Surface Modification of PDMS and Plastics with Zwitterionic Polymers

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Abstract: Surface modification of PDMS, polycarbonate, and acrylic resin was examined using various methacryl polymers bearing sulfobetaine, phosphoryl choline, and oligoethylene glycol units. We have found that zwitterionic polymers are adsorbed on the PDMS surface treated with plasma. The surface of PDMS is stable to keep high hydrophilicity after a month of the modification. On the other hand, one of sulfobetaine polymers showed distinguished adsorption behavior in the case of polycarbonate surface treated with plasma. Suppression effect for nonspecific adsorption of BSA was evaluated using polycarbonate and acrylic resin modified with the polymers. The modified surfaces showed suppression effect for nonspecific adsorption of BSA compared with the surface only treated with plasma.

Key words: surface modification, polymer, hydrophilicity, PDMS

1 INTRODUCTION

Plastics and elastomers are recognized as one of versatile materials, and hydrophilicity is sometimes required for their surfaces in biomedical application. It is well known that chemical modification of plastic and elastomer surfaces with covalent bond is quite troublesome, because of their surface properties, such as low chemical reactivity, low erosion resistance against organic solvents, and hydrophobicity. In the case of plastics, surface-treatments such as irradiation of UV light and plasma are recognized as an effective method to afford chemical reactivity and hydrophilicity for their surfaces, and those surface-treatments are also necessary for coating to lead the surface modification with covalent bond. However, in the case of elastomers such as PDMS (polydimethylsiloxane), it is reported that the treated surface with UV light and plasma recovers original hydrophobicity soon due to their molecule flexibility. Recently, an interface polymerization using atom transfer radical polymerization (ATRP) attracts attention as a new surface modification method with covalent bond. This method is intriguing because various surfaces of metals, oxides, carbons, plastics, and elastomers are modified by this method with covalent bond. This method could be a powerful tool for surface modification, but the introduction of an ATRP initiator to the surface is inevitable at the beginning. Furthermore, a considerable amount of monomer solution is required for ATRP surface modification. Those terms in ATRP method hamper general usage for surface modification.

For various applications, fabrication of materials in combination with surface modification and nanostructure formation is crucial. We have studied on surface modification materials and methods in application for biosensor systems, and established some methods how to modify surfaces with monolayer similar to self-assembled monolayer (SAM). We applied those methods to modify surfaces of plastics and elastomers, where plasma was adopted for surface-treatment. Although there is an example to report surface modification of PDMS with sulfobetaine-silane to form a monolayer, attempts to modify plastic and elastomer surfaces with a SAM-like monolayer were failed due to low reactivity and dissolving of the surface treated by plasma. Therefore, we turned our attention to modification with polymer as bulky polymer can cover surface effectively even with lower surface concentration than SAM. Furthermore, as a surface modification method of plastics, coating of bovine serum albumin (BSA) on the surface is an important procedure to suppress non-specific adsorption of proteins with hydrophilicity in biosensor field. This method is very simple, and BSA is attached on plastic surface by hydrophobic interaction, in other word, polymer effect. We are interested in the interaction of polymer with plastics and elastomers to lead such a simple surface modification method.

In this paper, we present a simple method for surface modification of polydimethylsiloxane (PDMS), polycarbon-
ate, and acrylic resin treated with plasma via polymer effect.

2 EXPERIMENTAL PROCEDURES

All chemicals were commercially available and used as received without additional purification. Details of synthesis, surface modification, and measurement procedures are described in Supplementary Material.

3 RESULTS AND DISCUSSION

3.1 Synthesis of polymers

Various polymers, such as polyethyleneglycol \( \text{PEG} \) \( ^{27-29} \), sulfobetaine \( ^{30-32} \), and phosphorylcholine \( ^{33-35} \), have been developed to suppress non-specific adsorption of proteins with hydrophilicity. As listed in Fig. 1, we synthesized several polymers by common radical polymerization using azobisisobutyronitrile (AIBN). In molecular design for the monomers, methacryl moiety was introduced with amido group to prevent hydrolysis of polymers, except for phosphoryl choline. Among those polymers, the polymers bearing sulfobetaine moiety are reported to be an attractive surface-modification material as the sulfobetaine moiety suppresses non-specific adsorption of proteins with excellent hydrophilicity, being easy to synthesis. We are also interested in surface modification with covalent bond. Therefore, a copolymer SB-Az (Fig. 1), which was a sulfobetaine polymer bearing photoreactive moiety, phenyl azide, was synthesized by AIBN polymerization, similarly \( ^{36,37} \).

3.2 Adsorption of polymers on PDMS

PDMS surface is notorious for poor hydrophilicity, and the surface is known to recover hydrophobicity soon after treatment with plasma. In order to examine interaction of polymers with the surface of PDMS treated by plasma, aqueous solution of the polymers (1 mg/mL) was prepared, and PDMS was dipped into the solution for 10 min. PDMS was rinsed with sonication for one min., and then, the contact angle of the PDMS surface was measured after 4 days and 1 month of the modification, respectively. The results are tabulated in Table 1. While the PDMS surface treated with plasma recovered hydrophobicity within four days, the surface modified with sulfobetaine and phosphoryl choline polymers showed excellent hydrophilicity. Those polymers are zwitterionic polymers, and it was demonstrated that the zwitterionic polymers were adsorbed on the PDMS surface treated with plasma. In control experiments, the PDMS surface modified with a monomer solution of C3SB by the same procedure recovered hydrophobicity soon. Therefore, it is evident that the adsorption of zwitterionic polymers on PDMS surface treated with plasma is derived from polymer effect. The modified surface kept hydrophilicity even after one month of the modification, although C2SB and MPC showed slight decrease of hydrophilicity. To the contrary, polymers derived from oligoethylene glycols afforded poor hydrophilicity. The results indicate that the zwitterionic polymers are adsorbed on the PDMS surface treated with plasma, and the adhesion derived from polymer effect is strong enough to restrict molecular mobility of PDMS to keep excellent hydrophilicity.

3.3 Adsorption of polymers on plastics

Similarly, we examined interaction of polymers with polycarbonate (PC) and acrylic resin (AC) surfaces treated with plasma. The plastics were modified with the same procedures as PDMS, and surface of the plastics was analysed by X-ray photoelectron spectroscopy (XPS). We used N/(N+C) atomic ratio as an indicator to evaluate adsorption of polymers on the plastic surfaces, as the nitrogen atom is derived from the amide group of polymers (Fig. S1). The results are summarized in Table 2 with N/(N+C) atomic ratio of polymers themselves for comparison. In the case of polycarbonate, the nitrogen atomic ratios were

| Table 1 Contact angle of PDMS surface modified with polymers. |
|-----------------|----------------|----------------|----------------|------|---------|--------|--------|
| none            | C2SB           | C3SB           | C6SB           | MPC  | EGOH    | EGOM   | MEGOM  |
| 4d              | 95.2           | 12.5           | 14.7           | 15.1 | 22.6    | 82.8   | 85.3   | 99.6  |
| 1m              | 96.3           | 18.6           | 16.8           | 17.7 | 32.7    | 91.6   | 90.2   | 97.1  |

Fig. 1 Synthesized polymers.
considerably high to show adsorption of polymers on the surface. Especially, the high nitrogen atomic ratio for sulfobetaine polymer C3SB indicated that C3SB was adsorbed on the polycarbonate surface more significantly than other polymers. On the other hand, the adsorption of polymers on acrylic resin surface was less than that on polycarbonate surface, and all sulfobetaine polymers were hardly adsorbed.

It is considered that electrostatic interaction, hydrophobic interaction, and hydrogen bond formation, and hydrophobic interaction could induce polymer adsorption. In the case of PDMS, electrostatic interaction could be predominant to induce polymer adsorption because all zwitterionic polymers were adsorbed well. In the case of polycarbonate, only C3SB was adsorbed with considerable amount, while MPC was adsorbed substantially on acrylic resin surface among zwitterionic polymers. Furthermore, there was no meaningful difference among EGOH, EGOM, and MEGOM in cases of plastics, where MEGOM does not have hydrogen to form hydrogen bond. Therefore, the adsorption amount of polymers on plastic surfaces seems to be depending on hydrophobic interaction.

### 3.4 Suppression effect of surface modification for non-specific adsorption of BSA

The polymers synthesized in this work are expected to suppress non-specific adsorption of proteins as various surface modification materials to suppress non-specific adsorption of proteins contain polyethyleneglycol, sulfobetaine, and phosphorylcholine moieties. Therefore, the suppressive effect against non-specific adsorption of proteins was evaluated using BSA for plastic surfaces modified with those polymers. Polycarbonate and acrylic resin were treated with plasma, and modified with the polymers. The non-specifically adsorbed BSA on the surface was evaluated by XPS measurement with silver staining method, which is one of common procedures to stain proteins via electrophoretic separation in biochemistry field\(^{[20]}\). The results are summarized in Table 3. The polycarbonate and acrylic resin surfaces without the polymer modification indicated the presence of BSA adsorbed non-specifically, as a significant amount of silver atom was detected with XPS measurement. On the other hand, in cases of surfaces modified with polymers, the amount of silver atom decreased significantly to show a suppressive effect against non-specific adsorption of BSA. The polycarbonate surface modified with C3SB showed excellent suppression effect against non-specific adsorption of BSA, reflecting the abundant amount of C3SB adsorption. Those results implied that immobilization of those polymers on plastic surface is promising to suppress non-specific adsorption of proteins.

### 3.5 Surface modification with covalent bond

It is considered that surface modification with covalent bond is more durable than that with physical adsorption. Therefore, copolymers incorporating photo-reactive cross-linking reagents, such as phenyl azide and diazirine, have been synthesized to immobilize polymers on substrate via covalent bond formation. We also synthesized a copolymer consisting of sulfobetaine and phenyl azide monomers, SB-Az (Fig. 1), and durability of the surfaces modified by physical adsorption and covalent bond were compared by 5-min-sonication treatment. The surface modification of polycarbonate by physical adsorption was performed with the same method as described before. The formation of covalent bond between SB-Az and polycarbonate surface was attained by UV-light irradiation for 5 min., and then, the surface modified polycarbonate was rinsed for 1 min. under sonication once more. The surface modified polycarbonates with SB-Az by physical adsorption and covalent bond were treated with 5-min-sonication in water, and the change in N/(N + C) atomic ratio was examined by XPS measurement. In the case of physical adsorption, the nitrogen atomic ratio was decreased from 5.82 to 5.18, however, that with covalent bond did not show meaningful change during sonication treatment, being 4.74 and 4.73%. This result suggests that surface modification with covalent bond is more durable than that with physical adsorption in accordance with general consideration.

In Table 3, C3SB showed good suppression effect against nonspecific adsorption of BSA reflecting considerable amount of adsorption on polycarbonate surface treated by

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### Table 2  \(\text{N/(N + C)}\) atomic ratio by XPS (\%)

<table>
<thead>
<tr>
<th></th>
<th>C2SB</th>
<th>C3SB</th>
<th>C6SB</th>
<th>MPC</th>
<th>EGOH</th>
<th>EGOM</th>
<th>MEGOM</th>
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<tr>
<td>PC</td>
<td>2.53</td>
<td>8.13</td>
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<td>2.26</td>
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<tr>
<td>AC</td>
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<td>1.16</td>
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<tr>
<td>Polym.</td>
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<td>11.8</td>
<td>8.33</td>
<td>9.09</td>
<td>8.33</td>
<td>7.69</td>
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</table>

### Table 3  \(\text{Ag/(Ag + C)}\) atomic ratio by XPS (\%)

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<th>none</th>
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<th>C3SB</th>
<th>C6SB</th>
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<tr>
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<td>0.03</td>
<td>0.13</td>
<td>0.08</td>
<td>0.12</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>AC</td>
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<td>0.15</td>
<td>0.13</td>
<td>0.13</td>
<td>0.09</td>
<td>0.13</td>
<td>0.14</td>
<td>0.12</td>
</tr>
</tbody>
</table>
plasma. Therefore, we expected that immobilization of the polymers with considerable amount by formation of covalent bond could lead to more effective suppression against nonspecific adsorption of proteins. The acrylic resin treated by plasma was immersed in the solution of SB-Az with the same procedure as described before and dried by nitrogen blow without rinse. UV-light was irradiated on the acrylic resin for 5 min. to immobilize SB-Az by covalent bond formation, and then, the acrylic resin was rinsed for 1 min. under sonication. The suppressive effect against nonspecific adsorption of BSA was evaluated with the same method as described for Table 3. The Ag/(Ag+C) atomic ratios for the surfaces modified with physical adsorption and immobilization by covalent bond formation were 0.16 and 0.06, respectively, showing significant effect. This result suggested that a considerable amount of polymer immobilization is effective for suppression of non-specific adsorption of proteins.

The surface modification of PDMS with SB-Az was carried out, and contact angles were measured before and after UV-light irradiation after 4 days of the modification. The results are summarized in Fig. 2. In Fig. 2, the contact angle before UV-light irradiation was 14.8°, indicating that physical adsorption of the copolymer, SB-Az, occurred on the PDMS surface treated by plasma similar to in cases of sulfobetaine polymers. After UV-light irradiation, the contact angle increased slightly, but the surface still kept high hydrophilicity. In the case of C3SB, similar increase of contact angle was also induced by UV-light irradiation (Fig. S2). Therefore, this tendency could be caused by molecular mobility activation of PDMS but not by SB-Az structure change derived from photochemical reaction of phenyl azide moiety.

4 CONCLUSION

The results demonstrate that zwitterionic polymers tend to adsorb on PDMS surface treated with plasma via electrostatic interaction, while hydrophobic interaction is predominant between the polymers and surfaces of polycarbonate and acrylic resin treated with plasma. It is noteworthy that the molecular mobility of PDMS is restricted by adsorption of zwitterionic polymers to keep hydrophilicity for more than a month. By using a copolymer consisting of sulfobetaine and phenyl azide monomers, surface modification with covalent bond is also possible to lead various methods for surface modification of PDMS and plastics. This simple method using polymers could be applicable to surface modification of micro flow channel, medical apparatus, and so on, which are made of PDMS and plastics.

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Supporting Information

This material is available free of charge via the Internet at http://dx.doi.org/jos.66.10.5650/jos.ess.17041

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