

Simple room temperature bonding of thermoplastics and poly(dimethylsiloxane)[†]

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We describe a simple and versatile method for bonding thermoplastics to elastomeric polydimethylsiloxane (PDMS) at room temperature. The bonding of various thermoplastics including polycarbonate (PC), cyclic olefin copolymer (COC), polymethylmethacrylate (PMMA), and polystyrene (PS), to PDMS has been demonstrated at room temperature. An irreversible bonding was formed instantaneously when the thermoplastics, activated by oxygen plasma followed by aminopropyltriethoxysilane modification, were brought into contact with the plasma treated PDMS. The surface modified thermoplastics were characterized by water contact angle measurements and X-ray photoelectron spectroscopy. The tensile strength of the bonded hybrid devices fabricated with PC, COC, PMMA, and PS was found to be 430, 432, 385, and 388 kPa, respectively. The assembled devices showed high burst resistance at a maximum channel pressure achievable by an in-house built syringe pump, 528 kPa. Furthermore, they displayed very high hydrolytic stability; no significant change was observed even after the storage in water at 37 °C over a period of three weeks. In addition, this thermoplastic-to-PDMS bonding technique has been successfully employed to fabricate a relatively large sized device. For example, a lab-on-a-disc with a diameter of 12 cm showed no leakage when it spins for centrifugal fluidic pumping at a very high rotating speed of 6000 rpm.

Introduction

Heterogeneous bonding, in which bonding occurs between two different materials, is a challenging task due to the difference in the physicochemical properties of the materials to be bonded. However, the diverse material properties of thermoplastics and elastomers offer unique opportunities for hybrid microfluidic devices. Therefore, it is important to develop techniques that are both simple and versatile in order to bond these materials together that maintain structural integrity of the pre-formed micro- and/or nanostructures.

One common method used for this purpose is surface modification-based bonding. Recently, Tang *et al.* have demonstrated a chemical gluing strategy for the permanent bonding of non-silicon-based thermoplastic substrates with silicon-based polydimethylsiloxane (PDMS) at room temperature.¹ The chemical gluing was achieved by anchoring amine terminated silane reagents on one substrate and epoxy terminated silane reagents on the other substrate *via* a silane coupling reaction followed by

amine-epoxy bond formation at the interfaces at room temperature.

Valchopoulou *et al.* have also reported a method for bonding PDMS to polymethylmethacrylate (PMMA) through surface modification using aminopropyltriethoxysilane (APTES)² and Tennico *et al.* have used tetraethyl orthosilicate (TEOS) for the same purpose.³ In both cases, however, the authors employed pressure and relatively high temperature, *i.e.* 80 °C and 50 °C, respectively, in order to realize the bonding.

Among the properties of bond strength, hydrolytic stability^{4,5} is particularly important for the processes that rely on an aqueous environment. However, it is not available for most of the reported bonding methods used for the hybrid devices.

Another important issue to be considered is large-area bonding. In most of the previous reports, bonding has been achieved between the substrate and cover material over a small surface area. However, for some practical applications, for example, multiplexed lab-on-a-disc devices, bonding over a large surface with minimal contact area is often required.^{6,7} In a rotating disc, the centrifugal forces drive the fluids outward at several thousands of rpm. Here, the fluidic channels in a disc should withstand the pressure of several hundreds kPa. To the best of our knowledge, irreversible large-area bonding of a plastic compact disc and a PDMS substrate has never been demonstrated.

In this paper, we describe a simple method for bonding thermoplastics to PDMS at room temperature. Hydrolytic stability of the bonded devices was studied and its applicability for large area bonding was also demonstrated. The bonding was performed through surface modification of the thermoplastic with a silane reagent, APTES. This bonding process was robust and

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could be applied to a variety of substrates. In this study, we have tested four kinds of thermoplastic materials, namely, polycarbonate (PC), cyclic olefin copolymer (COC), PMMA, and polystyrene (PS). This simple bonding method will provide an easy and powerful strategy for the irreversible bonding of thermoplastics to PDMS at room temperature for developing hybrid microfluidic devices with a design tailored to its specific needs and features on either of the materials or on both.

Experimental

Surface modification for bonding

Schematic representation of the bonding process is shown in Figure S1.† Thermoplastic samples were cut into 3 cm × 5 cm rectangular pieces using a CNC milling machine (3D modeling machine; M&I CNC Lab, Osan, Korea). They were cleaned with ethyl alcohol or isopropyl alcohol (IPA), dried and treated with a 60 W oxygen plasma (Cute plasma system; Femto Science, Korea) for 1 min and placed in an aqueous solution of 1% v/v APTES for 20 min. The substrates were then washed with DI water and dried under a stream of air. PDMS was cut into pieces of the desired size and treated with an oxygen plasma (60 W) for 1 min. The activated thermoplastic and PDMS substrates were kept in conformal contact at room temperature and the bonding was formed within a few minutes. For inlet and outlet ports of the microfluidic channel, holes were punched through the PDMS before bonding. The detailed information about the fabrication of microchannels in PDMS, materials and reagents, characterization methods of functional groups in surface, tensile strength, leakage and stability tests are shown in the ESI.†

Results and discussion

Surface characterization

The water contact angles for untreated, oxygen plasma-treated, and APTES modified thermoplastics immediately after modification and after drying at room temperature for 12 h are shown in Table S1.† The values for untreated PMMA and COC were in good agreement with literature values.⁸ A decrease in the water contact angle after plasma activation implies the generation of a hydrophilic surface. The initial water contact angle measured immediately after APTES treatment was almost similar to the values obtained for plasma-treated thermoplastics and could probably be explained by the hydrophilicity arising from the reaction solvent. The hydrophobicity of the substrates increased slowly and reached a stable value after aging them in ambient conditions for 12 h.

To ensure that the APTES was covalently tethered to the activated surface, a PC surface was characterized by XPS before and after the modification. The XPS spectra for the elemental composition of PC is shown in Figure S2.† The spectra of the untreated PC shows a ratio of 0.192 between the O1s and C1s photoemissions. After surface modification, the O1s/C1s ratio changed to 0.266 indicating the increased oxygen content of the surface (Table S2†). The presence of N1s, Si2s and Si2p peaks indicates that APTES was coated on the surface. The identical elemental composition for the spectra recorded on the same day

of modification and after aging for one day denotes the stability of the surface functionalization of PC.

Bonding of thermoplastic to PDMS and the effect of surface treatment on bonding

There are two critical steps in the bonding process as denoted in Fig. S1:† (i) Oxygen plasma treatment of both substrates; and (ii) surface modification of the thermoplastic with APTES reagent. When the surface functionalized thermoplastic comes into contact with the plasma activated PDMS, an irreversible bond was formed within 2 min at room temperature for PC, COC and PS. In the case of PMMA, the time required for realizing this bond was 15 min. This could be due to differences in the properties of the thermoplastics.⁹

The bonding characteristics of various thermoplastics and PDMS which were treated under different conditions and subjected to bonding is summarized in Table S3.† Strong bonding was formed in cases where the plasma activated and APTES coated thermoplastics were kept in contact with plasma activated PDMS with or without surface modification. Also, PDMS coated with APTES and the thermoplastic treated with an aqueous solution following plasma treatment also bonded strongly.

For plasma treated COC and PS, the bonding did not occur with the plasma treated PDMS but a strong and irreversible bond was formed when PDMS had an APTES layer. In the case of PC, which was treated with APTES without prior plasma activation, a strong bond was realized with the plasma treated PDMS. All other surface treatment conditions resulted either in weak bonding or no bonding. Further study is in progress to investigate the detailed mechanisms of the bonding as well as the unique plastic-material-dependent characteristics.

These results clearly indicate that the plasma activation of both thermoplastics and PDMS is necessary and treating thermoplastics with APTES facilitates the bonding process. The APTES treatment of PDMS only helps when the thermoplastics were treated with an aqueous solution. From the above observations, and to minimize the steps required for bonding, the best choice was to do surface modification of only thermoplastics after plasma activation of both substrates.

In addition, the times required for bonding aged thermoplastic surfaces with plasma activated PDMS and *vice versa* are shown in Table S4.† First, the APTES coated thermoplastics from the same batch of modifications were subjected to bonding with plasma activated PDMS at an interval of 30 min. For each experiment, the PDMS was activated just before bonding. The time needed to realize the bond increased with prolonged aging time of the surface modified thermoplastic. However, when the aged thermoplastics were soaked in DI water for 5 min at room temperature and brought into contact with the plasma activated PDMS, bonding occurred. In contrast, bonding was realised immediately after contact between the oxygen plasma activated PDMS and the surface modified thermoplastic irrespective of the aging time of the activated PDMS until 240 min of activation.

From the above experiments, it was apparent that the process of bonding was significantly dependent on the surface wettability of the APTES modified thermoplastic. Water contact angle data showed that the surface wettability changed as the aging time

increased. It was confirmed that the APTES layer on the surface was stable even after 24 h according to the XPS data (see Figure S2†). At this point, it is important to note that the APTES coated thermoplastics are stable for long periods of time – testing time now is over one month – and soaking them in DI water for 5 min at room temperature before bonding helps in the formation of the bond.

Tensile strength measurements

Quantitative evaluation of the bonding strength of thermoplastic-PDMS devices was done by using a tensile tester. The plastic-PDMS hybrid device bonded to an aluminium jig is shown in Figure S3.† The load-displacement curves for the bonded thermoplastic-PDMS devices are shown in Fig. 1a. The bond strengths obtained for PC and PMMA were significantly higher than the reported values obtained with different bonding method (see Table S5†).¹ Tensile strength values for the PC-PDMS devices that were kept at relatively harsh storage conditions, such as -20°C and at 37°C in DI water, also showed very strong bond strengths. Various methods that are available for bonding thermoplastic and PDMS are summarized in Table S6.†

Burst pressure measurements

To examine the maximum burst pressure that the bonded assemblies could withstand, air was infused through the inlet channel at a rate of 10 mL min^{-1} . The result shows

that the channels were able to withhold more than 528 kPa without delamination, which was the maximum limit at which the pressure sensor was used. The pressure value displayed by the thermoplastic-PDMS device exceeded the holding pressure value required for many microfluidic applications.^{10,11}

Stability tests

Hydrolytic stability of the microfluidic devices can be very important in cell culture studies. Usually, it takes a few hours to a few days to complete a growth cycle, during which the bonding should be strong enough to hold the aqueous solution at 37°C without delamination. Even though Mehta *et al.* have successfully demonstrated that hybrid devices made of hard and soft materials can be used for cell culture studies, the lifetime of their device was limited to 14 days at high humidity.⁴ The devices that utilized polyallylamine-polyglycidylmethacrylate chemistry for bonding showed bond strength degradation after 6 h in an aqueous environment and the device completely failed after soaking them in water for 18 h.⁵

In contrast, the hybrid device bonded with the proposed method was extremely stable as demonstrated in Fig. 1b–e. The channels of thermoplastic-PDMS devices were filled with water and the device was completely immersed in water for three weeks at 37°C and also for one day at 100°C . The devices at 37°C showed a constant bond strength and the bond was stable

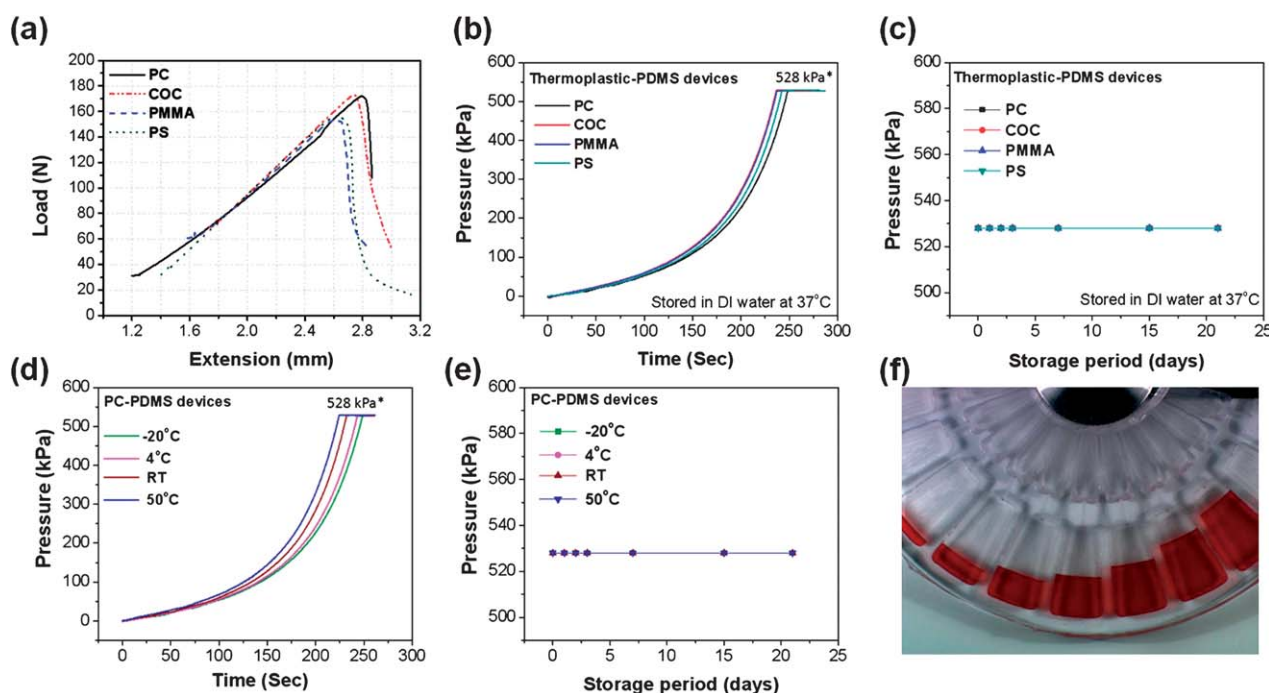


Fig. 1 (a) Tensile strength curves of the thermoplastic-PDMS hybrid devices. The highest load readings correspond to the point of rupture for each plastic. (b) Burst pressure measured after storing for three weeks to demonstrate the hydrolytic stability of thermoplastic-PDMS devices in DI water at 37°C . (c) Effect of storage time on burst pressure over a period of three weeks. (d) Stability of PC-PDMS devices at various temperatures (-20°C , 4°C , room temperature, and 50°C). The burst pressure was measured after storing for three weeks. (e) The effect of storage time on burst pressure over a period of three weeks. The devices show a constant result for the storage period of three weeks and the bonding remained unaffected. *Maximum limit of the pressure sensor. (f) A photograph of a PC-PDMS bonded disc with a diameter of 12 cm, rotating at 6000 rpm. The chambers were milled in PC and filled with 100–700 μL of aqueous red dye solution.

even after three weeks of storage. Fig. 1b shows the burst pressure measurements of thermoplastic–PDMS devices recorded after three weeks of storage in DI water at 37 °C and Fig. 1c shows the effect of storage time on the burst pressure of thermoplastic–PDMS devices over a storage period of three weeks.

To investigate the stability of the bonded hybrid devices, the PC–PDMS devices were kept at various temperatures including –20 °C, 4 °C, room temperature, and 50 °C. Fig. 1d and 1e represent the burst pressure measurements after three weeks of storage at a specified condition and the effect of storage time on the burst pressure respectively. The PC–PDMS devices stored at various temperatures and conditions for three weeks also exhibited constant pressure values indicating that the bond remained stable during the tested period.

Leakage tests

To study the integrity of sealed devices under hydrodynamic flow conditions, an aqueous solution of red dye was infused through the channels of bonded assemblies at flow rates from 5–60 mL min^{–1}. The channels were intact and leakage was not observed even when the infusion rate was 60 mL min^{–1} (see Figure S4 and ESI movie 1†), whose per minute injection volume was nearly 24 000 times higher than the total internal volume of the microchannel.

In addition, we have applied this bonding technique for the fabrication of a hybrid lab-on-a-disc to check the possibility of bonding for a relatively large device. A simple channel structure was designed and fabricated by micromilling on PC. Here, the bonding area was 42.85 cm², which is only 38.5% of the entire disc area. The gap of the bonding area at the outer wall of the disc, on which the centrifugal force is acting, was about 4.05 mm. The minimum distance between the channels was only 0.7 mm. Here, 100–700 µL of an aqueous solution of red dye was injected into each chamber and their movements by centrifugal forces were observed, as shown in Fig. 1f. At 6000 rpm, which is the maximum spin speed of our experimental setup, the pressure exerted on the wall of the disc due to 700 µL of dye solution was calculated to be 327 kPa. Even at the maximum spin rate with the largest sample volume, there was no leakage at the bonded interface. This leakage test using a PC–PDMS disc was the first attempt to demonstrate this large-area thermoplastic–PDMS bonding for centrifugal microfluidics.⁶

Conclusions

A novel and versatile room temperature bonding method for a hybrid device consisting of a thermoplastic and PDMS has successfully been demonstrated. The bonding was facilitated by the surface modification of the thermoplastic with APTES after plasma activation of both the thermoplastic and PDMS. Both tensile strength and burst pressure measurements showed very strong bonding characteristics for various thermoplastics such as PC, COC, PMMA and PS. Furthermore, all of the devices exhibited excellent hydrolytic stability even after three weeks of storage in water at 37 °C. They could also withstand large hydrodynamic flow with a per minute injection volume of nearly 24 000 times higher than the total internal volume of the microchannel. In addition, the lab-on-a-disc made of PC–PDMS bonded device with a diameter of 12 cm showed no leakage even at maximum spin speeds of 6000 rpm, suggesting the proposed method is also applicable for bonding relatively large sized devices.

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