

Electronic Supplementary Information for Simple Room Temperature Bonding of Thermoplastics and Poly(dimethylsiloxane)

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This supporting information includes:

Fig. S1 Schematic representation of bonding process. An irreversible bonding was formed between the thermoplastics and PDMS within a few minutes at room temperature. The channels were made either in PDMS using soft lithography techniques or in thermoplastic by CNC milling.

Fig. S2: XPS spectra for the detection of the atomic concentration of carbon, oxygen, nitrogen and silicon of pristine PC, APTES-modified PC and APTES-modified PC after 24 h of storage at ambient conditions

Fig. S3: Images of (a) a plastic-PDMS chip fixed to an aluminum jig before mounting in a tensile strength tester and (b) released devices after tensile strength measurements. The plastic sheets correspond to PC, COC, PMMA and PS, respectively.

Fig. S4 A photograph of PC-PDMS device having microchannel in PDMS, the tests were performed under flow condition infusing a red dye solution at the rate of 60 mL/min. The entire hybrid devices made of thermoplastics under investigation (PC, COC, PMMA and PS) showed the same result.

Table S1. Contact angle data of pristine and surface treated thermoplastics.

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Movie file 1: Result of leakage test done by infusing a red dye solution through the microchannel

Supplementary Experimental Information

Materials and reagents

PDMS prepolymer (Sylgard 184) and a curing agent were purchased from Dow Corning (MI, USA). SU-8 photoresist and 3-APTES were purchased from MicroChem Corp. (MA, USA) and Sigma-Aldrich Corp. (MO, USA), respectively. The thermoplastics used for the bonding test were as follows: PC was purchased from I-Components Co., Ltd (Seongnam, Korea); COC (5013 L10) was purchased from TOPAS Advanced Polymers GmbH (Frankfurt-Höchst, Germany); PMMA was Plexiglas 6N S000 from Evonik Industries (Essen, Germany); and PS was a petri dish purchased from SPL Life Sciences (Pocheon, Korea).

Fabrication of microchannels in PDMS

For making channels in PDMS, first an SU-8 master was fabricated on a silicon wafer using standard photolithography. SU-8 2025 was spin coated onto a silicon wafer at 2000 rpm for 30 s, baked at 65 °C for 3 min and at 95 °C for 5 min (soft baking), exposed to UV (170 mJ/cm²) and post exposure baking was done at 65 °C for 3 min and 95 °C for 4 min. After development, the mold was washed with IPA and dried. Then PDMS prepolymer was mixed in a 10:1 ratio of monomer and curing agent, degassed in a vacuum chamber and poured onto the SU-8 master mold and cured at 80 °C for 30 min. For making a flat PDMS substrate, the degassed prepolymer mixture was poured onto a clean Petri dish and cured at 80 °C for 30 min.

Effect of surface modification on bonding

Thermoplastics were cut into 6 cm × 8 cm rectangular pieces using a CNC milling machine, cleaned and dried. PDMS was also cut into 2 cm × 2 cm pieces. Both the thermoplastic and PDMS were treated under various conditions including; (i) oxygen plasma treatment (60 W, 1 min) and then treatment with 1% v/v aqueous APTES solution for 20 min; (ii) oxygen plasma treatment and then immersed in DI water for 20 min; (iii) oxygen plasma treatment; and (iv) immersed in an aqueous solution of 1% v/v APTES for 20 min without prior oxygen plasma treatment. All the substrates treated with a reagent were then washed with DI water and

blown dry with a stream of air. Different combinations of the activated thermoplastic and PDMS substrates were kept in conformal contact at room temperature for 1 h, bonding was evaluated by a manual peeling test. The results are summarized in Table S3

Surface characterization

In order to characterize the functionalized surfaces, X-ray photoelectron spectra (XPS) were recorded on an XPS analyzer (K-alpha; Thermo Fisher Scientific, UK). Water contact angles were measured using a goniometer (DSA100; KRUSS GmbH, Hamburg, Germany) for all the plastics before and after surface treatments.

Tensile strength measurements

The strength of bonded devices was determined with a tensile strength test. A flat 3 cm × 5 cm thermoplastic (1-mm-thick) piece with holes at four corners was made using a CNC milling machine and a planar 2 cm × 2 cm PDMS (5-mm-thick) was bonded at the center of the plastic. After bonding, the upper layer of PDMS was bonded to an aluminum jig using silicone sealant (LC909N, Henkel). The four corners of the thermoplastic piece were clamped to another aluminum jig using a bolt and nut. The two jigs were fixed in the tensile strength tester (5848 Micro Tester, Instron, USA) equipped with a 1800 N load sensor. The measurements were recorded at a displacement rate of 1 mm/min.

Burst pressure test

To determine the maximum pressure that the device could withstand, a burst resistance test was performed. For this, PDMS with a straight microchannel (depth = 45 μm; width = 1 mm or 600 μm; length = 27 mm) was bonded to the flat thermoplastic. Fluidic connections between the pump and chips were realized through the holes punched into PDMS using Tygon tubing (O.D. = 1.5 mm; I.D. = 0.5 mm) and the connections were sealed with an epoxy glue.

To measure the burst pressure, air was infused into the inlet of the channel at a flow rate of 10 mL/min through a syringe pump (Harvard PHD 2000) using a Hamilton gas tight syringe and the outlet of the channel was connected to a pressure sensor with a maximum pressure reading of 528 kPa (MPX5500D, Motorola). The pressure build within the device was recorded to determine the burst resistance of the device.

Stability test

To investigate the hydrolytic stability of the bonded interface, devices were submerged in DI water for three weeks at 37°C after filling the microchannels with DI water. Furthermore, to test the stability of the PC-PDMS devices with microchannels in PDMS, the bonded devices were kept at various temperatures (−20°C, 4°C, room temperature, and 50°C) for a period of three weeks. Stability of the bonded devices was determined by measuring the bond strength using the burst resistance test. Also, tensile strength was evaluated for the PC-PDMS devices kept at -20°C and in DI water at 37°C for 24 h.

Leakage tests

Hydrodynamic stability of the device was tested by performing a leakage test under fluid flow conditions. The PDMS with microchannel (depth = 45 µm; width = 800 µm; total length = 70 mm) was bonded to a planar piece of thermoplastic. Fluidic connections were realized through holes punched into the PDMS fitted with Tygon tubing (O.D. 1.5 mm, I.D. 0.5 mm). A red dye solution was infused through the channels using a syringe pump, initially at a flow rate of 5 mL/min and then increased gradually to 60 mL/min with an increasing flow rate of 5 mL/min.

To examine the capability of this bonding method for centrifugal microfluidics, leakage tests were also performed using a PC disc with a diameter of 12 cm. Microchannels in the PC disc were fabricated by micromilling using a CNC machine. The channels were sealed by bonding a flat PDMS layer (diameter = 12 cm; thickness = 4 mm) onto the disc. Several volumes of an aqueous red dye solution ranging between 100 - 700 µL was injected into each chamber of the disc and the disc was centrifuged at 1000 to 6000 rpm using a spin-stand equipped with a programmable spinning motor (200 W Servo Motor; Yaskawa Electronic Corp., Kitakyusu, Japan). The movement of fluids were recorded using a camera (Toshiba IK-TF5; Toshiba Corp., Tokyo, Japan) with a strobe light.

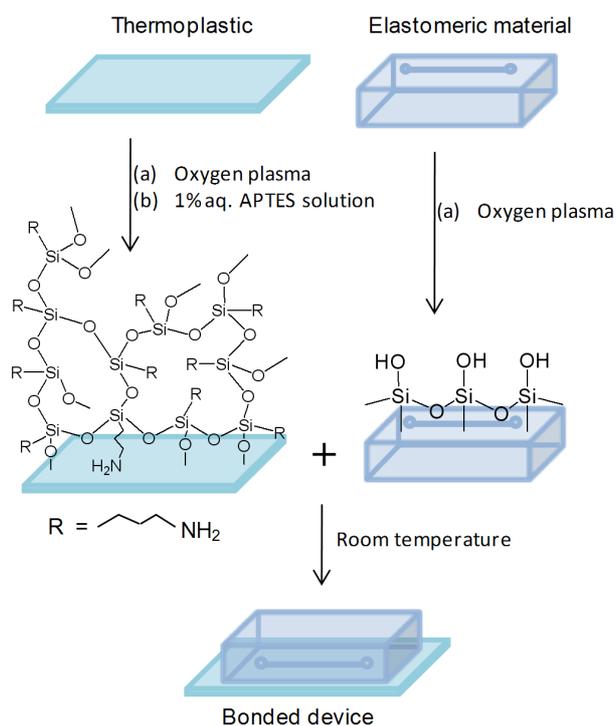


Fig. S1 Schematic representation of bonding process. An irreversible bonding was formed between the thermoplastics and PDMS within a few minutes at room temperature. The channels were made either in PDMS using soft lithography techniques or in thermoplastic by CNC milling.

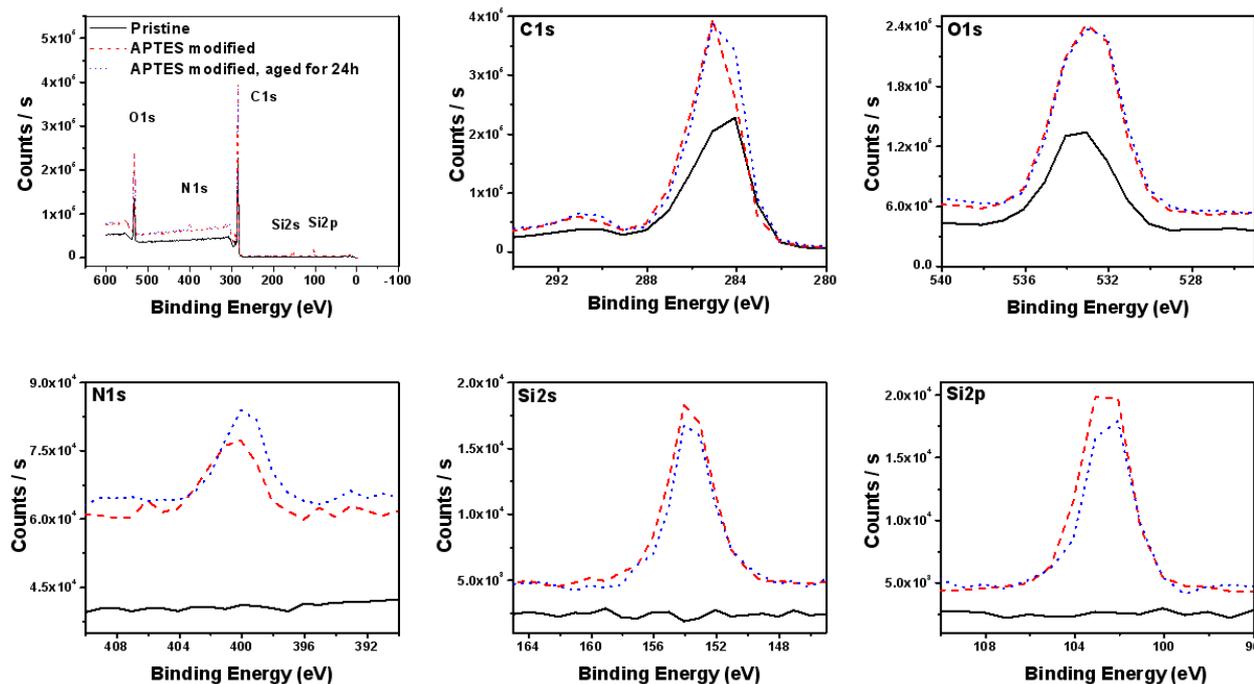


Fig. S2 XPS spectra for the detection of the atomic concentration of carbon, oxygen, nitrogen and silicon of pristine PC, APTES-modified PC and APTES-modified PC after 24 h of storage at ambient conditions. Almost identical elemental composition on the APTES modified substrates both with and without aging indicates the stability of the surface groups.

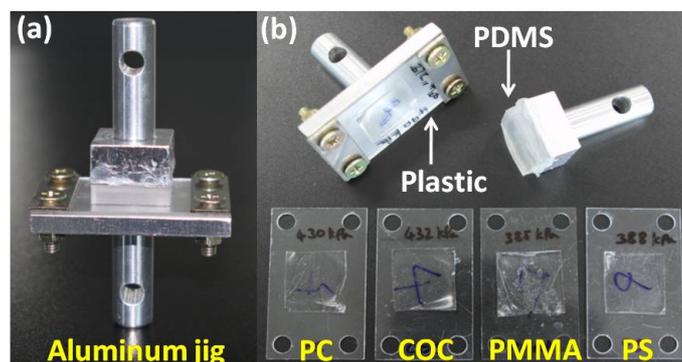


Fig. S3 Images of (a) a plastic-PDMS chip fixed to an aluminum jig before mounting in a tensile strength tester and (b) released devices after tensile strength measurements. The plastic sheets correspond to PC, COC, PMMA and PS, respectively. The jig was fixed in the tensile strength tester using bolts. The load was applied at a displacement rate of 1 mm/min until bond failure.

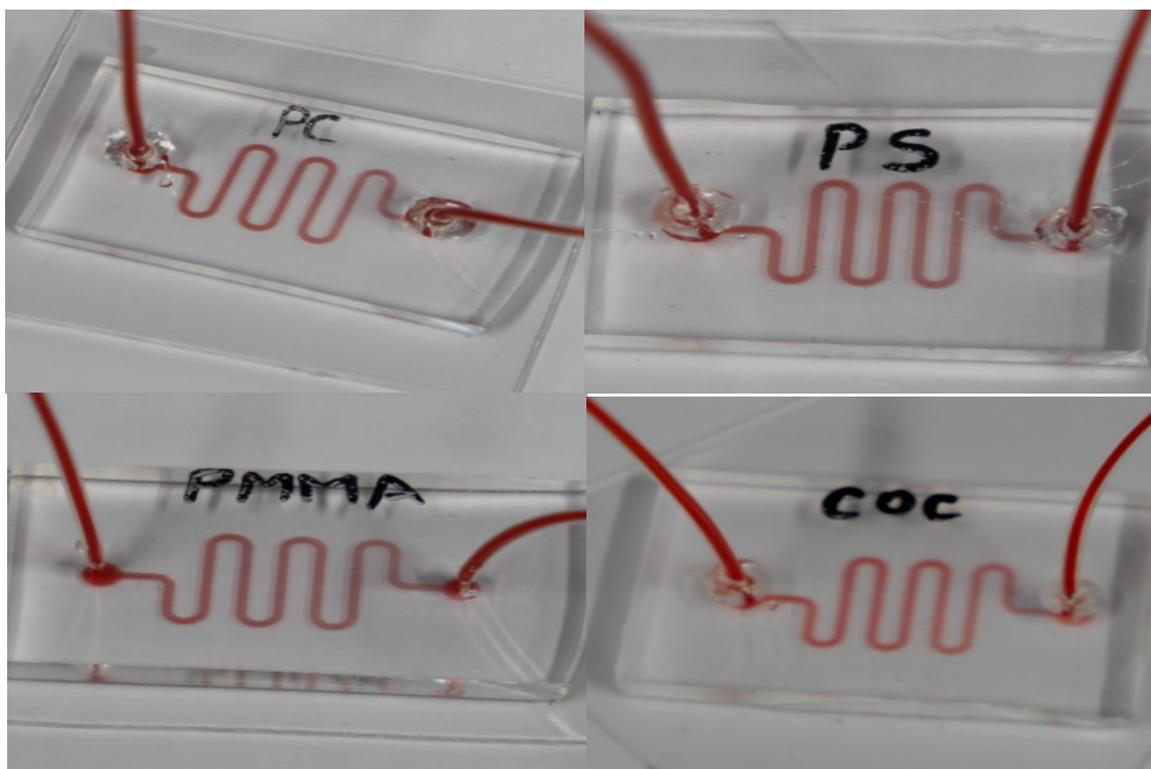


Fig. S4 A photograph of Thermoplastics-PDMS device having microchannel in PDMS, the tests were performed under flow condition infusing a red dye solution at the rate of 60 mL/min. The entire hybrid devices made of thermoplastics under investigation (PC, COC, PMMA and PS) showed the same result.

Table S1. Contact angle data of pristine and surface treated thermoplastics.

Thermoplastic	Pristine	Plasma	Plasma + APTES	
			Initial	After 12 h
PC	98 ±2	44 ±1	45 ±1	59 ±2
COC	93 ±2	46 ±1	45 ±1	63 ±2
PMMA	79 ±2	51 ±1	45 ±1	66 ±2
PS	83 ±2	56 ±1	57 ±1	68 ±2

Plasma: treated with oxygen plasma (60 W) for 1 min; APTES: immersed in 1% v/v aq. APTES solution at room temperature for 20 min; contact angle was measured immediately after modification (initial) and after drying for 12 h. Each value reported was the average of a minimum of five measurements secured at separate positions on any given substrate.

Table S2. XPS data for elemental composition of pristine and APTES modified PC.

PC	Atomic concentration (%)					O 1s/C 1s
	C 1s	O 1s	N 1s	Si 2s	Si 2p	
pristine	83.88	16.12	-	-	-	0.192
APTES modified	71.81	18.99	3.43	2.66	3.43	0.264
APTES modified, stored for 24 h	70.83	18.99	3.05	3.38	3.70	0.268

Table S3. Effect of various surface treatments on bonding characteristics

Thermoplastic		PDMS		Bonding characteristics*			
step 1	step 2	step 1	step 2	PC	PMMA	COC	PS
Plasma	APTES	Plasma	APTES or DI or None	S	S	S	S
		None	APTES	×	×	×	×
Plasma	DI	Plasma	APTES	S	S	S	S
		None	DI or None	×	×	W	W
Plasma	None	Plasma	APTES	×	×	S	S
		None	DI or None	×	×	×	×
None	APTES	Plasma	APTES	×	×	×	×
		None	APTES	×	×	×	×
None	None	Plasma	APTES or DI or None	S	×	×	×
		None	APTES	×	×	×	×

Plasma: Treated with oxygen plasma (60 W) for 1 min; APTES: immersed in 1% v/v aq. APTES solution at room temperature (RT) for 20 min; DI: immersed in DI water at RT for 20 min; None: no treatment. *The thermoplastic and PDMS were kept in contact for 1 hr at RT and the formation of bonding was evaluated by attempting to peel the PDMS layer manually. S: Strong bonding (highlighted cells); PDMS could not be peeled off from the surface, rupture occurred within the PDMS layer; ×: PDMS was peeled off easily indicating no bonding; W: Weak bonding, PDMS was peeled off with some traces of PDMS remaining on thermoplastic.

Table S4. Time required for irreversible bonding of thermoplastics with plasma activated PDMS

PDMS	Aging time (min)	Time required for irreversible bonding (min)			
	Thermoplastic	PC	COC	PMMA	PS
	<1	2	2	15	2
	30	5	5	15	5
<1	60	5	5	30	5
	120	15	15	30	15
	240	30	30	60	30
	24h + 5 min in DI	2	2	15	2
	<1				
30					
60	<1	2	2	15	2
120					
240					

PDMS was treated with oxygen plasma (60 W) for 1 min; Thermoplastic was treated with oxygen plasma (60 W) for 1 min and immersed in 1% v/v aq. APTES solution at RT for 20 min; Aging time: storage time of PDMS and thermoplastics individually, in between surface treatment and conformal contact. Six 2 cm × 2 cm pieces of PDMS were bonded on each 6 cm × 8 cm piece of thermoplastic. The formation of an irreversible bonding was evaluated by peel tests, which were conducted by peeling of one piece of PDMS manually at a time after 2, 5, 10, 15, 30 and 60 min of conformal contact at RT.

Table S5. Comparison of tensile strength values of thermoplastic-PDMS devices.

Thermoplastic	Storage Condition	Tensile Strength (kPa)	
		Measured	Ref.
PC	Ambient	430	178 ¹
PC	-20°C for 24 h	435	NA
PC	37°C in water for 24 h.	490	NA
COC	Ambient	432	NA
PMMA	Ambient	385	180 ¹
PS	Ambient	388	NA

Various examples of hybrid device made of thermoplastics and PDMS are given in the supplementary information; see **Table S2**. However, most of the chips were boned at relatively higher temperature (e.g. 50 ~ 80°C) and the tensile strength values were not available. Here, the available tensile strength values were compared with our result.

Table S6. Various methods for bonding thermoplastics and PDMS and bond strengths of the fabricated devices.

Ref.	Thermoplastic	Bonding Method	Applied Pressure	Temp (°C)	Time (h)	Tensile strength (kPa)	Burst Pressure (kPa)
Sensors & Actuators B 2010, 143, 799-804	PMMA	O ₂ Plasma treatment followed by Surface modification with TEOS (tetraethyl orthosilicate)	Clamp	50	1	NA	NA
	PC						
J. Micromech. Microeng., 2009, 19, 015007	PMMA	Silylation of PMMA with APTES, O ₂ Plasma activation of both substrates	0.5 kg weight placed on top of the sandwiched structure	80	1	NA	NA
	PS						
Lab Chip 2009, 9, 411	PC	Polymer (nano adhesive layer) coated substrates were bound	lightly pressed	70	12	NA	> 345
	PS						
Lab chip 2010, 10, 1274	PMMA	Chemical Gluing	---	RT	1	180	510
	PC					178	579
Chem. Mater., 2010, 22, 1732	PC	Initiated Chemical Vapor Deposition (iCVD)	--	50	24	NA	> 1000
	COC						
Anal. Chem., 2009, 81, 3714	PS	Plasma, oxygen & argon (2:1)	1 lb weight on top of the device	60	24	NA	> 120
	COC						