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Non-silicon substrate bonding mediated by poly(dimethylsiloxane) interfacial coating

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ABSTRACT

In this paper, we introduce a simple and robust strategy for bonding poly(dimethylsiloxane) (PDMS) with various thermoplastic substrates to fabricate a thermoplastic-based closed microfluidic device and examine the feasibility of using the proposed method for realizing plastic–plastic bonding. The proposed bonding strategy was realized by first coating amine functionality on an oxidized thermoplastic surface. Next, the amine-functionalized surface was reacted with a monolayer of low-molecular-weight PDMS, terminated with epoxy functionality, by forming a robust amine-epoxy bond. Both the PDMS-coated thermoplastic and PDMS were then oxidized and permanently assembled at 25 °C under a pressure of 0.1 MPa for 15 min, resulting in PDMS-like surfaces on all four inner walls of the microchannel. Surface characterizations were conducted, including water contact angle measurement, X-ray photoelectron spectroscopy (XPS), and fluorescence measurement, to confirm the successful coating of the thin PDMS layer on the plastic surface, and the bond strength was analyzed by conducting a peel test, burst test, and leakage test. Using the proposed method, we could successfully bond various thermoplastics such as poly(methylmethacrylate) (PMMA), polycarbonate (PC), polystyrene (PS), and poly(ethylene terephthalate) (PET) with PDMS without the collapse or deformation of the microchannel, and the proposed method was successfully extended to the bonding of two thermoplastics, PMMA, and PC.

1. Introduction

Plastic bonding with elastomeric poly(dimethylsiloxane) (PDMS) has wide practical applicability that cannot be achieved with a homogeneous assembly such as plastic–plastic or PDMS–PDMS. For example, a plastic–PDMS assembly can provide versatile surfaces for the targeted immobilization of cells, proteins, and other biomolecules to a predetermined location within a microchannel. In addition, a plastic substrate ensures the formation of submicron-scale patterns with high mechanical strength, preserving the high fidelity of the channel morphology without sacrificing optical transparency. Moreover, the build-up of microfluidic components such as microvalves and micropumps becomes possible, and their functions can be optimized when constructed from heterogeneous materials with various mechanical properties. Despite the numerous advantages of plastic–PDMS assemblies, however, the bonding of plastic with PDMS is not easily realized owing to differences in their chemical compositions, because plastics are generally non-silicon-based and PDMS is silicon-based.

Several researchers have endeavored to realize plastic–PDMS bonding [1–9]. Vlachopoulou et al. [6] treated the surface of poly(methylmethacrylate) (PMMA) with aminosilane and subsequently oxidized the aminosilane-treated surface to bond with plasma-treated, oxidized PDMS under a heated condition. Lee and Ram [9] proposed the bonding of a plastic–PDMS assembly mediated by the use of an organofunctional silane network at the interface, which could be applied for realizing a hydrolytically stable bond for microvalve application. Im et al. [7] proposed the bonding of various plastics with PDMS by grafting epoxy functionalities via an initiated chemical vapor deposition (iCVD) process followed by the plasma polymerization of amine functionalities under a heated condition. In our previous studies [8,10], we have proposed a facile route for realizing the irreversible bonding of PDMS–PDMS as well as plastic–PDMS assemblies by forming a robust and stable amine-epoxy chemical bond at room

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temperature under atmospheric pressure. This was realized because carbon backbones of thermoplastic substrates break after external energy input such as plasma treatment, and free carbons react with inorganic silicons of the silane coupling agent, which is used to functionalize substrate surfaces, to form Si–O–C bond [9,11–13]. Because of the high bond strength (~580 kPa) obtained when bonding polycarbonate (PC) with PDMS, the proposed bonding strategy is particularly suitable for applications where liquid injection with a high flow rate is required or when constructing arrays of biomolecules inside a closed microfluidic device for targeted immobilization purposes, because the capping of the biomolecule-patterned surface with a microchannel-engraved substrate is realized under mild conditions such as at room temperature. In this way, the immobilized biomolecules could be protected in the sealing process. Despite many advantages, however, the above-mentioned method is difficult to apply when homogeneous inner wall coating is desired.

In our previous study [14], we introduced a strategy for coating an anti-adhesion layer on the surface of a nanopatterned polymer mold to facilitate the transfer of the nanopatterns onto another polymer precursor. The anti-adhesion coating was realized by forming a monolayer of low-molecular-weight PDMS on the surface of the nanopatterned mold surface. The PDMS coating was realized by first functionalizing the surface of the nanopatterned mold with aminosilane and then reacting the amine group with low-molecular-weight PDMS, terminated with epoxy functionality, via amine-epoxy bond formation. Owing to the innate surface hydrophobicity of the coated PDMS layer, we could successfully replicate nanopatterns onto a polymer over 200 times with high stability without deforming the nanopatterns [15].

In this study, we adopt the anti-adhesion mold coating strategy to bond a thermoplastic with PDMS. In short, we first coat the epoxy-functionalized, low-molecular-weight PDMS, on either a patterned or flat surface of an amine-functionalized plastic substrate. Then, we oxidize both the PDMS-coated plastic substrate and the bare PDMS and simply assemble them, as in the typical silicon-based bonding process widely applied for bonding PDMS–PDMS or PDMS–glass assemblies. In this way, all four walls of the microchannel formed after the assembly displays PDMS-like property, which makes the device highly desirable particularly when homogeneous flow of liquid sample is demanded. We demonstrate the universal applicability of the proposed method by bonding PDMS with various thermoplastics such as PMMA, PC, polystyrene (PS), and poly(ethylene terephthalate) (PET). In addition, we perform various surface characterizations such as contact angle measurement, X-ray photoelectron spectroscopy (XPS) analyses, and fluorescence measurement to verify the successful coating of the PDMS monolayer. Furthermore, we analyze the bond strength by conducting a peel test, burst test, and leakage test. In this study, we further extend its application for bonding two thermoplastics, specifically, PMMA with PS.

2. Materials and methods

2.1. Materials

PDMS prepolymer (Sylgard 184) and a curing agent were purchased from Dow Corning (Midland, MI, USA). SU-8 3050 and SU-8 developers were purchased from MicroChem (Newton, MA, USA). 3-Aminopropyltriethoxysilane (APTES, 99%) and monoglycidyl ether terminated PDMS (average M_n 5000 g mol^{-1}) were purchased from Aldrich. PET (180 μm in thickness) was purchased from SKC (Korea). PMMA, PC, and PS were used, with widths, lengths, and thicknesses of 20, 20, and 3 mm, respectively. A custom-made pneumatic press machine was used to fabricate microchannels on plastic substrates by embossing. A Tesla coil (BD-10A) was purchased from Electro-Technic Products (Chicago, IL, USA).

2.2. Microchannel fabrication

Serpentine and spiral microchannels were fabricated on either the PDMS or plastic substrates. To fabricate the microchannels on a PDMS substrate, conventional photolithography and replica molding were performed [16]. In short, SU-8 3050 was spin-coated on a Si wafer at 4000 rpm for 30 s, followed by soft baking at 65 °C for 5 min and 95 °C for 30 min. The SU-8 spin-coated Si wafer was then exposed to UV light (365 nm, 15 mW cm^{-2}) for 20 s using a mask aligner (CA-6M, Shinu M.S.T, Korea). Post exposure, baking was performed at 65 °C for 1 min and at 95 °C for 5 min. After the development, a 10:1 (w/w) mixture of the PDMS prepolymer and a curing agent was poured onto the microchannel-patterned Si wafer. After thermal curing at 80 °C for 1 h, the cured PDMS replica was peeled off the Si master. To fabricate microchannels on a plastic substrate, a CNC milling machine was used to engrave the microchannels directly on the plastic substrate.

2.3. Surface characterizations

2.3.1. Contact angle measurement

The water contact angles were measured on the surfaces of a pristine plastic substrate, corona-treated plastic substrate, APTES-treated plastic substrate, and monoglycidyl ether terminated PDMS-treated plastic substrate by the sessile drop technique using a Phoenix 300 contact angle measuring system (Surface Electro Optics, Korea) and analyzed with Image Pro 300 software. The measurements were repeated five times and averaged.

2.3.2. XPS analyses

XPS analyses were conducted using an Axis-Hsi (Kratos Analytical, UK) equipped with a magnesium X-ray radiation source of dual gun (1253.6 eV) and pass energy of 20 eV. The pressure in the chamber was below 5×10^{-9} Torr before the data were taken, and the voltage and current of the anode were 15 kV and 10 mA, respectively. The take-off angle was set at 45°. The binding energy of C 1s (284.5 eV) was used as the reference. The resolution for the measurement of the binding energy was about 0.1 eV.

2.3.3. Fluorescence measurement

The surface autofluorescence values of pristine PDMS, PMMA, and PC, as well as the fluorescence values of PDMS-coated PMMA and PC, were measured. The substrates were thoroughly cleaned by sonicating them in isopropyl alcohol for 3 min; they were then dried completely to eliminate contaminants. The autofluorescence values of the selected substrates were measured using an Olympus IX-71 inverted fluorescence microscope, and they were analyzed using ProgRes® Capture Pro 2.8 software (Jenoptik).

2.4. Bonding process

The processes for bonding the thermoplastic and PDMS or two thermoplastics are schematically shown in Fig. 1. As shown in Fig. 1a, a thermoplastic substrate was treated with a corona discharge for 1 min and dipped in a 5% (v/v) aqueous solution of APTES at 80 °C for 20 min. After washing the surface with a copious amount of distilled water and drying the surface completely, the APTES-functionalized plastic substrate was reacted with monoglycidyl ether terminated, low-molecular-weight PDMS at 80 °C for 4 h to form an amine–epoxy bond. The unreacted monoglycidyl ether-terminated PDMS was removed by immersing the substrate in isopropyl alcohol and sonicating for 1 min, followed by complete