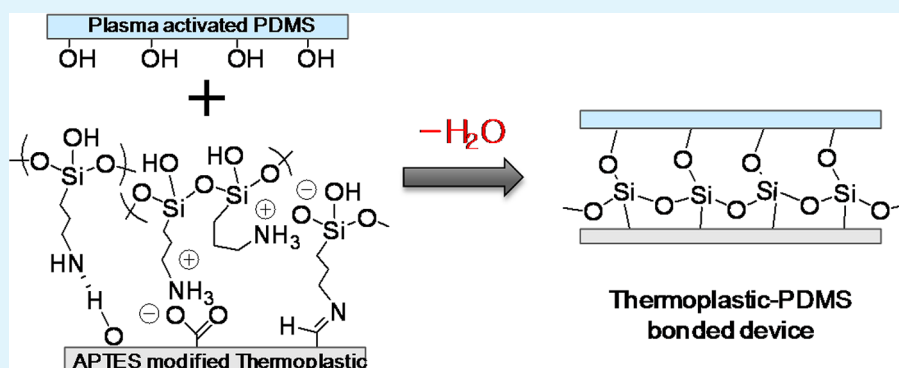# Investigation on the Mechanism of Aminosilane-Mediated Bonding of Thermoplastics and Poly(dimethylsiloxane)

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Ⓢ *Supporting Information*

ABSTRACT: A possible mechanism for the aminosilane-mediated room-temperature (RT) bonding of thermoplastics and poly(dimethylsiloxane) (PDMS) is presented. The plasma-activated thermoplastic or PDMS substrates were modified with alkoxy silanes having different organo functional groups, and their bonding characteristics were studied. Manual peeling tests revealed that strong bonding was realized only when the silane had a free amino group and at least two alkoxy groups on the silicon. Silanization was carried out in both aqueous and anhydrous conditions; bonding occurred readily at RT in the former case, but a longer incubation time or a higher temperature was needed for the latter. The presence of the silane on the surface was confirmed by contact-angle measurements and UV spectrophotometric, attenuated total reflectance infrared spectroscopic (ATR-IR) and X-ray photoelectron spectroscopic (XPS) analyses. In the case where the aminosilane was deposited from aqueous solution, the amino functionality of the silane-catalyzed siloxane bond formation between the silanol on the modified thermoplastic surface and the silanol of the plasma-activated PDMS. In the case of anhydrous phase deposition, the aminosilane first catalyzed the hydrolysis of the ethoxy groups on the silicon, and then, catalyzed the condensation between the silanol groups of both materials. Shelf life tests of the modified thermoplastics showed that the aminosilane was stable over 2 weeks, and that bonding occurred at RT when the substrates were soaked in water before bonding.

KEYWORDS: *thermoplastic−PDMS bonding, mechanism of bonding, plasma treatment, surface modification, aminosilane catalysis, plastic−PDMS interface*

■ INTRODUCTION

The field of microfluidics is becoming increasingly important in biomedical research, and one of the major concerns in microfluidics is device assembly.[1] Recently, silane reagents have been used widely to enhance the adhesion between thermoplastics and poly(dimethylsiloxane) (PDMS) hybrid microfluidic devices. For example, tetraethyl orthosilicate (TEOS) was used in conjunction with oxygen plasma treatment for the bonding of polymer microfluidic devices.[2] Gu et al. fabricated two valve arrays in a plastic/PDMS/plastic device through 3-(trimethoxysilyl)propyl methacrylate (TMSPMA)-mediated bonding after activation of the substrates with corona discharge.[3] A "chemical gluing" method was developed by Tang et al. for bonding thermoplastics and PDMS using an aminosilane and epoxysilane.[4] A similar approach was used by Cortese et al. to fabricate a cyclic olefin copolymer (COC-

PDMS-COC) microfluidic device with integrated valves[5] and by Ogilvie et al. to fabricate Viton membrane valves in COC and poly(methyl methacrylate) (PMMA) devices.[6] In all these cases, the substrates were activated with oxygen plasma prior to silane treatment, and then, one substrate was modified with aminosilane (3-aminopropyl trialkoxysilane) and the other with epoxysilane (e.g., 3-glycidoxypropyl trimethoxysilane). The authors believed that strong bonding could be realized through covalent bond formation between the amino and epoxy groups on the surfaces when these substrates were kept in contact with each other. In another approach, 3-aminopropyl trimethoxysilane (APTES) alone was used for bonding plastic substrates.

First, APTES was deposited on oxygen-plasma-activated thermoplastic surfaces, and then silanol groups were generated by the second plasma treatment. Subsequently, the modified thermoplastic substrate was kept in contact with plasma-oxidized PDMS. Here, the substrates could be bonded through siloxane (Si−O−Si) bond formation.[7,8] For the fabrication of a hydrolytically stable microfluidic device, a mixed silane solution was coated on corona-discharge-activated materials, and bonding was achieved through siloxane bond formation.[9]

In the case of aminosilane-mediated bonding, it was believed that the silanols reacted with the activated surface, leaving a free amino group for further reactions. In other words, the silane would be in "right-side-up"[10] orientation, and bonding would be achieved with the amino group facing upward. However, there was no experimental evidence to validate this hypothesis. In another study, Li et al. demonstrated that the amino group reacted with the carbonate functionality of the polycarbonate (PC) to form urethane linkages, leaving the ethoxy groups free for further interactions when the PC was treated with APTES in organic solvents such as chloroform or isopropyl alcohol.[11] However, no attempt was made to confirm this "upside-down"[10] orientation.

In our previous studies on the bonding of thermoplastics and PDMS, we found that bonding occurs between plasma-activated materials when the thermoplastic alone possesses the aminosilane group.[12−14] Here, it was interesting that no further treatment was necessary to generate silanols on the surface, and the bonding occurred readily at room temperature (RT). Moreover, bonding took longer when the PDMS treated with 3-glycidoxypropylmethyldiethoxysilane (GPDES) was subjected to bonding with APTES-treated thermoplastics. In addition, no bonding occurred when a GPDES-modified thermoplastic was treated with plasma to generate silanols on the surface and subjected to bonding with plasma-activated PDMS. Therefore, we considered it worthwhile to investigate the mechanism of aminosilane-mediated thermoplastic−PDMS bonding. In this paper, we discuss a possible orientation of aminosilane on plasma-activated thermoplastics and its role in the bonding mechanism. In addition, the influence of the silane functional groups on the bonding strength is investigated, and a possible bonding mechanism is proposed.

■ MATERIALS AND METHODS

Materials. The PDMS prepolymer and curing agent (Sylgard 184A and 184B) were obtained from Dow Corning (MI, USA). They were mixed in a 10:1 ratio, degassed, poured onto a Petri dish, and cured at 80 °C for 30 min. APTES and anhydrous ethanol were purchased from Sigma-Aldrich Corp. (MO, USA). The other silane reagents were from Gelest Inc. (PA, USA). The thermoplastic sheets (∼1 mm thick) used for the bonding tests were as follows: PC was purchased from I-Components Co., Ltd. (Seongnam, Korea); PMMA was Plexiglas 6N S000 from Evonik Industries (Essen, Germany); COC (5013 L10) was purchased from TOPAS Advanced Polymers GmbH (Frankfurt-Höchst, Germany); and PS was a Petri dish purchased from SPL Life Sciences (Pocheon, Korea). Au was purchased from Shin Woo metal, Korea. A 200-nm Au layer was evaporated onto a clean silicon wafer with a 20 nm chromium adhesion layer in an electron beam evaporator. All other chemicals and solvents were purchased from Samchun Chemicals (Korea).

Surface Analysis. The surfaces of the unmodified and modified substrates were assessed by water contact-angle measurements with a goniometer (DSA100; KRUSS GmbH, Hamburg, Germany). Ultra-pure water was used for the contact-angle measurements (18.2-MΩ resistivity at 25 °C); a volume of 4 μL was dispensed on the substrate and measurements were taken at five different positions on each thermoplastic sample. XPS analyses were performed on a K-alpha analyzer (Thermo Fisher Scientific, UK), UV spectra were recorded on a Carry 5000 UV spectrophotometer (Varian, US) and IR spectra were collected at a resolution of 2 cm^{-1} scans on a 670-IR spectropho-tometer (Varian, US) using a monolayer/grazing-angle specular reflectance accessory.

Surface Modification for Bonding. Aqueous solutions were made up by mixing 1% v/v silane reagent with deionized (DI) water and stirring at RT for 1 h. Thermoplastics were cut into pieces of 2 × 3 cm^2 using a CNC milling machine (3D modeling machine; M&I CNC Lab, Osan, Korea) and PDMS was cut into pieces of 2 × 2 cm^2. All materials were cleaned with isopropyl alcohol and treated with oxygen plasma (60 W, Cute plasma system; Femto Science, Korea) for 1 min, and then treated with aqueous silane solution for 20 min. The substrates were then washed with DI water and dried under an air stream. Here, the silane treatment was performed selectively on the thermoplastics or PDMS. Different combinations of the activated thermoplastics and PDMS were kept in conformal contact at RT for 1 h.

Anhydrous solutions were made up by mixing 1% v/v silane with anhydrous ethanol and stirring for 10 min under nitrogen at RT. The materials were treated with oxygen plasma (60 W, 1 min) and then placed in the reaction solution under nitrogen at RT. After 20 min, the substrates were washed with ethanol and blown dry with nitrogen. The silane treatment was performed selectively on the thermoplastics or PDMS, and they were kept in contact at RT for 1 h.

Effect of pH. A 1% v/v aqueous APTES solution was prepared, and the pH of the reaction solution was adjusted to 2.0, 7.0, or 8.4 with 1 N HCl. The plasma-activated PC was immersed in the APTES solutions kept under various pH conditions, including the natural pH of 10.5. After incubation (1 min, 5 min, and 20 min), the substrates were washed with DI water, blown dry with nitrogen, and kept in contact with plasma-activated PDMS at RT for 1 h.
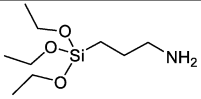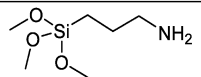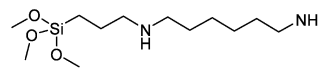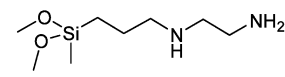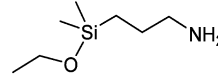
Bonding Strength Measurements. For all the devices, the bond strength was evaluated by attempting to peel the PDMS layer manually. The bonding was classified as follows: strong bonding, PDMS could not be peeled off from the surface or rupture occurred within the PDMS layer; moderate bonding, PDMS was peeled off with some traces of PDMS remaining on the thermoplastic substrate; 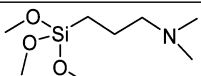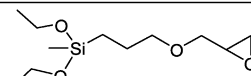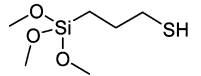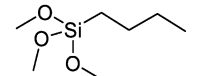weak bonding, PDMS was peeled off with minimal traces of PDMS left on the thermoplastic substrate; no bonding, PDMS peeled off easily.

For the quantification of the bond strength, we determined the tensile strength using a tensile strength tester (5848 Micro Tester, Instron, USA) equipped with a load sensor (1800 N). The measurements were recorded at a displacement rate of 1 mm/min. The sample preparation method has been reported in detail previously.[12] In brief, a flat 1-mm-thick thermoplastic substrate with holes at the four corners was prepared by using a CNC milling machine and bonded with a planar 5-mm-thick PDMS sample. Then, the upper surface of the PDMS was bonded to an aluminum jig using silicone sealant (LC909N, Henkel). At least three tests were performed per sample, and the bonding strength ranges were categorized as strong (tensile strength >200 kPa), moderate (tensile strength = 50−200 kPa), or weak (tensile strength <50 kPa).

Effect of Storage Time on Bonding. The PC samples were modified with aqueous APTES solution as described above and stored at RT. These substrates were treated under different conditions including (i) immersion in DI water for 10 min; (ii) oxygen plasma treatment; (iii) no treatment, then bonding with plasma-activated PDMS at RT and 65 °C. Manual peel-off tests were performed to evaluate the nature of the bonding after incubation for 5 min, 1 h, and overnight at RT, and after 1 h at 65 °C.

Substrates for IR Measurements. A layer of thermoplastic (3−4 nm thick) was deposited on the Au substrate by spin-coating of the polymer solution in chloroform (concentration 0.5 mg/mL) in order to pick up the signal of the thermoplastic surfaces and minimize interference from bulk materials in the IR spectra. These substrates were used for further modification, and the IR spectra were recorded for the pristine and aminosilane-modified surfaces.

Table 1. Bonding Characteristics of Thermoplastic and PDMS Hybrid Devices[a]

Silane	Silane on plastic				Silane on PDMS			
	PC	PMMA	PS[b]	COC	PC	PMMA	PS[b]	COC
APTES	S	S	S	S	x	x	S	W
APTMS	S	S	S	S	x	x	S	W
AHAPTMS	S	S	S	S	W	x	S	M
AEAPDMS	S	S	S	S	S	x	S	S
APDMES	x	x	S	W	x	x	S	x
DMAPTMS	x	x	S	x	x	x	S	x
GPDES	x	x	M	x	x	x	W	x
MPTMS	x	W	S	x	M	W	M	M
BTMS	x	x	W	x	x	x	W	x

[a]Surface modification was performed in aqueous solution and the surfaces were kept in contact for 1 h at RT. Silanes: APTES = 3-aminopropyltriethoxy; APTMS = 3-aminopropyltrimethoxy; AHAPTMS = N-(6-aminohexyl)-3-aminopropyltrimethoxy; AEAPDMS = N-(2-aminoethyl)-3-aminopropylmethyl- dimethoxy; APDMES = 3-aminopropyldimethylethoxy; DMAPTMS = 3-(N,N-dimethyl)-aminopropyltrimethoxy; GPDES = 3-glycidoxypropylmethyldiethoxy; MPTMS = 3-mercaptopropyltrimethoxy; BTMS = n-butyltrimethoxy. Bond strength: S = strong (tensile strength (TS) > 200 kPa); M = moderate (TS = 50−200 kPa); W = weak (TS < 50 kPa); x = no bonding. [b]PS and PDMS bond strongly with plasma treatment on both when they are kept in contact with each other immediately after plasma treatment.

Spectrophotometric Determination of Amino Groups. A reported procedure was used to determine the free amino groups on the surface.[15,16] In short, the aminosilane deposited PC substrates (1 × 3 cm^2) were immersed in an aqueous solution of methyl orange in acetate buffer for 10 min at RT. The substrates were washed with DI water for 5 times and immersed in a mixture of 1 M HCl and 0.5 M KCl and absorbance of the resulting solution was measured. As a positive and negative control, APTES and GPDES modified glass substrates (1 × 3 cm^2) were also used, which were prepared by anhydrous phase deposition of the silane in toluene at RT for 2 h followed by drying at 110 °C for 30 min.

■ RESULTS AND DISCUSSION

Effect of Chemical Reagents on Bonding Character-istics. For the assessment of the functional group participating

in the bonding of thermoplastics and PDMS, differently substituted organosilanes were used for surface modification of the plasma-activated thermoplastics and PDMS. These silanes were grouped into two categories on the basis of their terminal functional groups: aminosilanes containing amino or dialkylamino groups; and nonaminosilanes containing glycidoxy, mercapto, or alkyl groups. Various silanes with mono-, di-, or trialkoxy groups on silicon were selected for this study (Table 1).

The plasma treatment conditions such as plasma power and exposure time were optimized based on the contact angle value of the treated surface. The thermoplastics were exposed to oxygen plasma for the time periods ranging from 10 to 180 s and treated with various plasma powers. The contact angle
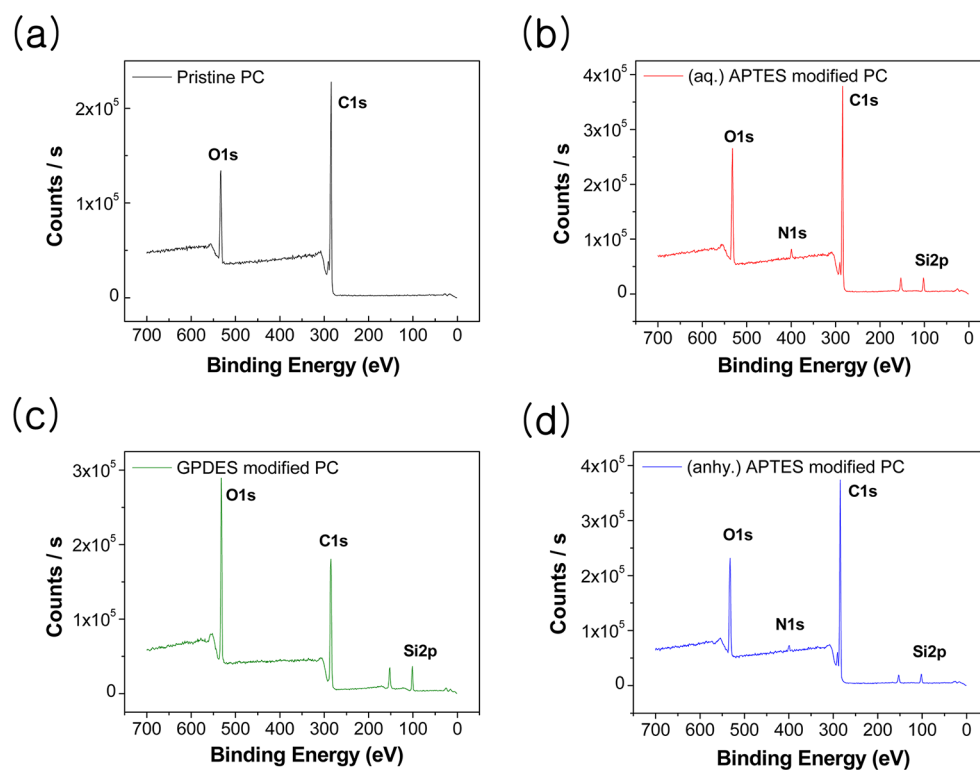
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Figure 1. XPS of PC: (a) pristine, (b) aq. APTES-modified, (c) GPDES-modified, and (d) anhydrous APTES-modified.

decreased up to 60 s exposure and reached a plateau. Similarly, the contact angle decreased and reached a plateau at 60 W plasma power. Table S1 in the Supporting Information shows the contact angle data obtained for PC at different treatment conditions. Other thermoplastics also showed similar results and 60s (1 min) treatment time and 60 W power were selected for treating the surfaces.

First, either thermoplastics (see Figure S1 in the Supporting Information) or PDMS substrates were activated with plasma and treated with aqueous silane solution. Then, different combinations of modified surfaces were kept in contact at RT for 1 h, and the bonding strengths were evaluated through manual peeling tests (see Figure S2 in the Supporting Information). Though it was found that the bonding happens within few minutes of contact, when the thermoplastics alone were treated with APTES,[12] the substrates were incubated for 1 h to make sure that the bonding does not happen with nonaminosilanes, even after incubating for prolonged time. The bonding characteristics of the thermoplastic−PDMS devices are summarized in Table 1. It is interesting to note that strong bonding was realized only for the silanes with an amino terminal group and at least two alkoxy groups on the silicon.

For example, APTES, APTMS, and AHAPTMS with three alkoxy groups and AEAPDMS with two alkoxy groups promoted bonding, whereas APDMES with only one alkoxy group and DMAPTMS with a dimethyl-substituted amino group could not assist the bonding. Similarly, the non-aminosilanes with dialkoxy or trialkoxy groups, i.e., GPDES, MPTES, and BTMS, did not facilitate bonding. In the case of PS and PDMS, strong bonding was achieved when they were kept in contact with each other immediately after plasma treatment, which is in agreement with earlier findings,[17] and also when either of the surfaces contained the aminosilane. On the other hand, reaction with the nonaminosilanes appeared to

be detrimental to bond formation. This may be because the organosilane reacted with the active functional groups on the surface of the PS, and thus, masked the available bonding sites. These results indicate that the presence of a free amino group and at least two alkoxy groups in the silane are necessary for strong bonding between thermoplastics and PDMS.

Furthermore, it is apparent that bonding was facilitated when the aminosilane was present on the thermoplastics, as shown in Table 1. There was either no bonding or weak bonding when the aminosilane was on the PDMS and was kept in contact with the plasma-activated thermoplastics. A possible reason for this result is that the orientation of the aminosilane group on the PDMS is different, and the active functional groups might not be accessible for reaction with the plasma-activated thermoplastic in the absence of water. In contrast, the devices made of PC and COC showed moderate bonding when MPTMS was present on the PDMS.

The XPS analysis results suggest that the silanes react with the plasma-activated thermoplastics irrespective of their terminal functional groups. General survey XPS results obtained for pristine PC, aqueous APTES, and GPDES-treated PC are shown in Figure 1a−c, respectively. The spectra show significant differences between the untreated and treated samples, and also between the samples treated with two different silanes. The peaks at 400 and 102 eV in Figure 1b correspond to the N 1s and Si 2p signals, indicating the presence of the aminosilane on the surface. Similarly, the peak at 102 eV for Si 2p in Figure 1c reveals the presence of GPDES on the surface. Also, the change in the O 1s and C 1s atomic concentrations after each treatment clearly shows the difference in chemical environment of the surfaces. The increase in O 1s concentration accounts for the increased oxygen content resulting from the plasma treatment, and the increase in the

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O 1s/C 1s ratio after silane treatment indicates the increased hydrocarbon content on the surface.

XPS analyses of other kinds of thermoplastic materials, for example, PMMA, PS, and COC, show analogous spectra for aqueous APTES treatment (see Figure S3 in the Supporting Information). The atomic concentrations of C 1s, O 1s, N 1s, and Si 2p are shown in Table 2. The presence of O 1s in

Table 2. XPS Data on Elemental Compositions of Pristine and Surface-Treated Substrates

thermoplastic	treatment condition	atomic concentration (%)				O 1s/ C 1s
		C 1s	O 1s	N 1s	Si 2p	
PC	pristine	84.09	15.92			0.189
	plasma-activated	73.86	26.14			0.354
	aq. APTES-modified	71.18	19.53	3.3	5.98	0.274
	anhy. APTES-modified	79.52	15.09	1.83	3.56	0.190
	GPDES-modified	66.71	27.53		5.76	0.413
PMMA	pristine	74.86	25.14			0.336
	plasma-activated	67.21	32.79			0.488
	aq. APTES-modified	63.69	27.81	3.01	5.49	0.437
PS	pristine	93.87	6.13			0.065
	plasma-activated	79.43	20.57			0.259
	aq. APTES-modified	70.81	17.85	4.97	6.37	0.252
COC	Pristine	92.57	7.43			0.080
	plasma-activated	80.64	19.36			0.240
	aq. APTES-modified	73.68	16.72	3.99	5.60	0.227

pristine PS and COC can be attributed to the adsorbed oxygen on the surface or additives that might be added during their molding process. The data obtained for all the samples are in accordance with the results for PC, and the O 1s/C 1s ratio increases with modification for all the samples, indicating that the chemical environments on these materials are similar.

Effects of Experimental Parameters on Bonding Characteristics. *Reaction Conditions.* Several silanes were used selectively to study the effect of anhydrous phase deposition on the surface reaction and bonding characteristics. The materials were activated by plasma and treated with silane under anhydrous conditions. Different combinations of modified surfaces were kept in contact at RT for 1 h, and manual peel-off tests were performed to evaluate the bond strength. It is somewhat surprising that bonding was not realized in all cases, including the aminosilanes. However, when the device was incubated for a longer time or at a higher temperature (i.e., 12 h at RT or 1 h at 65 °C), bonding was realized only for the aminosilane-treated thermoplastics (Table 3). This result may be explained by the fact that the hydrolysis of the alkoxy groups is slow under anhydrous conditions, so cross-linking takes longer or requires a higher temperature. It is also worth noting that the diaminosilanes (AEAPDMS and AHAPTMS) promote bonding faster than the monoaminosilanes (APTES and APTMS). Apart from the number of amines, the difference in molecular size also plays an important role in the catalysis process.[18] The aminoethyl group is more accessible

Table 3. Bonding Characteristics of PC−PDMS Devices under Different Incubation Conditions[a]

	silane	RT			65 °C
		1 h	3 h	12 h	1 h
amino	APTES	x	W	W	W
	APTMS	x	W	S	S
	AHAPTMS	x	W	S	S
	AEAPDMS	S	S	S	S
nonamino	GPDES	x	x	x	x
	MPTMS	x	x	x	x

[a]Surface modification was performed under anhydrous conditions. Bond strength: S = strong (TS > 200 kPa); M = moderate (TS = 50−200 kPa); W = weak (TS < 50 kPa); x = no bonding.

and will participate in catalysis faster than the aminohexyl group, and the methoxy groups of the silane are hydrolyzed faster than the ethoxy groups.

The difference in the chemical nature of the aminosilane on PC treated with APTES under aqueous and anhydrous conditions (Figure 1b, d) was also studied by XPS. Although the spectra are similar, the C 1s and O 1s atomic concentration values are different. It is seen from the data in Table 2 that the APTES-modified PC prepared under aqueous conditions shows a higher O 1s/C 1s ratio than that made under anhydrous conditions, which demonstrates the presence of silanol groups on the former and alkoxy groups on the latter. These results are in agreement with the contact-angle measurements (Table 4), which show that the substrate made under aqueous conditions exhibits a lower contact angle than that formed under anhydrous conditions.

Table 4. Contact-Angle Data of Pristine and Surface-Treated Materials[a]

thermoplastic	pristine	plasma	plasma + APTES	
			aqueous	anhydrous
PC	86 ± 2	40 ± 1	53 ± 1	73 ± 1
PS	83 ± 2	32 ± 2	55 ± 1	70 ± 1
PMMA	79 ± 2	44 ± 1	52 ± 1	65 ± 1
COC	92 ± 2	45 ± 1	54 ± 1	67 ± 1

[a]Plasma: treated with oxygen plasma (60 W) for 1 min; aq. APTES: immersed in 1% v/v aq. APTES solution; anhy. APTES: immersed in 1% v/v APTES in anhy. EtOH solution at RT for 20 min; contact angle was measured after drying for 12 h. Each value reported is the average of five measurements secured at separate positions on any given substrate.

To determine the presence of free amino groups on the surface, the aminosilane-treated substrates were reacted with methyl orange solution. As positive and negative control, APTES and GPDES modified glass (1 × 3 cm^2) were also subjected to methyl orange test and the spectra obtained are shown in Figure 2. The positive control, i.e., APTES-modified glass showed a broad signal representing free amino groups and the negative control, i.e., GPDES-modified glass does not show any signal. The PC modified by aqueous phase deposition shows lower intensity, suggests that the amino groups were either reacted with the functional groups generated on the surface or formed inter- and intramolecular hydrogen bonding.

Reaction Solution pH. For the investigation of the effect of the pH of the reaction solution on the bonding characteristics, the plasma-activated PC was treated with aqueous APTES
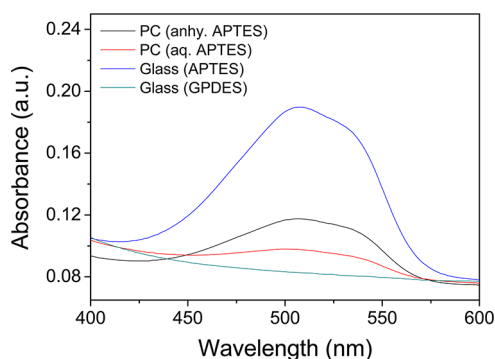
Figure 2. Spectrophotometric determination of amino groups.

solution at pH 2.0, 7.0, 8.4, and 10.5 (natural pH of aq. APTES solution); these substrates were kept in contact with the plasma-activated PDMS at RT for 1 h. Manual peel-off tests indicated that bonding occurs only when the pH of the solution is at its natural pH of 10.5 (Table 5). Earlier, it was shown that

Table 5. Effect of pH on Bonding Characteristics of PC−PDMS Device[a]

incubation time (min)	pH 2.0	pH 7.0	pH 8.4	pH 10.5
1	x	x	x	S
5	x	x	W	S
20	x	W	W	S

[a]Bond strength: S = strong (TS > 200 kPa); M = moderate (TS = 50−200 kPa); W = weak (TS < 50 kPa); x = no bonding.

APTES exists in the form of the ammonium hydrochloride salt, hydrogen-bonded amine, and free amine in aqueous solutions at pH 2, 10.8, and 12, respectively, and that the structure of APTES adsorbed on silica depends strongly on the pH of the solution.[19,20] Similarly, in the present study, different interactions are possible between the aminosilane and the plasma-activated thermoplastic materials depending on the pH of the solution (Figure 3). The amino group of APTES is protonated in acidic solutions and exists as an ammonium ion, which may experience repulsion from the plasma-activated surface, resulting in a "right-side-up" orientation (Figure 3a). As the amino group is protonated, its ability to interact with Si−OH of plasma-activated PDMS is lower, which could be the reason for the lack of bonding when the reaction is performed at a lower pH. At the same time, the amino group exists as a free amine in basic solutions, and at its natural pH, the amine is

prone to form inter- and intramolecular interactions because the molecules are oriented uniquely on the surface. Intermolecular interactions between the amine and the surface functional group result in an "upside-down" orientation (Figure 3b), whereas intramolecular interactions result in irregular orientations with hydrogen-bonded amines and silanols available for further reactions. These amines on the surface catalyze the condensation between the silanol groups on both surfaces and promote bonding.

The IR spectrum of APTES deposited from aqueous solution on plasma-activated PC (Figure 4) shows peaks for Si−OH,
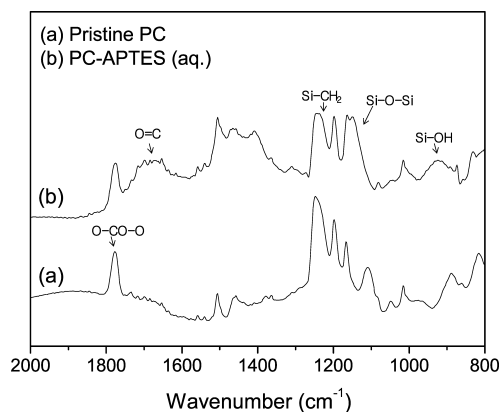

Figure 4. IR spectra of (a) pristine and (b) APTES-treated PC.

Si−O−Si, Si−CH₂, and −C=O (amide and carbonyl) in the regions 950−850, 1150−1100, 1220−1200, and 1750−1600 cm⁻¹, respectively.[21] The presence of Si−OH and Si−O−Si peaks supports the above explanation, and the IR spectra of APTES on other thermoplastics (see Figure S4 in the Supporting Informaiton) also show similar peaks. On this basis, we presume that the orientation of aminosilane on all plasma-activated thermoplastics is similar irrespective of their pristine nature or chemical composition, and that it is oriented in such a way that free silanols are available on the surface for bonding, and the amino group catalyzes the condensation of silanols and promotes cross-linking between the materials through the formation of −Si−O−Si− bonds (Figure 5).

Shelf life test of APTES-modified PC showed that the silane layer on the surface is intact and the surface is stable for over two weeks (maximum tested period). Soaking the substrates in water for a few minutes prior to contact helped the bonding, and the minimum incubation time required for the bonding was
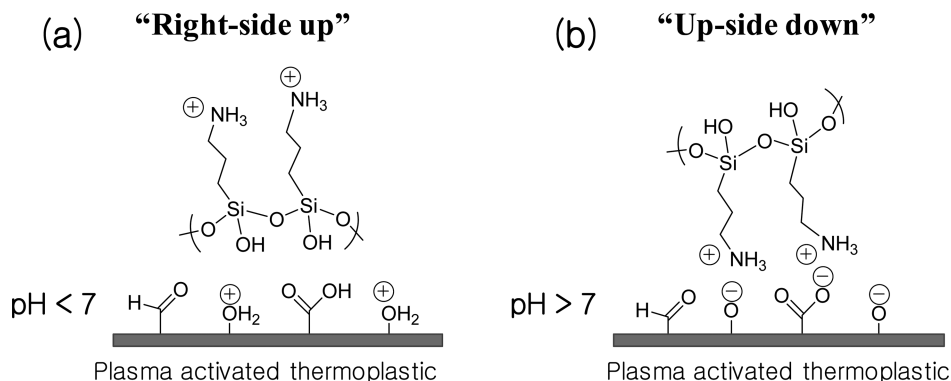

Figure 3. Possible orientations of APTES molecules under (a) acidic and (b) basic pH conditions.

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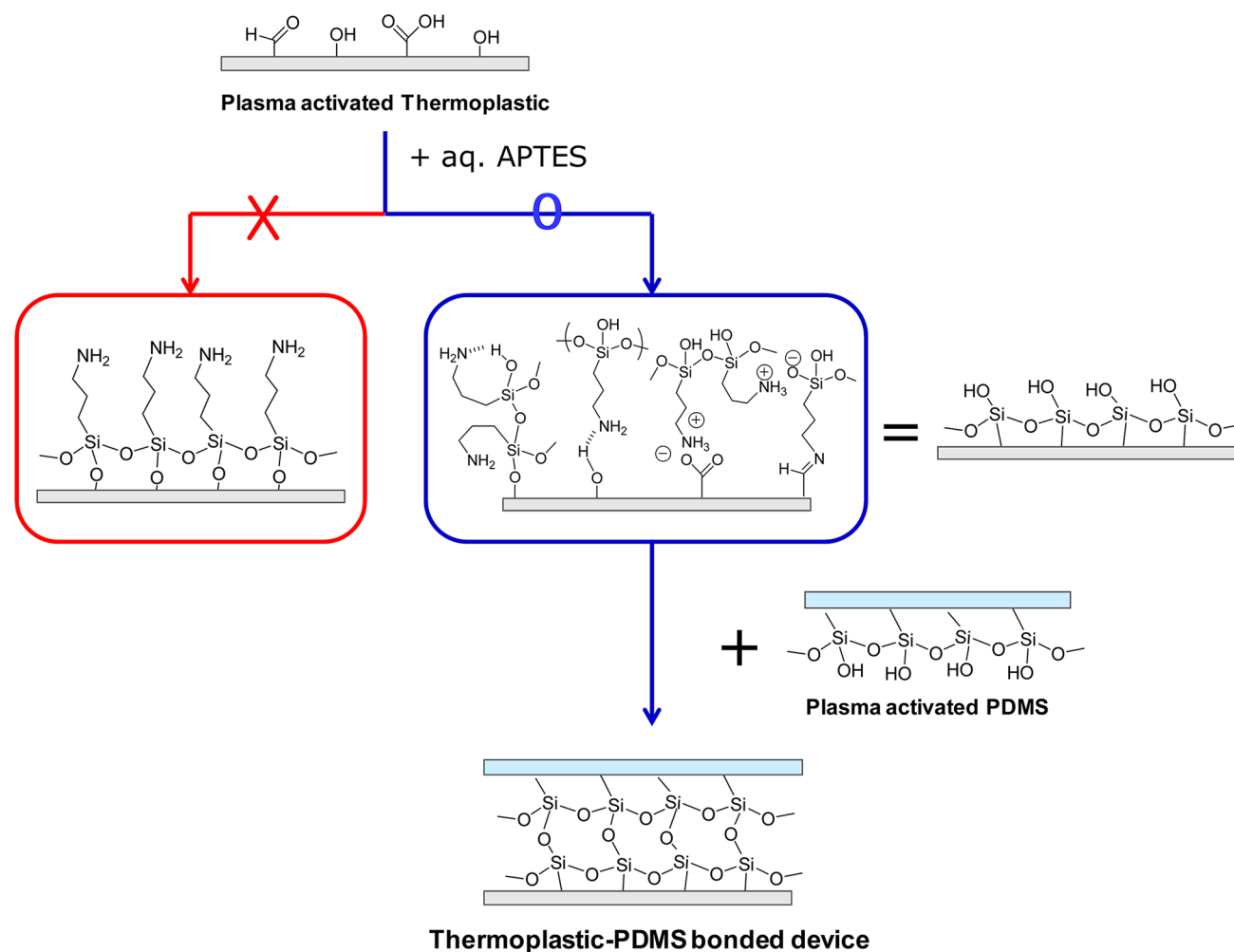
Figure 5. Schematic representation of the bonding process. Irreversible bonding was formed between the thermoplastics and PDMS within 1 h at RT through −Si−O−Si− bond formation.

1 h. If the substrates were subjected to bonding without any treatment, incubation was required overnight at RT, or for 1 h at a higher temperature of 65 °C. When the substrates were treated with oxygen plasma, strong bonding formed only after incubation for 1 h at 65 °C, and the bond strength decreased as the storage time increased (see Table S1 in the Supporting Information). Treatment of the aminosilane-modified substrates with oxygen plasma might damage the aminosilane layer, which could be the reason for the weak bonding and the decrease in bonding strength.

From the above data, it is evident that the silanes react with the plasma-activated materials to form a stable layer on the surface, and that only aminosilane promotes the bonding between the thermoplastics and PDMS. In the case of the other silanes, although the silanes were present on the surface, they could not assist the bonding even after incubation of the substrates for 12 h at RT. These results suggest that a free amino group is essential for bond formation between the thermoplastics and PDMS. The amines with exchangeable hydrogen atoms are known to catalyze the silylation reaction of alkoxy silanes on silicon.[22,23] Here, the aminosilane acts as a self-catalyst and participates in the condensation reaction.

The aqueous solutions of aminosilanes, at low concentrations, exist as silanol monomers or short oligomers.[10] These molecules react spontaneously with the functional groups generated on the plasma-activated surfaces. Various inter- and intramolecular interactions, including hydrogen bonding, covalent bonding, electrostatic attraction, etc., are possible between the surface and the aminosilane, and also between the aminosilane molecules.

Because of this, the molecules on the surface are oriented in such a way that free silanols are available to react with the silanol of the plasma-activated PDMS, and the amino group catalyzes the condensation of the silanols, resulting in the formation of −Si−O−Si− bonds between the surfaces of the thermoplastics and PDMS when they are kept together (Figure 5). In anhydrous phase deposition, the aminosilane first catalyzes the hydrolysis of the ethoxy groups, resulting in silanol groups on the surface, and then catalyzes the condensation reaction. The mechanism of bonding would be the same as that in aqueous phase deposition once the silanols are formed.

■ CONCLUSION

A plausible mechanism for the bonding between hard and soft materials has been demonstrated on the basis of the bonding characteristics under various treatment conditions. The effect of the silane functional group on the bonding between surface-treated thermoplastics and plasma-activated PDMS has been evaluated. Bonding occurs only when the surface is treated with

an aminosilane having a free amino group and at least two alkoxy groups on the silicon. Aqueous conditions are more favorable for the surface reaction, as the hydrolysis of the aminosilane is faster in water. The data also show that the hydrolysis of ethoxy groups and the formation of siloxane bonds are promoted either by the presence of water or by higher curing temperatures. The bonding is highly dependent on the pH of the reaction solution, which affects the aminosilane orientation on the surface, and occurs readily only when the thermoplastic is treated with a solution at its natural pH. Studies on the molecular structure of aminosilane on plasma-activated thermoplastics indicate that the combination of plasma activation and aminosilane treatment yields a unique surface that is ideal for bonding with plasma-activated PDMS at room temperature. The aminosilane-modified substrates show good stability, and can be stored for a few days after modification.

ASSOCIATED CONTENT

Supporting Information

Figures S1–S4 and Table S1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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