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Surface Modification of Polymers with 3-Aminopropyltriethoxysilane as a General Pretreatment for Controlled Wettability

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ABSTRACT: Various polymer surfaces were analyzed for reactivity toward 3-aminopropyltriethoxysilane (APTES). Results indicate that the method described here is useful as a general surface-selective modification technique for polar polymers such as polyesters, polyamides, polycarbonates, polyimides, cellulosics, polyacrylics, etc. X-ray photoelectron spectroscopy (XPS) showed an average of 10% silicon and nitrogen atomic concentrations at 75° takeoff for all successfully modified surfaces. The APTES multilayers were subsequently hydrophobized with perfluorinated chlorosilanes giving 40% fluorine atomic concentration by XPS and 120°/90° (advancing/receding) dynamic contact angle averages. APTES modifications were successful in all solvents with the exception of protic solvents. On the basis of these and other observations, a new model for the reaction pathway is proposed. We propose the reaction proceeds by initial APTES adsorption (likely through hydrogen bonding by the amine) to the substrate, lateral bond formation, and subsequent multilayer formation. The model is thus analogous to silane multilayer formation on silica.

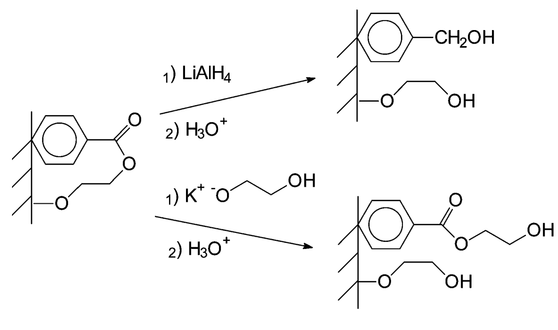
Introduction

A number of synthetic routes to create chemically modified polymer surfaces have previously been developed. The approach has, in general, been to introduce covalently attached functional groups (e.g., alcohol) that can then be derivatized through well-controlled chemical reactions. Chemically resistant polymers such as poly(tetrafluoroethylene),[1,2] polypropylene,[3] poly(chlorotrifluoroethylene),[4−7] and poly(ether ether ketone)[8] have a number of advantages for surface chemistry applications, in particular, acting as inert supports for harsh chemical reactions.

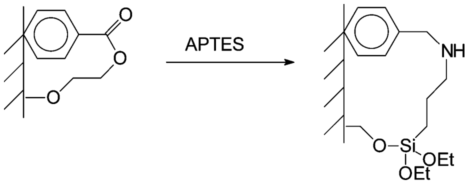
Similar modifications on more reactive polymers is of interest but is often more difficult as conditions that only affect specific functional groups, not the entire polymer chain, are desired. Modification of poly(ethylene terephthalate) (PET)[9−11] has been shown to mitigate the inherent low surface energy that limits its use in many applications. PET glycolysis and reduction (Scheme 1) are common methods used to prepare surfaces with alcohol functionality. These methods are limited in their usefulness since both techniques cause chain cleavage; therefore, surface functionalization must be balanced against bulk polymer degradation.

Other methods of modifying PET using ester chemistry have been reported including plasma treatment,[12] graft polymerization,[13−15] activation with *p*-toluenesulfonyl chloride,[16,17] and reduction of silicate salts.[18] Thompson et al.[19] reported that the reaction of PET with 3-aminopropyltriethoxysilane (APTES) proceeds to create a cross-linked siloxane network with a thickness larger than the X-ray photoelectron sampling depth. Unlike previous attempts to selectively modify its surface, the PET showed no degradation. Thompson et al. suggest that the primary method of modification is the formation of an amide bond between the PET and APTES; however, Thompson et al. imply that a multitude of other reaction pathways may also be at play. The insertion of APTES into the PET chain (Scheme 2) was proposed where nucleophilic attack of the APTES amine on the carbonyl breaks the ester bond forming the amide with the resultant alcohol reacting with the silicon−oxygen bond.

Scheme 1. Reaction Scheme of Reduction (upper) and Glycolysis (lower) of PET



Scheme 2. Reaction Scheme Reported by Thompson et al. for APTES Reacting with an Ester Surface[19]



On the basis of the work by Thompson et al., Fadeev and McCarthy[20] furthered the understanding of the reaction mechanism. On the basis of XPS data, they proposed a similar insertion mechanism but, instead, argued intuitively that PET chain loops would react with two APTES molecules (Scheme 3). Using this method, surfaces with silica-like reactivity were prepared. Reactive silanol functionality was introduced to the surface of PET by subsequently hydrolyzing the APTES modified film. This silanol surface was shown to be reactive to various chlorosilanes while polycondensation of tetraethoxysilane (TEOS) on these silanol surfaces produced ultrathin silica films. These surfaces, as well, were reactive toward chlorosilanes. Thus, Fadeev and McCarthy[20] produced a general method for surface modification of PET with the techniques demonstrated for silica surfaces. Further investigation by Loch et al.[21]

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Scheme 3. Resultant Polymers by the Modified Chain Insertion Mechanism from Fadeev and McCarthy[20]

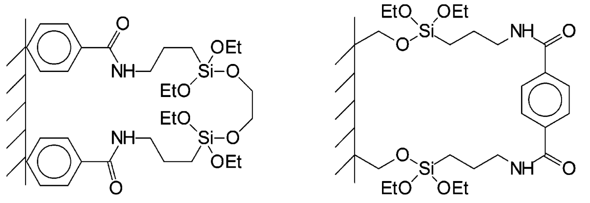

Table 1. 75° Takeoff Angle XPS Results of APTES Reaction on Various Polymer Surfaces

polymer	solvent	% Si	% N
poly(ethylene terephthalate)	toluene	11.6	11.1
poly(ethylene naphthalenate)	toluene	9.8	8.9
poly(butylene terephthalate)	toluene	9.3	7.6
poly(1,4-cylcohexanedimethylene terephthalate-*co*-ethylene terephthalate)	toluene	5.4	5.0
poly(methyl methacrylate)	hexane	8.5	8.0
cellulose acetate	toluene	10.0	9.4
poly(bisphenol A carbonate)	hexane	10.8	8.8
nylon-6,6	toluene	11.7	9.0
poly(methacrylic acid)	toluene	8.4	7.4
polyimide	toluene	12.1	9.1
poly(allyl amine)	toluene	9.0	7.7
poly(vinyl alcohol)	toluene	8.1	7.3
polystyrene	hexane	0.8	0.5
poly(tetrafluoroethylene)	toluene	0.8	0.7

established that hydrogen bonding was responsible for the initial adsorption of APTES at the PET surface. Loch et al. interpreted this result as a precursor step to the amidation reaction. Thus, given enough time, a covalent bond would be formed.

Similar to the work with PET surfaces, Hu and Siddiqui[22] successfully used APTES modification on poly(ethylene napthalate) (PEN) surfaces. Recently, the PET−APTES system has been used to form silica layers for applications ranging from micropatterning,[23] photocatalysis,[24] and as a gas barrier.[25] Polymers such as poly(butylene terephthalate) and poly(1,4-cylcohexanedimethylene terephthalate-*co*-ethylene terephthalate), being esters analogous to PET, are prime candidates for APTES modification. Other polymers such as poly(methyl methacrylate) and poly(bisphenol A carbonate) also have potential applications for surface modification; however, APTES modification may be ineffective for surface selective chemistry due to their structural differences from PET. The currently held mechanism for surface modification by APTES does not suggest that side-chain esters and non-esters can be modified in the same manner as PET.

We report here silica-like reactive surfaces by preparation of thin multilayers of 3-aminopropyltriethoxysilane on various polar polymers, thereby extending the process to a general method of polymer surface-selective modification. On the basis of variations in substrate, solvent, and reagent, we establish that previous notions of the primary mode for surface modification (main-chain amine insertion) are incorrect. Instead, a new model for the dominant reaction mechanism is proposed.

Experimental Methods

PET film (Mylar) was obtained from DuPont and cleaned by rinsing with toluene and distilled water. Toluene, hexane, chloroform, ethanol, tetrahydrofuran, formamide, 1-octanol, carbon tetrachloride, dichloroacetic acid, hydrochloric acid, and diethyl ether were all purchased from Aldrich and were anhydrous grade solvents (used as received). Ethyldiisopropylamine, butylamine, and ethylenediamine along with reagents of 3-aminopropyltriethoxysilane (APTES), 3-aminopropylmethyldiethoxysilane (APMDS), 3-aminopropyldimethylethoxysilane (APDES), and *n*-propyltriethoxysilane (*n*PTES) were also purchased from Aldrich and used as received.

Table 2. 75° Takeoff Angle XPS Results of APTES Reaction in Various Solvents

solvent	% Si	% N
toluene	11.6	11.1
hexane	11.5	9.8
carbon tetrachloride	11.4	10.1
diethyl ether	12.5	9.0
tetrahydrofuran	10.4	9.9
formamide	2.9	3.9
ethanol	2.8	2.6
1-octanol	3.3	1.6

Table 3. 75° Takeoff Angle XPS Results of PET Modified with Various Aminosilanes

reagent	functionality	% Si	% N
APTES	$(-OEt)_3$	11.6	11.1
APMDS	$Me/(-OEt)_2$	2.4	2.4
APDES	$Me_2/(-OEt)$	0.8	0.5

Table 4. 75° Takeoff Angle XPS Results of PET Modified with Combinations of Silanes and Alkylamines Each at 1% Concentration

reagent	% Si	% N
PET neat	0.0	0.0
*n*PTES	0.0	0.0
butylamine	1.1	0.0
*n*PTES + butylamine	1.4	0.0
APTES	11.6	11.1

The following polymers were purchased from Aldrich and were either granular or pelletized: poly(ethylene terephthalate), poly(ethylene naphthalenate), poly(butylene terephthalate), poly(1,4-cylcohexanedimethylene terephthalate-*co*-ethylene terephthalate), poly(bisphenol A carbonate), poly(methyl methacrylate), polystyrene, cellulose acetate, poly(vinyl alcohol), poly(allyl amine), and nylon-6,6. Kapton polyimide was obtained from DuPont. Polytetrafluoroethylene was obtained from Berghoff America. The fluorinated silane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane, was purchased from Gelest and used as received.

Samples were spin-cast onto silicon wafers at 2000 rpm using 2.5% solutions. All annealing was performed under vacuum for 24 h at 150 °C. Solutions were prepared in dichloroacetic acid for polyesters and nylon-6,6, chloroform for poly(bisphenol A carbonate), toluene for polystyrene and poly(methyl methacrylate), and in water for poly(vinyl alcohol) and cellulose acetate. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer Physical Electronics 5100 spectrometer with Al $K\alpha$ excitation (15 kV, 400 W) at a takeoff angle of 75° (between the plane of the sample surface and the entrance lens of the detector optics). Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C_{1s}, 0.200; O_{1s}, 0.501; N_{1s}, 0.352; F_{1s}, 1.00. Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively.

APTES, APDES, APMDS, or *n*PTES (0.3 mL) was syringed into a flask containing 30 mL of anhydrous toluene (or other solvent such as hexane). The flask was previously purged with nitrogen; all transfers were done under nitrogen. The flask contained up to seven samples in a custom holder and a Teflon stir bar. The reaction was held at 75 °C in an oil bath for 72 h. The samples were washed with copious amounts of flowing toluene and dried at reduced pressure. Samples to be hydrolyzed were immersed in 30 mL of H_2O with a catalytic amount of HCl for 24 h, washed with copious amounts of flowing water, and dried at reduced pressure. Silanization reactions were performed to hydrophobize the surfaces for contact angle analysis. Ethyldiisopropylamine (0.3 mL) was

Table 5. 75° Takeoff XPS Results, Water Contact Angle, and Hexadecane Contact Angle of APTES Pretreated Polymer Surfaces after Secondary Silanization Step with (Tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane

polymer	% F	% N	θ_A(deg)/θ_R(deg)^{H_2O}	θ_A(deg)/θ_R(deg)^{Hex}
poly(ethylene terephthalate)	40.2	2.1	120/86	79/47
poly(ethylene naphthalenate)	43.8	1.2	120/90	75/44
poly(butylene terephthalate)	42.7	0.9	120/90	74/44
poly(1,4-cylcohexane dimethylene terephthalate-*co*-ethylene terephthalate)	38.9	1.5	117/80	75/43
nylon-6,6	46.7	0.8	122/89	74/34
poly(vinyl alcohol)[a]	39.3	2.3	140/60	71/0
poly(methyl methacrylate)[b]	19.0	2.9	132/77	59/0
poly(bisphenol A carbonate)[b]	25.1	3.9	130 /76	70/26
silicon	43.2		119/92	80/50

[a] Nonhydrolyzed. [b] APTES modification and silanization done in hexane.

syringed into a flask containing 20 mL of toluene. Subsequently, 0.5 mL of (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane was added to the reaction mixture. The reaction was heated for 72 h at 75 °C in an oil bath. The samples were washed by immersion in the order toluene, toluene/ethanol, ethanol, ethanol/water, water and dried at reduced pressure.

Results

General Polymer Surface Modification. APTES surface modification was performed on a variety of substrates. The spin-cast samples were reacted at 75 °C and 1.0% concentration in toluene for 72 h. Table 1 gives XPS results for all substrates tested. Initially, only main-chain and side-chain polyesters were tested: PET, poly(ethylene naphthalenate), poly(butylene terephthalate), poly(1,4-cylcohexanedimethylene terephthalate-*co*-ethylene terephthalate), poly(methyl methacrylate), and cellulose acetate. As poly(methyl methacrylate) is soluble in toluene, the alternative medium of hexane was used (the use of alternative solvents is explored more in depth later in this section). XPS results indicate that all surfaces were reactive toward APTES modification. Samples have approximately 8−11% silicon and nitrogen atomic concentration with little difference between 15° and 75° takeoff angle data (15° data not shown). The lack of angle dependence indicates a thick multilayer of 40 Å or more. This is surprising as the Fadeev and McCarthy[20] and Thompson et al.[19] schemes propose reactions with a side-chain ester attaching the silane to the surface through a C−O−Si bond, which is easily cleaved by water hydrolysis subsequently removing the APTES from the surface during rinsing. The data indicate no difference between the main-chain and side-chain esters.

Substrates containing other functional groups were also investigated, such as carbonate, acid, amide, and imide. Poly(bisphenol A carbonate), poly(methacrylic acid), nylon-6,6, and Kapton polyimide were analyzed after attempted APTES surface modification. Looking at Table 1, these polymers were successfully modified. The silicon and nitrogen atomic concentrations fall within the same range as with esters. To confirm the experimental protocol, controls were performed with substrates that should have no possible mode of interaction. Poly(vinyl alcohol) and poly(allyl amine) were also tested with our modification protocol. Other than possessing polar functionality, these polymers are dissimilar from those with ester functionality. However, these polymers were successfully modified, as evidenced by the silicon and nitrogen atomic concentrations observed.

Although success with poly(methacrylic acid) is not unexpected, successful modification of other substrates is surprising as, based on previously supposed mechanisms, the reactions are equal to or uphill in energy with respect to the current states. For example, imides are extremely stable materials. For this material to revert to amic acid in order to form an amide with the APTES molecule is highly unlikely. Based on these results, the reaction mechanism proposed by Thompson et al.[19] and subsequently by Fadeev and McCarthy[20] is not the dominant pathway of surface modification. Poly(styrene) and poly(tetrafluoroethylene) were analyzed for APTES modification and did not have any interaction with APTES. Silicon and nitrogen atomic concentrations of less than 1% were observed after reaction (Table 1).

Samples were hydrolyzed in water with catalytic HCl for 24 h after reaction to introduce silanol functionality reactive toward chlorosilanes. After hydrolysis, water contact angles on all successfully reacted ester samples and nylon-6,6 were approximately 57°/0° (advancing/receding) (except poly(1,4-cylcohexanedimethylene terephthalate-*co*-ethylene terephthalate) which was 77°/0°), indicating a relatively large amount of silanol functionality and similar surfaces on all samples. Poly(methyl methacrylate) and poly(bisphenol A carbonate) had contact angles somewhat higher (75°/30°) possibly due to hexane being a poor solvent compared to toluene for this reaction. Hydrolysis of nonreactive substrates marginally altered the surfaces; hydrolysis of poly(methacrylic acid), poly(vinyl alcohol), cellulose acetate, and poly(allyl amine) was not performed as they are soluble in water.

Effects of Solvent and Reagent. APTES modifications were carried out in alternative reaction media to determine whether these changes would have any effect on the reaction. Results are presented in Table 2. As with reactions in toluene, APTES modifications in other nonpolar solvents such as hexane and carbon tetrachloride work well as evidenced by the silicon and nitrogen atomic concentrations. Even with ether solvents such as tetrahydrofuran and diethyl ether, the surface modifications were successful. However, formamide and ethyl alcohol inhibit surface reaction. The silicon and nitrogen atomic concentrations were lower relative to the other solvents. It is not likely that the hindered reaction is resulting from just solvent quality and polarity changes as reactions carried out in 1-octanol are similarly inhibited.

In an effort to gather more information as to the possible mechanistic origins of the APTES surface modification, surface modifications of PET were performed with reagents where the reactive ethoxy functionality of the APTES molecule was replaced with nonreactive methyl groups. Although the ethoxy group is a required element of previous reaction schemes, only one ethoxy is required for the reaction to proceed. Removing excess ethoxy groups from APTES should have little effect until all of them are replaced, as even one ethoxy group should allow the reaction to continue. What actually occurs, however, is completely different (Table 3). Replacing just one of the ethoxy groups as in APMDS nearly prevents the reaction completely.

Silicon and nitrogen atomic concentrations between 2% and 3% were seen. Replacing two ethoxy groups (APDES) results in surfaces nearly the same as those that are unmodified—no reaction occurred as supported by the less than 1% silicon and nitrogen seen by XPS. Again, this is strong evidence that the currently held ideas of APTES modification are incorrect: amidation is likely not an important feature of the reaction (or the reaction is competitively disfavored).

An additional set of control experiments were performed to probe the ability for other reactions that may occur at the PET surface due to the presence of amine and ethoxysilane. Reactions of a silane without amine (nPTES), neat butylamine, and nPTES in combination with butylamine were performed at standard reaction conditions. No effect was observed with nPTES, butylamine, or a combination of the two, as seen in Table 4. This result indicates that the reagents are not simply acting in concert or as cocatalysts, but the amine functionality must be attached to the silane for APTES modification to be effective.

Hydrophobization of APTES Treated Polymer Surfaces. In order to test the usefulness of the APTES modification technique toward control of the wetting behavior for the various polymer surfaces, covalent attachment of a monochlorosilane on these surfaces was performed. (Tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane was used as it provides an efficient XPS label for subsequent analysis and also provides a highly nonwettable surface. Additionally, the chlorosilane will selectively modify the APTES, while remaining nonreactive toward the potentially exposed polymer substrate, thus exposing any potential defects in the APTES films. Although better hydrophobization could no doubt be achieved through the use of trichlorosilanes, by using monochlorosilanes, one can get an idea of the number and accessibility of silanols with silica-like reactivity. No other silanes are used as the intent is to characterize the APTES pretreatment and prove its general utility in subsequent modification, not to duplicate previous silanizations with the technique.

After hydrophobization, the polymers were analyzed by XPS. Table 5 gives 75° XPS fluorine and nitrogen atomic concentration. Effective fluorination of the surfaces modified with APTES is evident. Esters modified in toluene as well as the nylon-6,6 samples have fluorination values approaching that of the silicon wafer (>40%) while displaying little nitrogen, indicating a relatively defect-free fluorination. Both water and hexadecane contact angles of these esters are also high and approach those of, but are not quite as high as, the modified silicon. APTES treated poly(vinyl alcohol) was also silanized with mixed results. However, the sample could not be hydrolyzed due to polymer solvation. The sample was spectroscopically similar (by XPS) to the other hydrophobized samples; however, the contact angle results differ. This behavior was not unexpected as poly(vinyl alcohol) has a specific interaction with the water. Two polymers, poly(methyl methacrylate) and poly(bisphenol A carbonate), were silanized in hexane due to their solubility in toluene. However, hexane is an inferior medium for silanization, providing rougher, less homogeneous surfaces. Macroscopic "snowing" was observed in the reaction mixture, possibly indicating higher water contents in the reaction media. There was fluorination on the surface; however, it was much less than on the previous samples. More nitrogen was also observed. Water contact angle shows much higher hysteresis, indicating an incomplete layer of silane. Hexadecane also shows higher hysteresis along with lower angles. Again this is indicative of poor surface coverage. This being said, there was a hydrophobization of the surface, although not to the degree of the other surfaces.

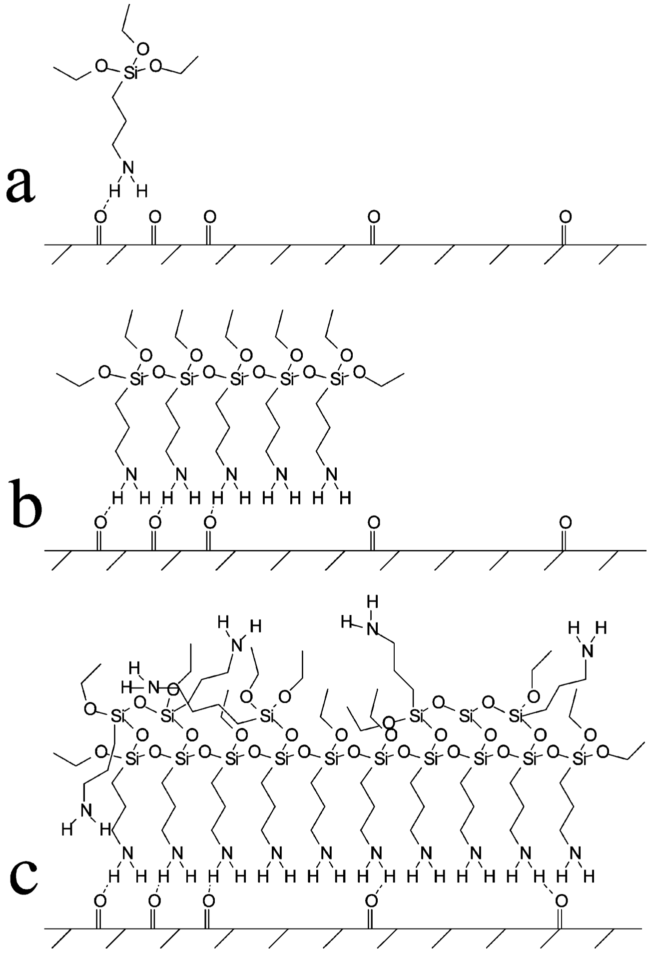

Figure 1. Proposed mechanism of APTES surface modification: (a) initial adsorption via hydrogen bonding, (b) subsequent lateral bond formation to the nearest neighbors, and (c) multilayer formation.

Discussion

An explanation of the nature of the APTES surface modification cannot be given that is consistent with the currently held view of the chain-insertion and amidation (amides that have not been spectroscopically observed) of PET. Rather, a new scheme is proposed (Figure 1), where APTES adsorbs to and then cross-links on PET, forming a multilayer siloxane much as in silane multilayers on silica. The first step in this process (a) is the physisorption of APTES to the polymer surface through hydrogen-bonding an H-bond acceptor on the surface.[21] Siloxane bond formation through the ethoxy groups with neighbors H-bonded to the surface or with free APTES molecules in solution then occurs as shown in (b). In contrast with prior models,[19-21] we assert that covalent bonding between APTES and the polymer substrate does not occur, even with extended reaction time. Furthermore, perfect registry between the donor amine and the acceptor groups is not required. It is likely that some of the APTES molecules are not actually H-bonded to the surface; however, the lateral bonds ensure that the layer will not come off. The inter-APTES reaction to form siloxane cross-links thus becomes the driving force of the reaction. After (or concurrently with) the lateral cross-linking occurs, the layer builds up in thickness to form a thin multilayer as evidenced by the lack of angle dependence of the XPS atomic concentrations. Some subtleties concerning the role of water in this proposed mechanism should be addressed. Water does not need to be initially available at the polymer surface to create a film, as physisorption occurs independent of water content.

However, as has been previously established for silane deposition, for the cross-linking reaction to proceed, trace amounts of water are necessary.[26,27] With respect to the polymer films created, we assume most of the water present in the system is in solution due to an inherent amount of water present in the solvents, and the ability of the solvents to abstract water from the surfaces of the vial and substrate at elevated temperatures.[28,29] For in-situ cross-linking to occur, either water must diffuse to the already physisorbed surface or some of the APTES molecules react in solution and contribute to film formation en masse. The implication of such small amounts of water being present in the reaction system is that the surfaces as initially created are poorly hydrolyzed and have a limited degree of cross-linking. This points to the necessity of an additional hydrolyzation step in which the films were immersed in water.

Using this model of APTES modification, previous results can readily be explained, and the reason for all of the polymers except polystyrene and poly(tetrafluoroethylene) to be heavily modified becomes clear. All modified polymers have polar, H-bond accepting groups allowing for the initial adsorption event of the chain reaction. Lacking groups such as these, polystyrene and poly(tetrafluoroethylene) do not support the reaction. The influence of solvent on the effectiveness of the reaction also supports our proposed model. Protic solvents such as the three with negative results (formamide, ethanol, and 1-octanol) would interfere with H-bonding and prevent APTES modification. Barring this, varying the medium of reaction should have little effect. Exactly this is observed. The effects of replacing the reagent ethoxy groups are also congruent with our model of reaction. Lateral bond formation is a necessary event. Interfering with this process would have negative consequences on the reaction. With just two possible linking points, APMDS can at most form linear chains that are not as effective as cross-linked networks at anchoring the layer on the surface. When two ethoxy groups are replaced, the APDES layer cannot maintain its integrity at all due to its ability to form only dimers. Last, while nPTES/butylamine results do not suggest that previously held models are wrong, the necessity of the amine being attached to the silane also supports the proposed model. In short, the evidence is incongruent with the previous held notions of the reaction yet is consistent with our hydrogen-bonding cross-linking model.

Summary

The utility of the modification of polymer surfaces with 3-aminopropyltriethoxysilane (APTES) was tested with a variety of polymer surfaces. Poly(ethylene terephthalate), poly(ethylene naphthalenate), poly(butylene terephthalate), poly(1,4-cylcohexanedimethylene terephthalate-*co*-ethylene terephthalate), poly(bisphenol A carbonate), poly(methyl methacrylate), polystyrene, cellulose acetate, poly(vinyl alcohol), poly(allyl amine), nylon-6,6, Kapton polyimide, and polytetrefluoroethylene were tested, and all polymers but polystyrene and poly(tetrafluoroethylene) were successfully modified by the evidence of 9%−12% silicon and nitrogen atomic concentrations by 75° XPS takeoff angle. Water contact angle analysis also confirms the modification. The ability of some of these polymers to undergo reaction with APTES was found to be contrasting with the chain-insertion model of reaction currently held. A new model is proposed analogous to SAM formation of silanes on silica, whereby initial H-bonding of the APTES followed by lateral bond formation occurs. Substrate reactivity and the inability of the reaction to proceed in polar protic solvents support the new model. An experiment was performed where the ethoxy groups were substituted for nonreactive methyl groups of the APTES reagent, and modifications were carried out with these. The reduction of reagent at the surface with one ethoxy substituted and the complete shutdown of the reaction with two substituted are further arguments for the new model. Hydrophobization of the APTES-modified surfaces was also carried out using (tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane after hydrolysis of the APTES layers. Effective hydrophobization was observed with water contact angles of 120°/86° (advancing/receding) and hexadecane angles of 79°/47° (advancing/receding) for PET film. Fluorine atomic concentrations are approaching those of, but are not quite as high as, similarly treated silicon wafers.

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