

Aminosilane layers on the plasma activated thermoplastics: Influence of solvent on its structure and morphology



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ABSTRACT

The chemistry and the structure of aminosilane layer on the plasma activated thermoplastic substrates, e.g., polycarbonate (PC), polystyrene (PS), poly(methyl methacrylate) (PMMA), and cyclic olefin co-polymer (COC) were investigated at the molecular level. The nature of the surface functional groups of the silane layers prepared by solution phase deposition in aqueous and anhydrous solvents were studied using various techniques including ellipsometry, goniometry, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and attenuated total reflectance infrared spectroscopy (ATR-IR). The XPS analyses revealed the presence of various oxygen functionalities on the plasma activated thermoplastics. Considerable differences were observed for the structure of aminosilane depending on the solvent used for the reaction. Deposition from aqueous solution resulted in relatively flat and smooth surfaces with consistent thickness compared to the anhydrous solution deposition. In the former case, 33% of the total nitrogen accounted for protonated amine and 16% for the free amino groups. In the latter, only 6% accounted for the protonated amine. The point of zero charge (pzc), on the aminosilane modified PC was found to be around 7, indicated that the surface is positively charged below pH 7 and negatively charged above pH 7. The surface analysis data suggested that various interactions are possible between the plasma activated thermoplastic surface and the aminosilane. In general, they are bound to the surface through covalent bond formation between the oxygen functionalities on the thermoplastic surface and the amino or the silanol groups of the aminosilane.

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1. Introduction

Thermoplastics are gaining attention as an alternative to the silicon materials for micro-analytical devices [1–3]. The main advantages of thermoplastics include low cost, optical transparency, ease of handling, and biocompatibility. However, altering the surface chemistry of thermoplastics is a challenging task owing to their solvent compatibility. Hence, non-solvent based methods such as plasma or UV were used to generate reactive functional groups on the surface, which were subjected to further modifications or biomolecule immobilizations [4–6].

Oxygen plasma is known to alter the surface properties of various substrates [7–10]. Recent report suggests that the oxygen radicals react on the surface and change the properties of thermoplastic surface [11]. Several groups have characterized the plasma oxidized thermoplastics like PC and PMMA, and concluded that different functional groups including carboxyl, carbonyl, hydroxyl, etc. are generated on these plasma activated surfaces [12,13]. However, still it is not clear which group predominates.

Combinations of plasma/UV and silane treatment have been used for microfluidic device assembly [14]. The most commonly used silane is 3-aminopropyltriethoxysilane (APTES), which is also used to modify the surface of various materials for bio-sensing applications [15,16]. Much has been studied about the structure and the orientation of aminosilane on silicon surfaces [17,18]. Several techniques such as ellipsometry, goniometry, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy have been used to characterize the amino groups on silicon surfaces and to evaluate the effect of the reaction conditions such as solvent type, pH, and reaction time [19–23]. However, still there is considerable debate on its structure and stability and new methods are still being developed to make stable aminosilane layers on silicon substrates [24,25].

On the other hand, very little is known about the structure of APTES on plasma activated thermoplastics. Though characterization of aminosilane layer on thermoplastics by contact angle or XPS could reveal the presence of silane on the plastic surfaces, no information has been available on the orientation of the amino or silanol groups [26]. It was often assumed that the silanols react with the functional groups on the plastic surface leaving the amino

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groups free for further reactions [26–28]. However, there is no reliable evidence to validate this hypothesis.

In this study, the aim is to investigate the molecular mechanism of the interactions between silane, e.g. APTES, with the plasma activated thermoplastic surfaces. In our previous studies, focus was on the device fabrication using aminosilane mediated bonding between thermoplastics including PC, PMMA, PS, COC etc. with polydimethylsiloxane (PDMS) [29,30]. As discussed above, the aminosilane is being used for device assembly in microfluidic field and it is important to know its structure and orientation as the surface properties within the channel could be changed due to the charges associated with the aminosilane layer. Furthermore, it is also important to know the orientation as people believe that the aminosilane layer exists in right-side up orientation leaving terminal amino group for further reactions. We strongly believe that it is necessary to investigate the structure and orientation of aminosilane layer on the plasma activated thermoplastic surfaces to develop biomedical devices for desired applications. Accordingly, the effect of solvent during the silane deposition step on the thickness, surface morphology, stability, and chemical properties of the APTES layer on plasma treated thermoplastics were explored. To this end, various surface analysis techniques such as ellipsometry, goniometry, AFM, XPS, and ATR-IR were utilized to examine the chemistry and the structure of silane layer on the plasma activated thermoplastics.

2. Experimental

2.1. Materials and methods

APTES and anhydrous ethanol were purchased from Sigma–Aldrich Corp. (MO, USA). 3-Glycidypropylmethyldiethoxysilane (GPDES) was from Gelest Inc., (PA, USA). 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. The thermoplastic sheets (~1 mm thick) used were as follows: PC was purchased from I-Components Co., Ltd. (Seongnam, Korea); PMMA was Plexiglas 6 N 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). All other chemicals and solvents were purchased from Samchun chemicals (Korea).

2.2. Substrates for surface analysis by ellipsometry, XPS and ATR-IR

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 pristine and aminosilane-modified surfaces were analyzed by ellipsometry, XPS and IR.

2.3. Surface modification

2.3.1. Plasma activation

The substrates were cleaned by sonication in isopropyl alcohol for 5 min and dried. Surface activation was done in a plasma system (Femto Science, Korea) using 60 W power, 50 sccm oxygen for 1 min.

2.3.2. Silane grafting

Aqueous phase deposition: 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 desired size using a CNC milling machine (3D modeling machine; M&I CNC Lab, Osan, Korea). 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 immersed in the aqueous silane solution and incubated over a period of time from 5 to 720 min. The substrates were then washed with DI water and dried under an air stream.

2.3.2.1. Anhydrous phase deposition. 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 and incubated over a period of time from 5 to 720 min. The substrates were then washed with ethanol, blown-dried with nitrogen, and stored under nitrogen until analyses.

2.4. Surface analysis

The surfaces of the unmodified and modified substrates were assessed by thickness measurements on a M2000 Ellipsometer (J.A. Woollam Co., Inc., US) and water contact-angle measurements with a goniometer (DSA100; KRÜSS GmbH, Hamburg, Germany). Ultrapure water was used for the contact-angle measurements (18.2-M Ω resistivity at 25 °C); a volume of 4 μ L was dispensed on the substrate and measurements were taken at five different positions on each thermoplastic sample, which was dried under vacuum for 2 h prior to contact angle measurement. To measure the contact angle as a function of pH, ultrapure water with varying pH was prepared by adding HCl or NaOH and controlling the pH values with a pH meter (AB15, Fisher Scientific). XPS analyses were performed on a K-alpha analyzer (Thermo Fisher Scientific, UK), and AFM images were recorded using Multimode V microscope (Veeco, US). The images presented were treated by use of flatten algorithm using the Nanoscope software, and average roughness (Ra) was calculated using the software provided by the instrument vendor. IR spectra were collected at a resolution of 2 cm⁻¹ scans on a 670-IR spectrophotometer (Varian, US) using a monolayer/grazing-angle specular reflectance accessory.

3. Results and discussion

3.1. Ellipsometric thickness measurements

The nature of aminosilane layer on the plasma activated materials was studied by ellipsometry. The aminosilane was

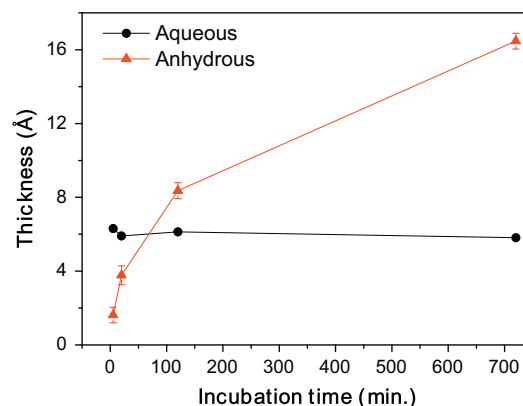


Fig. 1. Variations in thickness of APTES on plasma activated PC, with incubation time, for aqueous and anhydrous phase deposition.

deposited on the surface by solution phase in aqueous (at its natural pH of 10.5) and anhydrous conditions. As shown in Fig. 1, the thickness of aminosilane layer deposited on the PC surface was found to be about 6.0 ± 0.2 Å when aqueous solution was used and there was no significant difference in the thickness even if the incubation time was increased. However, it was increased as a function of the incubation time, from 1.6 ± 0.4 Å to 16.5 ± 0.4 Å, under anhydrous conditions. The thickness of aminosilane layer on other thermoplastics also showed similar tendency and the values are presented in Table 1. The results obtained are in accordance with the thickness of aminosilane layers on the silicon, where the deposition of aminosilane in aqueous solution resulted in lower thickness compared to the anhydrous solution due to the nature of aminosilane in these solvents [22]. To check the nature of binding of the silane layer on the plasma activated PC, the effect of sonication on the thickness of the silane layer was tested. Sonication usually removes the weakly bound, physically adsorbed layers from the surface while retaining the covalently bound molecules. As shown in Table 2, sonication of the substrates in water (3 min) did not affect the thickness of the film deposited from aqueous solution irrespective of its incubation time. However, the thickness of the film deposited from anhydrous solution varies, after sonication in ethanol (3 min), depending on its incubation time. The thickness decreased significantly for layers prepared at shorter incubation time, but it did not change when the substrates were

incubated for longer time. This suggests that the hydrolyzed form of aminosilane in aqueous solution reacts spontaneously with the surface forming a stable aminosilane layer. Whereas in anhydrous solutions, weak hydrogen bonding forms initially between the ethoxy or the amino groups of the silane and the oxygen functionalities on the surface. And a covalent bond forms between them by elimination of small molecules like water and ethanol, when the samples are incubated for longer time or at higher temperature (see Figure S1).

3.2. Surface analysis by contact angle measurements

The wettability of aminosilane-modified PC surface was examined by measuring contact angle on both aqueous and anhydrous phase aminosilane deposited PC made with various incubation times. Fig. 2A shows the plot of contact angle versus incubation time. The contact angle increased slightly with increasing time and is constant after 20 min for aqueous phase deposition. On the other hand, the hydrophobicity increased with increasing time for anhydrous phase deposition. The range of contact angle was between 48 – 54° and 66 – 82° for aqueous and anhydrous phase depositions, respectively. This difference in contact angle could be due to the nature of aminosilane under the specified reaction conditions. In aqueous phase, the aminosilane gets hydrolyzed to silanetriol and results in a hydrophilic surface compared to the anhydrous phase, where the molecules exist as triethoxysilanes.

Table 1
Thickness (Å) of aminosilane layer on plasma activated thermoplastics.

Incubation time (min)	Aqueous phase, pH 10.5			Anhydrous phase		
	PS	PMMA	COC	PS	PMMA	COC
20	5.6 ± 0.1	5.9 ± 0.2	5.2 ± 0.2	3.6 ± 0.4	3.8 ± 0.3	3.1 ± 0.4
120	5.6 ± 0.3	6.1 ± 0.1	5.1 ± 0.1	7.5 ± 0.4	8.5 ± 0.4	6.9 ± 0.4
720	5.7 ± 0.2	5.9 ± 0.2	5.0 ± 0.2	15.4 ± 0.5	16.9 ± 0.4	14.7 ± 0.3

The values presented here are an average of four independent measurements.

Table 2
Effect of sonication on the thickness of aminosilane layer on plasma activated PC.

Incubation time (min)	Aqueous phase, pH 10.5		Anhydrous phase	
	Initial thickness (Å)	Thickness (Å) after sonication	Initial thickness (Å)	Thickness (Å) after sonication
5	6.3 ± 0.3	6.0 ± 0.5	1.6 ± 0.4	0.6 ± 0.3
20	5.9 ± 0.1	5.8 ± 0.2	3.8 ± 0.5	2.5 ± 0.6
120	6.1 ± 0.1	6.1 ± 0.3	8.4 ± 0.4	8.0 ± 0.4
720	5.8 ± 0.2	5.9 ± 0.4	16.5 ± 0.4	16.3 ± 0.2

The values presented here are an average of four independent measurements.

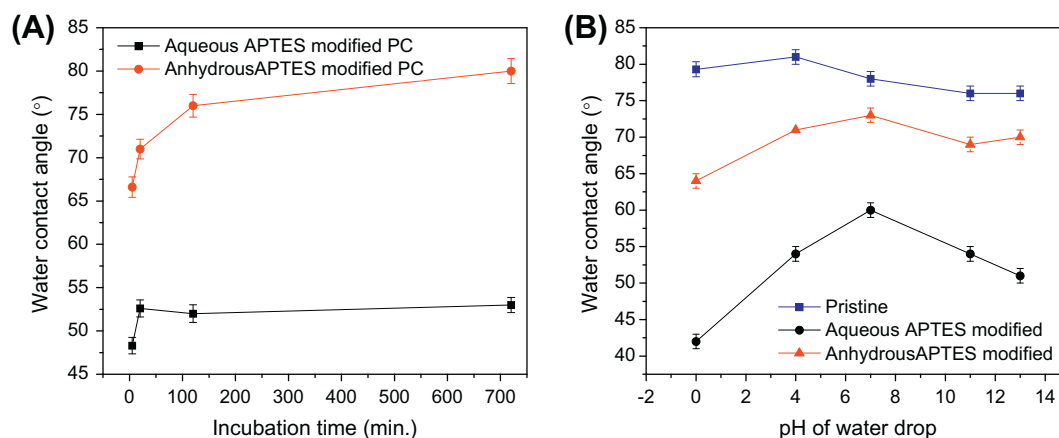


Fig. 2. Variation of water contact angle as a function of incubation time (A) and pH of water (B).

The point of zero charge (pzc) of the pristine and modified PC was also determined by measuring water contact angle, as a function of pH of the water drop. Fig. 2B shows the plot of water contact angle versus pH. As can be seen from the figure, the water contact angle exhibits a maximum at pH 4 and pH 7 for pristine and aminosilane modified PC, respectively. This implies that the pzc of pristine PC and aminosilane treated PC is around pH 4 and 7, respectively. The PC modified in both aqueous and anhydrous solvents shows the same pzc, i.e., 7. Here, the effect of solvent used for aminosilane deposition was negligible as the substrates were dried under vacuum for 2 h prior to contact angle measurements. Though the amine functions are positively charged up to pH \sim 11, the aminosilane modified PC is positively charged below pH 7 and negatively charged above pH 7. This neutrality of the aminosilane treated PC at pH 7 can be attributed to the presence of negatively charged species such as —COO^- , —O^- and —C—O^- which might have formed during the oxygen plasma treatment of the substrate, to compensate the positively charged amine functions on the surface.

3.3. Surface topographical analysis using AFM

To monitor the changes in surface morphology with each step of surface treatment conditions, AFM images were recorded for pristine and surface treated thermoplastics. The images of PC are shown in Fig. 3. The average roughness (R_a) of pristine, plasma activated, aqueous, and anhydrous phase aminosilane deposited PC are 2.53, 0.83, 0.64, and 0.72 nm, respectively. It is interesting to note that the overall R_a value decreased after plasma activation while the R_a value at a local area increased (See Figure S2). This is because the surface of pristine PC is composed of peaks and valleys yielding large height variation (Fig. 3A) while the plasma treated PC shows relatively flat but locally embossed micro domain

(Fig. 3B). These tiny and embossed microstructures could be formed due to the surface rearrangement by scission and cross-linking of the polymer fragments during the plasma process or by etching due to the bombardment of high energy species on the surface. The surface becomes flat and smooth after the silane treatment (Fig. 3C and D) and suggests that the silane is anchored on the substrates. An interesting difference found between aqueous and anhydrous phase aminosilane deposition is that it is featureless for the silane surface prepared in aqueous phase, but it contains a few features in anhydrous phase. This roughness can be attributed to the presence of APTES aggregates that could be formed under anhydrous reaction condition.

The AFM images of PS, COC, and PMMA are shown in Figures S3–S5, respectively. Even though these thermoplastics exhibit different surface features, they show similar trend in change of surface morphology as that of PC, that is, the surface shows embossed micro domains after plasma treatment and becomes relatively flat after the silane treatment.

3.4. Surface characterization by XPS analysis

The XPS, with a probing depth ranging between 0.5 and 10 nm, is a sensitive technique which gives valuable information about the chemical composition on the surface. As the thickness of the aminosilane layer formed on the surface was less than 1 nm, the signals of bulk PC predominated over the signals of aminosilane layer. Although the analysis results indicate the presence of silane on the surface, they provide little information on chemical nature of the aminosilane (data not shown). To avoid the ambiguity in the surface characterization and to precisely understand the chemistry on the plasma activated and aminosilane treated surfaces, a thin film of PC was spin-coated on the Au substrates and the

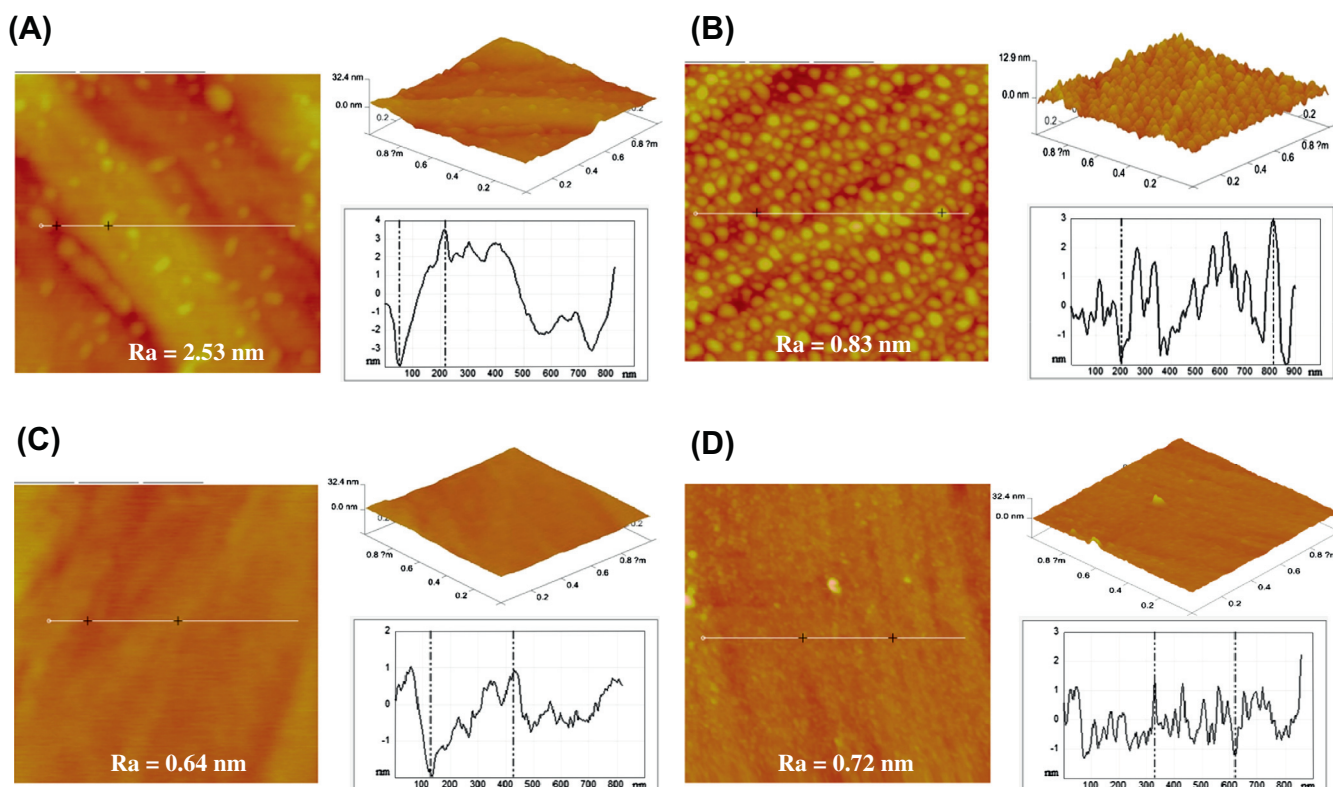


Fig. 3. Atomic force microscope (AFM) image (left), 3D image (right top), and surface cross sectional profile (right bottom) of (A) pristine, (B) plasma-treated, (C) plasma & aqueous APTES treated and (D) plasma & anhydrous APTES treated ($1\ \mu\text{m} \times 1\ \mu\text{m}$) PC.

change in chemical environment on the surface with the treatment condition was investigated by XPS analyses.

The spectra were obtained before and after plasma activation, as well as after APTES treatment of the PC film deposited on Au. The change in elemental compositions after each step of the treatment indicates a change in surface functionality. To determine the nature of the functionality, the C 1s, O 1s, and N 1s peaks were curve fitted and are shown in Fig. 4. The functional groups are assigned based on the differences in their binding energies [31]. A peak-fit of the C 1s high resolution spectrum of pristine PC (Fig. 4A) shows the signals for different bonding states of carbon which correspond to aromatic $\text{C}-\text{C}/\text{C}-\text{H}$, aliphatic $\text{C}-\text{C}/\text{C}-\text{H}$, $\text{C}=\text{O}$, and $\text{O}-\text{C}(\text{O})-\text{O}$ at binding energies (BE) of 284, 284.5, 286.1, and 290.4 eV, respectively. The fitting of the O 1s spectrum shows two peaks at 532 and 533.6 eV that correspond to $\text{C}=\text{O}$ and $\text{O}-\text{C}(\text{O})-\text{O}$, respectively. The curve-fit of C 1s spectrum of plasma activated PC (Fig. 4B) shows signals at 283.9, 284.3, and

284.9 eV for aromatic and aliphatic $\text{C}-\text{C}/\text{C}-\text{H}$ and broad peaks at 286.2 and 288.2 eV for $\text{C}=\text{O}$, $\text{C}=\text{O}$ and $\text{O}-\text{C}(\text{O})-\text{O}$, $\text{O}-\text{C}(\text{O})-\text{O}$, respectively. The O 1s spectrum shows a broad peak which was deconvoluted into multiple peaks with BE's 530.9, 531.9, 532.5, 533.1, and 533.8 eV corresponding to various functional groups including aliphatic and aromatic moieties of $\text{C}=\text{O}$ (carbonyl), $\text{C}-\text{O}$ (alcohol, ether), $\text{O}-\text{C}=\text{O}$ (carboxyl), $\text{O}-\text{C}(\text{O})-\text{O}$ (carbonate). These results reveal the incorporation of new polar functionalities such as carboxyl ($-\text{COOH}$), carbonyl ($-\text{CO}-$) and hydroxyl ($-\text{OH}$) on the surface, by the reaction of active oxygen species generated by the plasma treatment. In the spectra of aqueous phase APTES modified PC (Fig. 4C), the C 1s deconvolution shows peaks at 283.8, 284.3, and 284.7 eV corresponding to $\text{C}-\text{H}/\text{C}-\text{C}$, and $\text{C}-\text{Si}$, and at 285.6, 289.4 eV corresponding to $\text{C}=\text{O}$, $\text{C}-\text{N}$ and $\text{O}-\text{C}(\text{O})-\text{O}$ bonding states of PC and APTES. The O 1s deconvolution shows peaks at 531.1 (aromatic $\text{C}=\text{O}$, $\text{O}-\text{C}(\text{O})-\text{O}$), 531.7 (aliphatic $\text{C}=\text{O}$, $\text{N}-\text{C}(\text{O})-\text{O}$), 532.2 ($\text{C}-\text{O}$, $\text{Si}-\text{O}$), and 533.3 ($\text{O}-\text{C}(\text{O})-\text{O}$). Interestingly, in the N 1s decon-

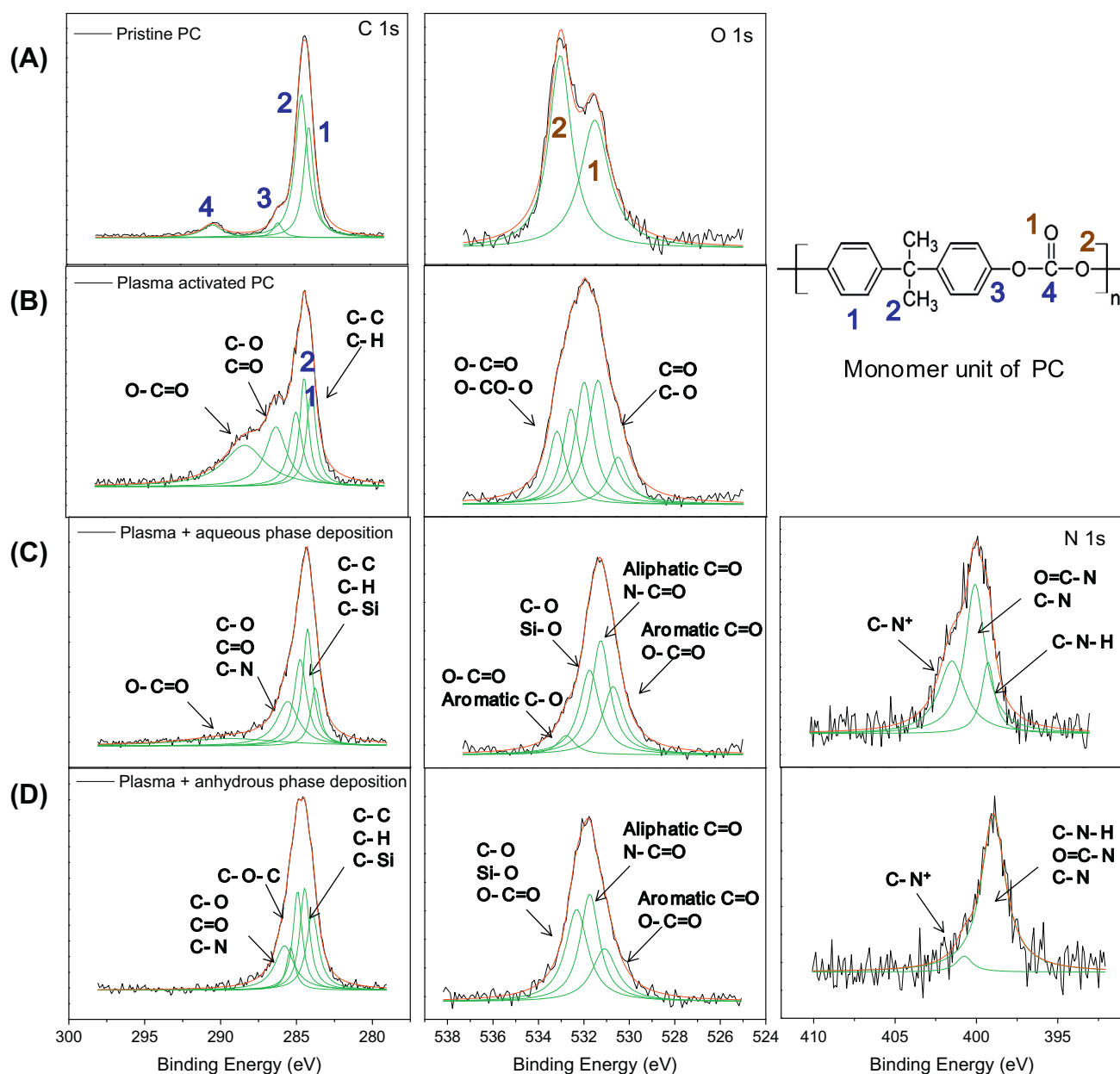


Fig. 4. XPS deconvolution spectra for C 1s, O 1s and N 1s binding energies of (A) pristine, (B) plasma activated, (C) aqueous phase APTES modified, and (D) anhydrous phase APTES modified PC.

volution, three peaks for different bonding states of nitrogen were found at 398.6 eV (C–N–H, free amino), 399.4 eV (O=C–N, C–C–N) and 400.9 eV (C–N⁺, protonated amine). From the peak area calculation, the amount of amine and protonated amine were found to be 16% and 33%, respectively and remaining 51% accounts for other bonding states of nitrogen including amide, imine, alkyl amine, etc. Anhydrous phase APTES modified PC also shows similar C 1s and O 1s spectra with a few differences in the percentage area under each peak accounting for the difference in the structure of APTES (Fig. 4D). The main difference is the ethoxy group of the silane, which would be present only on the surface prepared under anhydrous condition. As shown in the N 1s spectra, the percentage of protonated amine (at 400.7 eV) is very small which is only 6% of total nitrogen content and the peak at 398.9 eV is for the remaining 94% nitrogen which accounts for other possible bonding states of nitrogen under anhydrous conditions. From this data, it is evident that in aqueous phase, majority of the amino groups tend to form inter and intra molecular hydrogen bonding with the hydroxyl group of silanol and exists as a protonated amine. Also, the average C/N ratios for the aqueous and anhydrous phase depositions are 23 and 42, respectively (see Table S1), shows that the carbon content in the aqueous phase deposition is lower compared to the anhydrous phase deposition, which further confirms the hydrolyzed form of APTES in aqueous phase.

The XPS spectra of pretreated hydrocarbon polymers, e.g., PS and COC show the C–H/C–C peaks at BE's 283.8, 284.3 eV for aromatic and aliphatic carbons of PS and at 284.2 eV for aliphatic carbons of COC. In both cases, after plasma treatment and aqueous APTES deposition, a broad peak corresponding to C–O, C=O, and C–N was appeared at 285 eV along with the peaks for other bonding states of carbon. The O 1s spectra of both PS and COC show a broad peak that was deconvoluted into two peaks corresponding to C–O, C=O, Si–O and N–C=O bonding states of oxygen indicating successful incorporation of polar oxygen functionalities and APTES molecule on the surfaces. The N 1s spectra of these polymers also showed three peaks at BE's 398.6, 399.4, and 400.9 eV corresponding to free amino, covalently bonded amine and protonated amine, respectively. The percentage of these bonding states of nitrogen was 30, 26 and 44, respectively, for PS and 20, 28, and 52, respectively, for COC (see Figures S6 and S7). The spectrum of oxygen containing polymer, e.g., PMMA shows similar spectral characteristics to that of PC. New peaks corresponding to polar functionalities and APTES were observed in C 1s and O 1s spectra. The N 1s spectrum of aqueous APTES deposited PMMA also shows three bonding states of nitrogen, of which 48% accounts for protonated amine (see Figure S8). These results indicate that most of the amino groups exist as protonated amines on plasma activated thermoplastics, when deposited from aqueous solution. The high resolution XPS data of C 1s, O 1s, and N 1s binding energies and their corresponding atomic percentages of thermoplastics are given in Table S2. The data suggest that the reaction between amino group of silane and the functional groups generated on the surface is predominating on PC compared to other thermoplastics. This may be because of the carbonate functional groups on the PC surface which are known to react with amines forming urethane linkages [17].

3.5. Surface functional group determination by ATR-IR spectroscopy

In order to assess the functional groups on the APTES modified thermoplastics and to avoid the interference of signals from bulk PC, a thin layer of PC was deposited on Au and subjected for modifications. The ATR-IR spectra were recorded for pristine (Fig. 5A) and surface modified PC (Fig. 5B and C). The spectra of modified PC show distinct peaks for aminosilane layer depending on the reaction conditions. The spectrum of aqueous phase deposition

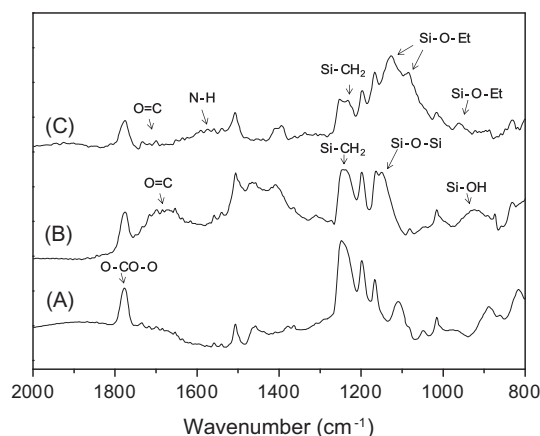


Fig. 5. ATR IR spectra of (A) pristine, (B) aqueous APTES modified, and (C) anhydrous APTES modified PC.

(Fig. 5B) shows a broad band between 950 and 850 cm^{−1} due to Si–OH and [32] confirms the presence of silanols on the surface. Presence of new bands in the regions 1150–1100 and 1220–1200 cm^{−1} corresponding to Si–O–Si and Si–CH₂, respectively, further confirms the cross-linked silane on the surface. While the C=O stretching vibrations (amide, carboxyl and carbonyl) appear as a broad band between 1720 and 1650 cm^{−1} confirms the interaction of amino group with polar functionalities on the plasma activated surface. On the other hand, the spectrum of anhydrous phase deposition (Fig. 5C) showed a broad band between 970 and 940 cm^{−1} and a doublet at 1100 and 1075 cm^{−1}, which are characteristics peaks of Si–O–Et, and indicates the presence of ethoxy silane of a non-hydrolyzed aminosilane. Other peaks include a strong band at 1200 cm^{−1} for Si–CH₂, a peak between 1600 and 1550 cm^{−1} for N–H bending vibration and a broad peak around 1700 cm^{−1} for C=O stretching vibration. The region between 3500 and 2800 cm^{−1} for CH, OH, and NH stretching are excluded from the discussion as the peaks are broad and could not be distinguished from the peaks of pristine PC.

The above analytical data suggest that the activation of thermoplastics with oxygen plasma produces a highly functionalized surface with the incorporation of oxygen functionalities such as hydroxyl, carbonyl, and carboxyl groups on the surface. These functional groups readily react with the silanol or amino groups of the hydrolyzed APTES when deposited from aqueous solution. It is well known that the ethoxy groups of APTES molecules hydrolyze rapidly in water and the aqueous solutions of APTES exists as silanetriol or short oligomers [17]. The presence of Si–O–Si and Si–OH bands in the IR spectrum of the aminosilane layer deposited from aqueous solution also indicates that the silane is in fully hydrolyzed and partially condensed form. The amino group in the hydrolyzed form of APTES interacts with the silanols and exists as a protonated amine. Also, a number of interactions are possible between APTES and the plasma activated surface, which are illustrated in Fig. 6. In aqueous phase deposition, the amino and silanol groups of APTES react with the functional groups on the surface through the formation of amide, imine, and silane (Si–O–C) bonds and also it interacts with the surface through electrostatic attraction and inter/intra molecular hydrogen bonding and forms protonated amine.

In the case of anhydrous phase deposition, as the ethoxy groups of APTES molecules are not completely hydrolyzed, the intramolecular hydrogen bonding is rare. The amino group reacts with the surface forming amide and imine bonds and weak interactions exist between the ethoxysilane of APTES and the thermoplastic surface. The surface bound water on the plasma treated thermoplastics can

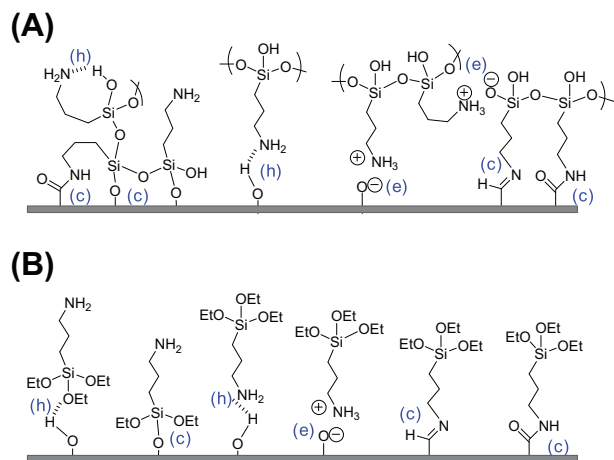


Fig. 6. Schematic representation of structure of APTES on plasma activated thermoplastics (A) aqueous phase deposition, (B) anhydrous phase deposition. Different types of interactions between APTES–APTES and APTES–surface. (h) inter-/intra molecular hydrogen bonding (e) electrostatic attractions (c) covalent bond formation.

hydrolyze the ethoxy groups which are oriented near the surface and helps in silane ($\text{Si}-\text{O}-\text{C}$) bond formation. Also, APTES molecules aggregate (see Fig. 3D) on the surface due to the physisorption, leading to a thicker film as the reaction proceeds (Fig. 1).

Although there are a few interactions similar to that of silicon surfaces, the main difference between the aminosilane on silicon and the thermoplastic surfaces is the formation of covalent bonds between the active functional groups generated on the surface during plasma activation. Formation of these covalent bonds is observed in both aqueous and anhydrous phase deposition indicates that this is a general reaction and happens irrespective of the reaction conditions.

4. Conclusion

For the potential applications of thermoplastic materials in bio-medical engineering, it is important to understand the mechanism of silane modification on thermoplastic surfaces. For example, a microfluidic device assembled with a surface modification method may have different surface properties within the channel which could affect the fluid dynamics. Understanding the structure and chemistry of silane helps in tailoring the surface for specific applications. To this end, the nature of APTES films formed on the plasma activated thermoplastics is investigated using various surface characterization techniques such as ellipsometry, goniometry, XPS, AFM, and ATR-IR. The differences and similarities of the APTES film deposited from aqueous and anhydrous solutions are examined. Information on the un-reacted ethoxy groups, siloxane ($\text{Si}-\text{O}-\text{Si}$) bond formation, and the interaction of other functional groups on the surface is provided by both IR and XPS spectra. It is important to note that unlike the amino group of APTES on silicon substrates, where it interacts with the surface through physical attractions, the amino group on the plasma activated thermoplastics can form covalent bonds with the functional groups generated on the surface during the plasma activation. Therefore, the number of free amino groups available on thermoplastic surface could be

lower and irregularly oriented compared to the silica surfaces. To the best of our knowledge, this is the first report to present the structure of APTES layer on the surface of plasma activated thermoplastic materials and we believe that the results presented here will make a significant impact on the microfluidic field.

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Appendix A. Supplementary material

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