively low amount of them in the polymer chain.

The thermal treatment is thus an effective means for reducing the adhesive forces. The extent of degradation ranged from 10% to 30%. The initial contact angles are reduced by the thermal treatment owing to crystallization of hydroxyl groups. On the other hand, the temporal changes in the contact angles indicate

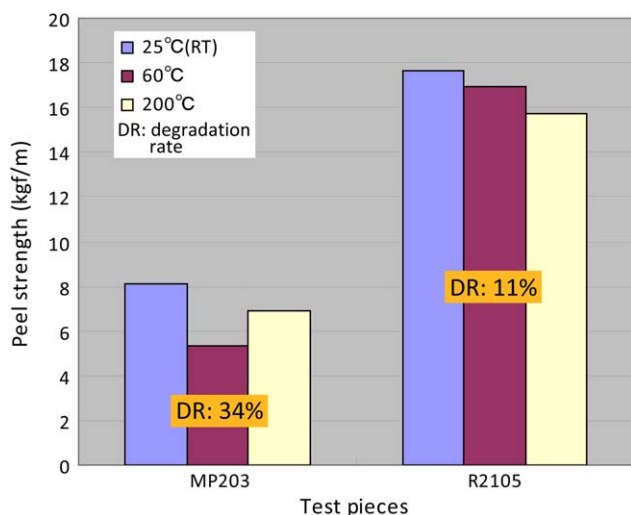


**Figure 5.** Time dependence of contact angles on (a) PVA105-, (b) PVA205-, and (c) PVA405-coated glass substrates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

various characteristics dependent on the PVA DH. The data shown in Figure 5 provide an understanding of the quantitative relationship between the hydrophilic and hydrophobic groups with respect to the DH.

#### Effects of PVA Modifications

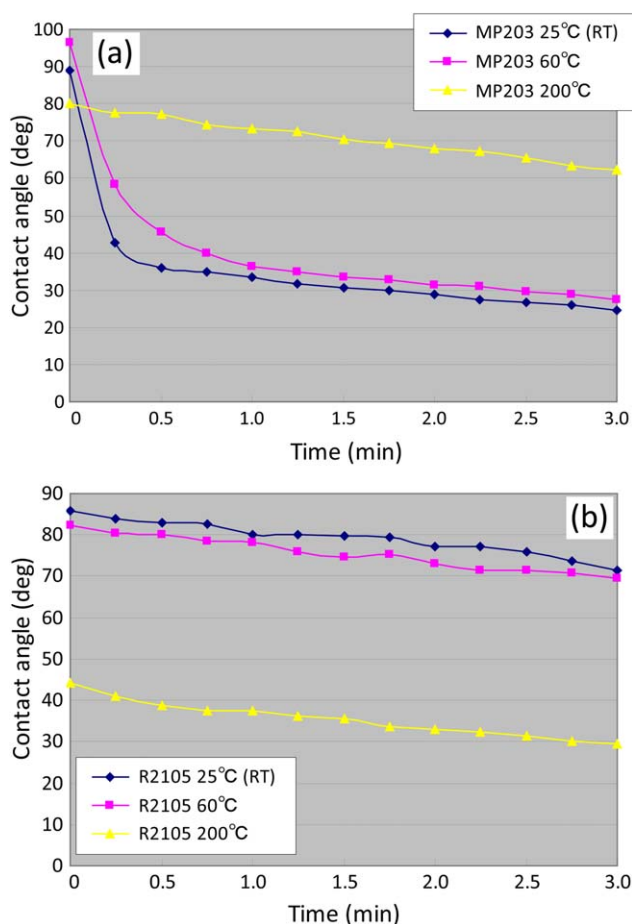
In Figure 2, the adhesive force of MP203 is lower than that of PVA205 despite a close DH. Similarly, the adhesive force of R2105 is lower than that of PVA105. The benefits of their



**Figure 6.** Influence of thermal treatment on peel strength of PDMS from MP203- and R2105-coated glass substrates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

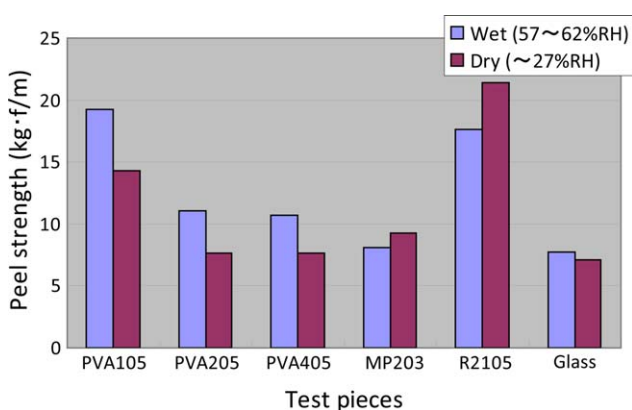
modifications are still uncertain except for the variation displayed in Figure 2. The effect of the thermal treatment on the adhesive forces was investigated for the MP203 and R2105 test pieces as discussed above for PVA105, PVA205, and PVA405. The results are shown in Figure 6. For the MP203 annealed at 60°C, the peel strength was reduced 34% to that prepared at RT. However, the peel strength of the test piece annealed at 200°C increased relative to that of the one annealed at 60°C. This behavior is different from that of the other PVAs. We also measured the contact angle time dependences, as shown in Figure 7(a). Furthermore, the contact angles increased with increasing annealing temperature. This trend is similar to that for PVA205. As a result, relatively high contact angles were observed. The interfacial activity increased with decreasing free hydroxyl groups, and hydrophobic groups (alkyl end groups) balanced the hydrophilic groups. The result also reveals that alkyl end groups are present in the PVA–PDMS interface. The increase in the adhesive force following the 200°C thermal treatment is attributed to interaction of the long MP203 alkyl groups with PDMS chains produced during thermal curing.

The R2105 data in Figure 6 are similar to that of the other PVAs, except for MP203. The degradation was 11%, and the contact angle time dependence resembles that of PVA105. Therefore, we attempted to enhance the siloxane bonding of the silanol groups in R2105. Siloxane bonding is normally formed by the dehydration reaction of the hydrogen bonds formed by silanol groups under dry conditions or by thermal treatment. We prepared several test pieces at ~27% RH and RT. The results of the peel strength test are shown in Figure 8 for “dry (~27% RH)” and “wet (57–62% RH)” test pieces. The “wet (57–62% RH)” data are the same as that in Figure 2. The data can be classified into two groups. In one group (PVA105, PVA205, PVA405, and bare glass), the peel strengths are reduced by preparation under dry conditions. In the other group (MP203 and R2105), the peel strengths increased by preparation

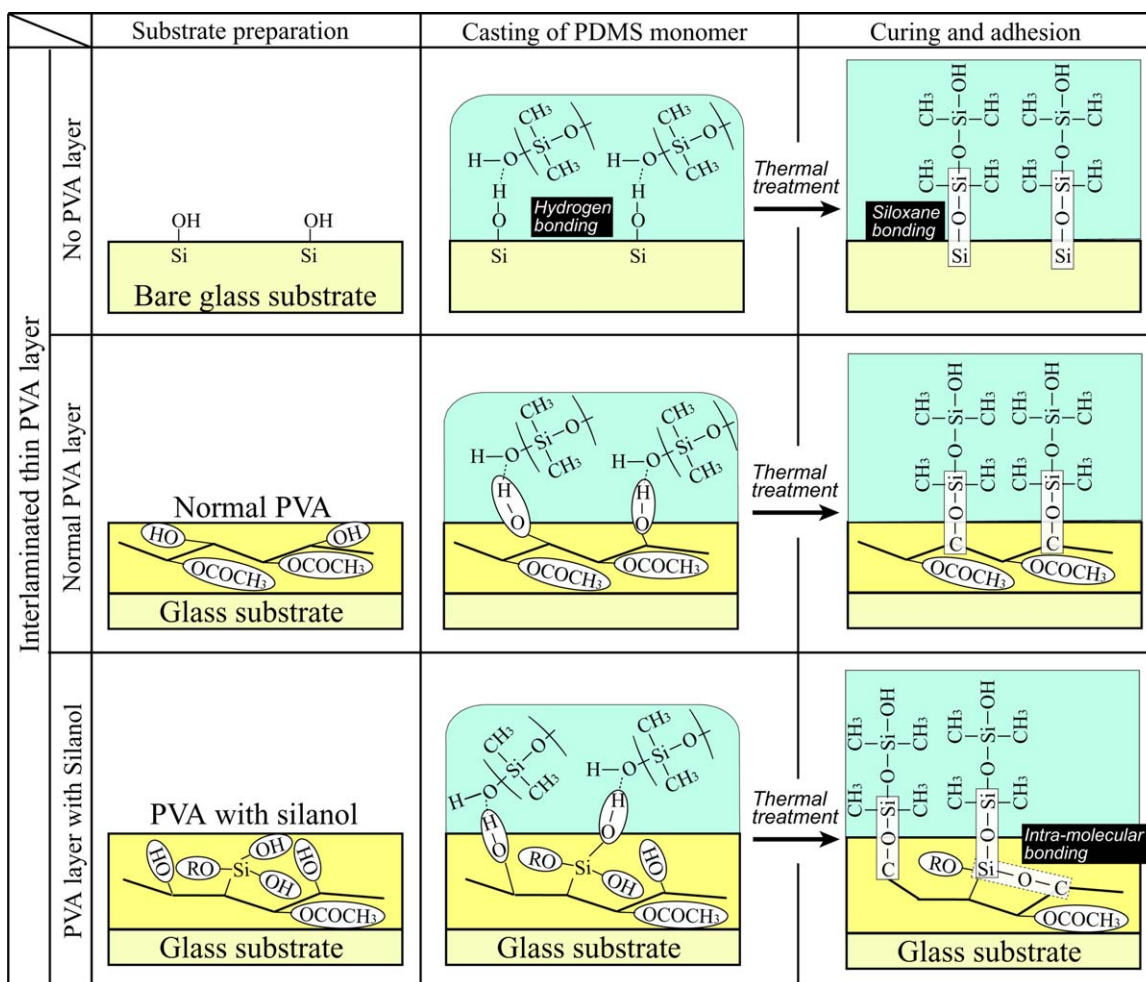


**Figure 7.** Time dependence of contact angles on (a) MP203- and (b) R2105-coated glass substrates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

under dry conditions. This classification can be regarded as normal and modified PVAs, respectively. The adhesive force of R2105 is particularly improved by the dry conditions, as expected.



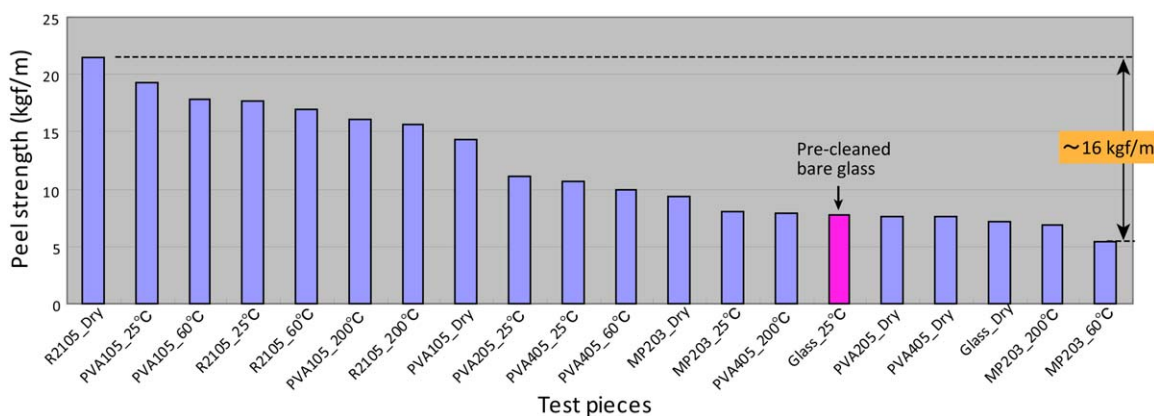
**Figure 8.** Influence of ambient humidity on peel strength of PDMS from PVA-coated glass substrates and bare glass substrates. The test pieces were prepared under the “wet” condition of RT and 57–62% RH and the “dry” condition of RT and ~27% RH. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** Chemical reactions and bonding for a PDMS-bare glass substrate (upper row), a PDMS-normal PVA-coated glass substrate (middle row), and a PDMS-modified PVA with silanol group (bottom row). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Adhesion mechanisms for the various substrates are illustrated in Figure 9. Bare glass is the initial reference (upper left). Silanols (Si—OH) were formed by moisture in the atmosphere and the SiO<sub>2</sub> groups of the glass surface. When PDMS pre-polymer was cast on the surface, the end silanols of PDMS monomers hydrogen-bonded with silanols on the glass. Siloxane bonding (Si—O—Si) is formed by thermal dehydration, resulting in adhesion of the PDMS to the glass substrate. The same mechanism occurs for silane coupling agents.<sup>14,22,23</sup> For normal PVA-coated glass substrates (middle row in Figure 9), hydroxyl groups are distributed according to the DH of the PVA and are hydrogen-bonded by the hydroxyl groups of the PDMS monomers. After thermal treatment, the PDMS and PVA are bonded by C—O—Si structures. For both PDMS-bare glass and PDMS-normal PVA-coated glass, the adhesive forces are determined by the number of chemical adsorption sites forming hydrogen bonds. Therefore, the fundamental adhesive force is determined by the PVA DH, and is weakened if the thermal treatment that enhances crystallinity by being prepared in dry conditions. The PDMS/PVA/Glass structure is similar to the Si—O—PVA—O—Si bonding structure in PVA binders for silica particles.<sup>24,25</sup> For the silanol-modified PVA (bottom left in Figure 9), the initial chemical adsorption is

also attributed to hydrogen bonding between the hydroxyl groups on the main chain and on the silanol group. The adhesive force is generated by both Si—O—Si and C—O—Si bonding after the thermal treatment. Because Si—O—Si bonding is dominant in the case of PDMS-bare glass and C—O—Si bonding is dominant in the case of PDMS-normal PVA-coated glass, this does not explain why the adhesive force of R2105 was improved by the dry preparation conditions. The main reason for the improvement is the internal bonding due to dehydration in the PVA layer. In silanol-modified PVA, the two bonding structures can be considered. One is intra-molecular C—O—Si bonding formed under thermal treatment between hydroxyl groups on the main chain and those on the silanol groups. Si—O—Si bonding is also formed when silanol groups are reacting in the same chain. The other is C—O—Si and Si—O—Si inter-molecular bonding between vicinal PVA molecules. These results indicate a proper procedure to obtain strong adhesive forces: the substrate is prepared under relatively wet conditions until just before PDMS pre-polymer casting in order to obtain many chemical adsorption sites, and the PDMS curing is performed under relatively dry conditions to obtain sufficient dehydration reactions, including inside the PVA layer.



**Figure 10.** Variation in the peel strength of PDMS from PVA-coated glass substrates and bare glass substrates. The adjustment range was 16 kgf/m. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The results of all the peel strength tests are summarized in Figure 10, where they are sorted in order of the peel strength. The range of adhesive forces extends to 16 kgf/m, where it can be tailored either strongly or weakly with respect to that of bare glass. This result means that the normal and modified PVAs can be used as primers for tailoring adhesion between PDMS and glass or similar inorganic substrates.

## CONCLUSIONS

In this work, various PVAs were used as primers to adjust the adhesive (peel) forces between PDMS and glass substrates. It was found that the fundamental adhesive force was determined by the DH (saponification value) in the PVAs. This is because the hydroxyl groups in the PVAs form chemical adsorption sites for the PDMS monomers by way of hydrogen bonding. Those weak bonds were transformed into strong C—O—Si bonding by dehydration reactions during thermal treatment. For silanol-modified PVA, the C—O—Si and Si—O—Si bonds result in strong adhesion. Their adhesive strength can be tailored by both annealing the PVA layer and by controlling the ambient humidity. Thus, a relatively wide range of tailoring the adhesive forces was demonstrated. The advantages of using PVAs as a primer are water solubility, a facility of application, the variation of chemical composition, cost effectiveness, and biodegradability.

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