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**Sol-gel based fabrication of hybrid microfluidic devices composed of PDMS and
thermoplastic substrates**

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Abstract

Fabrication of microfluidic devices using both rigid and flexible plastic substrates offers benefits for making pressure-actuated membrane valves, mechanically active components, and low-cost but highly-functional 3-D microchannel networks. Here we present a simple and versatile process for bonding flexible polydimethylsiloxane (PDMS) and rigid thermoplastics like poly(methyl methacrylate) (PMMA), by utilizing the sol-gel method. The silica sol, obtained by oligomerizing tetraethoxysilane monomers, was spin-coated on a thermoplastic plate and further polymerized to form a thin silica layer (silica gel) with a thickness of 140 to 300 nm. The silica-coated surface could be covalently and strongly bonded with an O₂ plasma-activated PDMS plate, just by bringing them into contact. We applied the presented process to preparing multilayer PDMS-PMMA microdevices having 3-D crossing channels or pneumatically-controlled membrane valves, and demonstrated the parallel flow distribution, mixing, and droplet generation. In addition, bonding strengths between PDMS and various thermoplastics, including PMMA, polyvinyl chloride (PVC), polycarbonate (PC), and polypropylene (PP), were examined.

Keywords: Sol-gel method, Microfluidic device, Polydimethylsiloxane, Thermoplastics,

Microfabrication

1. Introduction

Polydimethylsiloxane (PDMS) is a widely used polymeric material for microfabricated structures, because of its biocompatibility, optical transparency, and simplicity in fabrication processes via soft lithography and replica molding [1-3]. Especially, the easiness in oxidation-base bonding with other silicon-base substrates including Si wafer, glass, and other PDMS plate has resulted in its popularity as the material of microfluidic devices [4]. Additionally, its elastic nature is suitable for preparing pressure-actuated membrane valves as well as peristaltic pumps, which are essential components for transporting and dispensing fluids in integrated microdevices [5-7]. However, this elasticity is often a cause of channel deformation under the application of high pressure, affecting the reliability in fluid manipulation. On the other hand, thermoplastics are becoming popular as the substrate for microdevices [8-11]. For instance, poly(methyl methacrylate) (PMMA) is mechanically rigid, optically transparent, and gastight, and PMMA devices are easily manufactured by employing injection molding, micromachining, or hot embossing technique together with the thermal bonding process. Although the precision of these fabrication processes is not so high compared with the usual soft lithography for PDMS microdevice, the low cost and rapidness in fabrication are attractive for general microfluidic applications. Hybrid microfluidic devices composed of PDMS and thermoplastic substrates like PMMA would therefore be advantageous for integrating flexible components into rigid devices and compensating their shortcomings, although making a chemical bond between these substrates is a non-trivial task.

In order to bond these different-type polymer substrates, several methods have hitherto been explored: for example, chemical vapor deposition of polymers on plastic substrates [12], silane-chemistry based surface modification [13-15], and UV-ozone treatment [16]. Although these methods are able to make a chemical bond between PDMS and thermoplastics, and most of these bonding schemes are stable under the pressure application of 50 psi ($\sim 3.5 \times 10^5$ Pa), a new method to easily and strongly bond PDMS and thermoplastics would facilitate the wider application of the low-cost and highly-functional hybrid devices, which can exploit the advantages of both rigid and flexible substrates.

Here in this study, we propose a simple and versatile method of bonding PDMS and thermoplastic plates, by employing a sol-gel method. Sol-gel methods have been employed for the preparation of organic solvent-resistant PDMS microchannels [17] and the development of capillary-based monolithic columns for biomolecule separation [18,19], both of which formed and utilized a silica-layer inside the microchannel or capillary. We applied the sol-gel procedure to coat thermoplastic plates (mainly PMMA plate) with a thin layer of silica, which can be covalently bonded with the O₂-plasma treated PDMS. The silica surface can further be functionalized with a variety of silane chemicals. In this study, we characterized the silica-coated PMMA surface, and evaluated the bonding strengths between PDMS and thermoplastics including PMMA, PC, PVC, and PP. In addition, we fabricated multi-layer microdevices composed of multiple PDMS/PMMA plates, and demonstrated the actuation of pressure-actuated valves and the parallel formation of multiple streams and droplets with different compositions.

2. Materials and Methods

2.1. Materials

Polydimethylsiloxane (PDMS; Sylpot 184) was obtained from Dow Corning Toray Corp., Tokyo, Japan. PMMA plates ($70 \times 30 \times 1$ mm) were obtained from PMT Corp., Fukuoka, Japan. Negative photoresists, SU-8 2025 and 2050 were obtained from Microchem Corp., MA, USA. Glass slides were obtained from Matsunami Glass Ind. Ltd., Osaka, Japan. Tetraethoxysilane (TEOS) was obtained from Wako Pure Chemical Ind. Ltd., Osaka, Japan. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (HTTS) was obtained from Gelest Inc., PA, USA. All other chemicals were of analytical grade.

2.2. Bonding procedure

The fabrication procedure of PDMS and thermoplastic (mainly PMMA) hybrid microdevices is shown in Fig. 1. As the start material for sol-gel chemistry, we employed tetraethoxysilane (TEOS). Initially, TEOS and ethanol were mixed, and then 0.1 M HCl was added. The volume ratio of 0.1 M HCl was fixed at 10%, while those of TEOS and ethanol were changed. The mixture was stirred at 30°C overnight to obtain TEOS oligomer (sol) as a result of hydrolysis and polycondensation. Thermoplastic plates were treated with O₂ plasma using a plasma reactor (PR-500, Yamato Scientific Corp., Japan) at 200 W for 3 min, and then, the TEOS sol was spin-coated on the treated surface at 2000 rpm for 30 sec. The coated TEOS sol was further polymerized and dried by heating at 80°C

for 1 h in a convection oven. The formed silica layer on the thermoplastic plate and a flat PDMS plate were treated with O₂ plasma (at 100 W for 10 sec), and they were covalently bonded by bringing them into contact. The bonded plates were incubated at a room temperature at least for 2 h before conducting further examination or inserting the inlet tubing.

2.3. Fabrication of multilayer hybrid microdevices

As the first application of the presented bonding process, we fabricated and actuated membrane valves in three-layer PMMA-PDMS-PMMA devices. PDMS prepolymer (a mixture of the base and the curing agent at a volume ratio of 10:1) was spin-coated on a silicon wafer ($\Phi = 100$ mm) at 400 rpm for 30 sec, and then it was baked at 85 °C for 30 min to obtain a flat PDMS membrane with a thickness of ~180 μ m. Microchannels were micromachined on PMMA plates by using a NC-micromachining device (Micro MC-2, PMT Corp.) equipped with an end mill ($\Phi = 0.1$ – 0.5 mm). Micromachined PMMA surfaces, either with the pressure-controlling chamber or the fluid channels, were silica-coated by the sol-gel procedure. After treating the PDMS membrane and the PMMA plates by O₂ plasma, the valve area on the PMMA plate having the fluid channels was treated with silane; a small aliquot of methanol containing 1% (w/v) HTTS was dropped, in order to avoid the permanent bonding between the PDMS membrane and the actuation area of the valve. The PDMS membrane and the PMMA plate were brought into contact, and by repeating this procedure twice with aligning the channels positions, the PDMS membrane was sandwiched by two PMMA plates.

Second, as the microdevice for multiple-flow distribution and parallel droplet generation, we

fabricated three-layer PDMS-PMMA-PDMS devices. Initially, SU-8 molds on silicon wafers were prepared by using the usual soft lithography, and PDMS plates having microchannel structures were prepared by using the replica molding technique as described elsewhere [1,2]. On the other hand, through-holes ($\Phi = 0.3$ or 2.0 mm) were precisely drilled on the PMMA plate by using the micromachining device, and then the top and bottom surfaces of the PMMA plate were coated with the silica layers stepwise. After forming the silica layers, these PDMS and PMMA plates were bonded with aligning the positions of the microchannels and the through-holes. Finally, after attaching silicone tubes for inlets and outlets, the inner surface of microchannels was modified to be hydrophobic; ~ 20 μL of methanol containing 1% (w/v) HTTS was introduced into the channel, and after 1 min of incubation at a room temperature, the solution was removed and the microchannel was dried. The silanized surface of the silica-coated PMMA became hydrophobic, being suitable for the stable formation of water-in-oil droplets.

3. Results and Discussion

3.1. Evaluation of coated PMMA surface

We first examined the effect of initial concentration of TEOS monomer on the uniformity of the formed silica layer, by changing the TEOS concentration (the volumetric ratio of TEOS) from 10 to 50%. Fig. 2 (a) shows the optical micrographs of the coated PMMA plates when the TEOS concentrations were 20 and 40%, respectively. As a result, when the initial TEOS concentration was higher than 30%, we observed cracks formed on the PMMA plate. The number of cracks

increased with the increase of the TEOS concentration, and these cracks caused fluid leakage when microchannel experiments were conducted (data not shown). On the other hand, when the TEOS concentration was 20% or lower, uniform coating was achieved and no cracks were observed. Fig. 2 (b) shows the SEM images of an identical micromachined PMMA plate before and after coating with the silica layer, and Fig. 2 (c) shows the cross-section of the PMMA microchannel coated with the silica layer for 5 times, when the TEOS concentration was 20%; uniform coating was achieved even inside the microchannel structure. The thicknesses of the silica layer were ~ 140 and ~ 300 nm for TEOS sol solutions obtained from 10% and 20% of TEOS, respectively, which were deduced from SEM images of five-time multiplied surfaces. In this study, the TEOS concentration was therefore fixed at 20% unless noted otherwise.

To further elucidate the presence of the silica layer on the coated surface, we conducted IR spectroscopy by using a FT-IR spectrophotometer (FTIR-8400, Shimadzu Corp., Kyoto, Japan). The IR spectrum of the coated surface using the silica sol of 10% TEOS solution is shown in Fig. 3 (a). As the number of coating increased, the characteristic signal at 1058 cm^{-1} (Si-O-Si bonding) increased, while the signals at 1726 cm^{-1} (C=O bonding of PMMA) and 1130 cm^{-1} (C-O) decreased, confirming the presence of the silica layer. In addition, the uniformity of the silica layer on the coated PMMA plate (30×70 mm) was estimated by comparing the peak heights at 1058 cm^{-1} and 1726 cm^{-1} . As a result, the variation of the coating thickness was $\sim 20\%$, and the silica layer at the plate center was thinner than that near the edges. Then, we examined if the organic-solvent tolerance is improved in the case of silica-coated PMMA. We dipped the coated and non-coated

PMMA plates in toluene at a room temperature and analyzed the amount of dissolved PMMA molecules by measuring the absorbance at 220 nm by using a spectrophotometer (Spectrophotometer 100-10, Hitachi Corp., Tokyo, Japan). As a result, the dissolution amount from the coated PMMA was less than 10% of the bulk PMMA, showing the dramatic improvement of the organic-solvent tolerance in the case of the coated PMMA (Fig. 3 (b)). The small amount of dissolution would be attributed to the non-coated edges of the PMMA plate.

3.2. Evaluation of bonding strength

The bonding strengths between PDMS and various thermoplastic plates were examined. Non-treated, O₂-plasma treated, and silica-coated thermoplastic plates were prepared, and they were respectively bonded with a small PDMS plate (5 × 5 mm). The other side of the PDMS plate was covalently bonded with a glass slide by O₂-plasma treatment, and the break-off pressure was estimated by gradually increasing the load to pull off the bonded plates and measuring the critical force using a spring scale when the bonded substrates were detached or the PDMS plate was torn. The results are shown in Table 1. When the PMMA plate was not coated with the silica layer, the bonding strength was much lower than that of the coated PMMA plate, regardless of the O₂-plasma treatment (at 100 W for 10 sec for PDMS, and 200 W for 3 min for PMMA). While in the case of the coated PMMA, the bonding strength was higher than 1.0×10^6 Pa, despite we could not measure the accurate bonding strength since the PDMS plate was torn before the bonded PDMS-PMMA plates were completely detached. This value is comparable to the values reported previously

[12-14] and those of the PDMS-glass and PDMS-PDMS bondings with the O₂-plasma treatment, in which the PDMS plate was also torn, showing that the bonding strength is high enough to prepare hybrid devices and conduct fluidic experiments. In the experiment, we used the TEOS sol solution within 1 day from the oligomerization process, since the long-time storage of the sol solution is not recommended. The bonding strength of PDMS and PMMA gradually decreased with the increase in the storage period of the sol solution; after 1 month of storage at 4°C, the break-off pressure became about the half of the value shown in Table 1 ($5.18 \pm 1.18 \times 10^5$ Pa). In addition, it should be noted that the bonding is not so stable under the presence of the hydrophilic solvent at a high temperature. The bonded PDMS-PMMA plates were completely detached after dipping in distilled water at 70°C for 24 h, although the bonding was not significantly degraded in water at a room temperature (the break-off pressure was $8.24 \pm 1.94 \times 10^5$ Pa, after 48 h of dipping).

In the case of other thermoplastic plates including PC, PVC, and PP, we also examined the bonding strengths as shown in Table 1. Although the bonding strengths of PC and PVC were slightly lower than those of PMMA and PP, we confirmed that the presented scheme can be applied to strongly bond PDMS with various types of thermoplastic substrates. Note that the initial O₂ plasma treatment prior to spin-coating of TEOS oligomer was essential to achieve the uniform silica coating on the surface, especially in the case of PC, PVC, and PP.

3.3. Fabrication of membrane valves

Active microvalves are one of the essential components in integrated microfluidic devices such

as a total gene analyzer or single-cell analysis systems [7], which require multiple liquid mixing and dispensing processes. Microvalves made of a flexible PDMS membrane and rigid fluidic channels would be superior to the entirely PDMS-base valves, since the channel deformation would be prevented even under the high-pressure application. Here, to address the applicability of the presented bonding method for fabricating membrane valves, we demonstrated the pressure-controlled valve actuation.

Fig. 4 (a) shows the schematic image of the microvalve structure, which is closed by the positive-pressure application. Valve actuation as well as the fluid (distilled water containing a blue dye) transportation was performed by controlling the applied pressure using a pressure controlling apparatus (HIP-240, Arbiotech Corp., Tokyo, Japan). As shown in Fig. 4 (b), we could accurately control the on-off switching of the valve by changing the applied pressure to the pressure controlling chamber, P_{valve} . We measured the relation between P_{valve} and the fluid-forward pressure (P_{fluid}) applied to the fluid channel, as shown in Fig. 4 (c). To open the valve, P_{fluid} should be slightly higher than P_{valve} , due to the relatively thick ($\sim 180 \mu\text{m}$) PDMS membrane. Additionally, we could precisely control the valve opening and closure even under high-pressure conditions; we did not observe the fluid leakage from the seam of the bonded surfaces even when the applied pressure was $\sim 500 \text{ kPa}$, owing to the strong chemical bonding formed between these substrates.

3.4. Demonstration of parallel droplet generator

One of the general advantages of the microfluidic devices is its ability to precisely form parallel

streams with different concentrations or compositions, which is essential for conducting high-throughput chemical/biological experiments [20-23]. In the case of forming multiple flows from two kinds of fluids, usually fluid flows are split into multiple branch flows and they are combined downstream. Then by adding a third fluid into the multiple flows with different compositions, one can conduct combinatorial chemical reactions, generate droplets with different compositions, or perform parallel biochemical analyses by simple operations. A microchannel network for these purposes needs to equip overpass/underpass crossings to distribute and mix the multiple flows, and thus, the multi-layer structures with through holes should be employed. Since it is not an easy task to precisely make through-holes with a diameter of several hundred micrometers through the PDMS plates, we employed a PMMA plate with through-holes created by micromachining, and bonded the PMMA plate with two PDMS plates.

In this study, we demonstrate the parallel droplet formation with different compositions, by adopting the concept of the parallel flow-distributor generating multiple concentration conditions from two kinds of fluids [22]. The microchannel design is shown in Fig. 5 (a). This microchannel network comprises (1) a bottom PDMS layer for distributing multiple aqueous flows with different compositions, (2) a middle PMMA plate having through-holes, and (3) a top PDMS layer for generating water-in-oil droplets. Ideally, the mixing ratio of two aqueous fluids is inversely proportional to the ratio of the branch lengths (L_{Rn}/L_{Ln}) in the flow-distributor on the bottom layer; the theoretical mixing ratios for channels 1~5 are 1:5, 2:4, 3:3, 4:2, and 5:1, respectively. The flow resistances of the branch channels on the top layer are equal, to achieve the uniform

flow-distribution and obtain the uniform-size droplets.

In the experiment, we used distilled water either with a blue (10 mM methylene blue) or red (10 mM safranin) dye as the disperse phases from Inlets 1 and 2, and olive oil as the continuous phase from Inlet 3, respectively. The flow rates from Inlets 1, 2, and 3 were 5, 5, and 30 $\mu\text{L}/\text{min}$, respectively, and the droplets generated at the T-shape confluence points on the top layer were observed by using a microscope. When we did not treat the inner surface of the microchannel with HTTS, droplet breakup did not precisely occur at the confluence, and the droplet volumes were not uniform, due to the relatively hydrophilic silica surface on the PMMA plate. On the other hand, when the surface was treated with HTTS, we observed the formation of uniform-size droplets as shown in Fig. 5 (b), indicating the equal flow distributions through the multiple branch channels and the through-holes. Fig. 5 (c) shows the red and blue dye concentrations in the droplets, measured by the colorimetric analysis from the captured images. We confirmed that the mixing ratios were changed stepwise, which were almost equal to the theoretical values. The presented technique of making hybrid devices would be useful for conducting digital-microfluidic experiments or preparing monodisperse particles in a low-cost and relatively-complicated microfluidic network, since the coated PMMA have the tolerance to organic solvents, while the channel deformation of PDMS would be suppressed. In addition, further functionalization of coated PMMA surface would be possible, by utilizing the various types of silane chemistry.

4. Conclusions

We presented a new process for making a strong bond between chemically inert PDMS and relatively rigid thermoplastics, by utilizing the TEOS-based sol-gel chemistry. Due to its simplicity and versatility, this process enables a variety of microfabricated devices which take advantage of both rigid and flexible polymeric substrates, and would accelerate the development of inexpensive and highly-functional microfluidic apparatus. Although here we just demonstrated the applications of PMMA-PDMS hybrid devices, this process would be applied to the fabrication of microdevices utilizing various polymeric substrates like PC, PVC, or PP, which also showed the high bonding strengths with PDMS. In addition, sol-gel based coating offers additional advantages in terms of organic-solvent tolerance and surface functionality by utilizing silane chemistry, which provides uniqueness for general microfluidic applications.

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Biographies

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Table

Table 1. Bonding strengths between PDMS and thermoplastics, glass, or PDMS, bonded either by self-sealing, O₂-plasma treatment, or the presented sol-gel scheme. Unit, 10⁵ Pa.

Substrate	Self-sealing [†]	O ₂ -plasma treatment [‡]	Sol-gel method
PMMA	0.19 ± 0.02	0.33 ± 0.06	10.7 ± 1.60*
PC	0.24 ± 0.03	0.32 ± 0.04	6.01 ± 1.38
PVC	0.25 ± 0.05	0.33 ± 0.06	5.75 ± 1.49
PP	0.20 ± 0.03	0.27 ± 0.07	12.6 ± 2.96*
Glass	0.34 ± 0.09	10.2 ± 1.57*	
PMDS	0.33 ± 0.06	9.56 ± 1.97*	

*The PDMS plate was torn.

[†]Both substrates were not treated with O₂ plasma.

[‡]PDMS and thermoplastic substrates were treated with O₂ plasma at 100 W for 10 sec and at 200 W for 3 min, respectively.

Figure Legends

Figure 1. Fabrication/bonding process of PMMA-PDMS hybrid devices by using the sol-gel method.

Figure 2. (a) Optical microscopic images of silica-coated PMMA plates with initial TEOS concentrations of 20 and 40%, respectively. (b) Scanning electron microscopy (SEM) images of the PMMA plate having a microchannel structure, before and after coating with the silica layer using the 20% TEOS sol solution. (c) SEM image of a microchannel cross-section, coated by the silica layer using the 20% TEOS solution for 5 times. In the right photograph, the area between the two arrows indicates the silica layer. Scale bar, (a) and (b): 200 μm , and (c): 20 μm .

Figure 3. (a) IR spectrum of the non-coated (blank) or coated PMMA plate with the sol-gel procedure. A: peak at 1058 cm^{-1} is attributed to Si-O-Si bonding. B: peak at 1726 cm^{-1} is attributed to C=O bonding. (b) Dissolution amount of PMMA molecules in toluene, either from the bulk or coated PMMA plate.

Figure 4. (a) Schematic illustrations of the micro membrane valve composed of PMMA-PDMS-PMMA substrates and its actuation by applying positive or negative pressure. (b) Micrographs showing the valve opening/closing with the applied pressures as indicated. (c)

Relation between the valve-controlling pressure (P_{valve}) and the critical pressure of P_{fluid} to open/close the valve. Dashed line indicates $P_{\text{valve}} = P_{\text{fluid}}$.

Figure 5. (a) Design and photograph of the parallel droplet generator composed of PDMS-PMMA-PDMS substrates. In the right photograph, aqueous solutions of red, blue, and yellow dyes were respectively introduced from Inlets 1, 2, and 3, at a constant flow rate (10 $\mu\text{L}/\text{min}$). (b) Micrographs showing the droplets generated at the T-shape confluence points on the top plate. (c) Red (safranin) and blue (methylene blue) dye concentrations in the formed droplets in each branch channel, measured by colorimetric analysis.

Figure(s)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5