Controlled Monomolecular Functionalization and Adhesion of Solid Surfaces

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Pulsed plasma polymerization of maleic anhydride leads to the deposition of well-defined anhydride functionalized films. These layers readily undergo reaction with amine-terminated nucleophiles to produce surface amide linkages that convert into cyclic imide groups upon heating. Potential applications include adhesion and biocompatibility.

1. Introduction

Well-adhered polymeric surfaces containing anhydride groups are widely sought after for improving interfacial bonding[1] and polymer/polymer compatibility,[2] as well as providing anchoring sites for chemical derivatization reactions,[3] (e.g., adhesive coupling reagents). Conventional bulk homopolymerization,[4] copolymerization,[5] and graft polymerization[6] of maleic anhydride have been extensively studied in the past. Formation of films from these materials in order to generate reactive surface anhydride groups requires organic solvents[7−9] or reactive polymer extrusion,[10,11] in conjunction with elevated temperatures and/or pressures. Alternative approaches have encompassed self-assembled monolayers[12] and maleic anhydride copolymers coupled to solid surfaces.[13,14] These systems also suffer from drawbacks related to the requirement for specific functional groups at the surface of the underlying substrate as well as geometric constraints.

A more straightforward methodology has been recently developed comprising pulsed plasma polymerization of maleic anhydride, where the overall anhydride composition in the film can be controlled by simply programming the electrical discharge parameters (e.g.,

duty cycle, power, etc.).[15] Pulsing the plasma in this way restricts monomer fragmentation and damage of the growing polymer layer during the duty cycle on-time, as well as encouraging conventional polymerization reaction pathways during the off-period.[15−17] A major benefit is that the surfaces of complex shaped substrates can be easily functionalized via subsequent chemical derivatization of anhydride groups contained in the plasma polymer layer (e.g., nucleophilic attack by amine- or alcohol-terminated moieties to produce amides/imides and ester linkages respectively[18,19]).

In this article, the functionalization of pulsed maleic anhydride plasma polymer surfaces with 2,2,2-trifluoroethylamine and Jeffamine-D230 (poly(propylene glycol) bis(2-aminopropyl ether)) is reported. The former has been chosen as a model nucleophile in order to demonstrate the viability of the proposed derivatization chemistry, while surfaces functionalized with the latter reagent (an amine-terminated polyether) are of potential interest for adhesion and biomedical purposes (e.g., controlled attachment of heparin[20] and DNA synthesis).

2. Experimental Section

Briquettes of maleic anhydride (Aldrich, 99% purity) were ground into a fine powder and loaded into a monomer tube. Plasma polymerization experiments were carried out in an electrodeless cylindrical glass reactor (4.5 cm diameter, 460 cm^3 volume, base pressure of 5.2×10^{-3} mbar, with a leak rate lower than 1.0×10^{-10} kg s^{-1}) enclosed in a Faraday cage. The reactor was fitted with an externally wound copper coil (4 mm diameter, 9 turns, spanning 8−15 cm from the gas inlet), a gas inlet, a thermocouple pressure gauge, and a 30 L min^{-1} two-stage rotary pump attached via a liquid nitrogen cold trap. All joints were grease-free. An L−C matching network was used to match the output impedance of the rf generator (13.56 MHz) to that of the partially ionized gas load;

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Table 1. Infrared Assignments of Maleic Anhydride Plasma Polymer, Nucleophilic Reagents, and Corresponding Derivatized Plasma Polymer Surfaces

| peak position/ cm^{-1}	assignment	MA	TFEA	MA + TFEA	Jeffamine	MA + Jeffamine
1849	C=O anhydride stretch[12]	*		*		*
1780	C=O anhydride stretch[18]	*		*		*
1725−1700	carboxylic acid stretch[14]			*		*
1772, 1710	imide bands[14]			* (after heating)		* (after heating)
1660−1563 (broad band)	amide I (C=O stretching) and amide II (NH bending)[12]			*		*
1627−1590	NH$_2$ bands[40]		*		*	
1625−1560 and 1550−1505	NH$_3^+$, antisymmetric and symmetric deformations[40]					*
1490−1400	CNH stretch of monosubstituted amide[40]		*			*
1400−1000	CF$_3$ stretches[40]		*	*		
1288−1240	cyclic anhydride stretch[25]	*				
1180−1000	CN stretch[40]		*	*	*	
1150	imide stretch[40]			* (after heating)		* (after heating)
1150−1060	COC stretch[25]				*	*
958−935	cyclic unconjugated anhydride[25]	*				
950−780	C−C skeletal bands[40]				*	*
850	NH$_2$ wag[40]		*		*	*

this was achieved by minimizing the standing wave ratio (SWR) of the transmitted power. Pulsed plasma polymerization experiments were carried out using a signal generator to trigger the rf power supply. The pulse width and amplitude were monitored with a cathode ray oscilloscope. The average continuous wave power output (P_{cw}) of the rf supply spanned 5−90 W. Pulse on-times (t_{on}) and off-times (t_{off}) could be varied between 5−800 and 5−1200 μs, respectively. The average power $\langle P \rangle$ delivered to the system during pulsing was calculated using the following expression

$$\langle P \rangle = P_{cw}\{t_{on}/(t_{on} + t_{off})\} \qquad (1)$$

where $t_{on}/(t_{on} + t_{off})$ is defined as the duty cycle.[21]

Prior to each experiment, the reactor was cleaned by scrubbing with detergent, rinsed in isopropyl alcohol, and oven-dried, followed by a 30 min high-power (50 W) air plasma treatment. Next, the chamber was vented to air and the substrate to be coated (e.g., glass, silicon, polypropylene, etc.) placed at its center, followed by evacuation back down to base pressure. Subsequently, maleic anhydride vapor was introduced into the reactor at a constant pressure of 2.6 × 10^{-1} mbar, and a flow rate of approximately 1.6 × 10^{-9} kg s^{-1}. At this stage, the plasma was ignited and left to run for 10 min. Upon completion of deposition, the rf generator was switched off, and the monomer feed allowed to continue to flow through the system for a further 5 min prior to pumping down to base pressure. The coating thickness was measured using a quartz crystal sensor (Kronos QM300) assuming a film density[18] of 1.49 g cm^{-3}; this was positioned adjacent to the substrate in the plasma reactor.

Next, the deposited maleic anhydride plasma polymer coatings were reacted with either 2,2,2-trifluoroethylamine (Fluorochem, 99.5%) or Jeffamine-D230 (H$_2$N−CH(CH$_3$)−CH$_2$−[OCH$_2$CH(CH$_3$)]$_n$−NH$_2$, Aldrich, average molecular weight M_n = 230, which corresponds to 2−3 repeat units). This was done without exposure to air in order to avoid hydrolysis of the maleic anhydride plasma polymer layer[18] or reaction of amine groups with atmospheric CO$_2$.[12,22,23] The vacuum pump was isolated and amine vapor allowed to fill and equilibrate into the empty chamber (trifluoroethylamine, 68.5 mbar; Jeffamine, 10.6 mbar) at ambient temperature (∼25 °C). At this stage, timing of the surface functionalization reaction
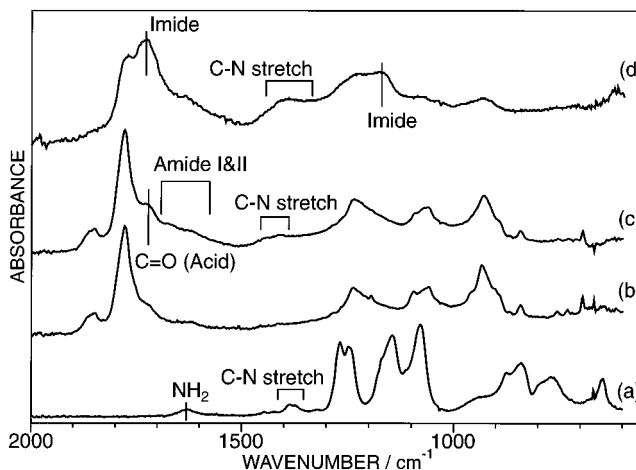
Figure 1. Infrared absorbance spectra of (a) trifluoroethylamine liquid, (b) untreated maleic anhydride pulsed plasma polymer layer, (c) plasma polymer functionalized with trifluoroethylamine, and (d) heating of (c) to 120 °C.

commenced. Upon termination of exposure, the amine reservoir was isolated, and the whole apparatus was pumped back down to its initial base pressure. Corresponding control experiments examined the reaction of ammonia (Aldrich, +99.99% purity) and diethylamine (Sigma, 98% purity) with the deposited maleic anhydride plasma polymer layers. Also the vapor-phase functionalization of poly(acrylic acid) (Aldrich, +99.5%, average M_w = 450 000) with trifluoroethylamine, Jeffamine, ammonia, and diethylamine was carried out for comparison.

Infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the functionalized surfaces. Maleic anhydride plasma polymer layers deposited onto preformed NaCl disks were employed for infrared absorption analysis using a Graseby Specac Golden Gate ATR accessory fitted to a Mattson Polaris instrument. This was operated at 4 cm^{-1} resolution over the 400−4000 cm^{-1} range.

XPS analysis of plasma polymer films deposited onto flat glass substrates was carried out using a VG ESCALAB electron spectrometer equipped with an unmonochromated Mg Kα$_{1,2}$ X-ray source (1253.6 eV) and a concentric hemispherical analyzer. Photoemitted electrons were collected at a take-off angle of 30° from the substrate normal, with electron detection in the constant analyzer energy mode (CAE = 20 eV). XPS envelopes were fitted using a Marquardt minimization com-

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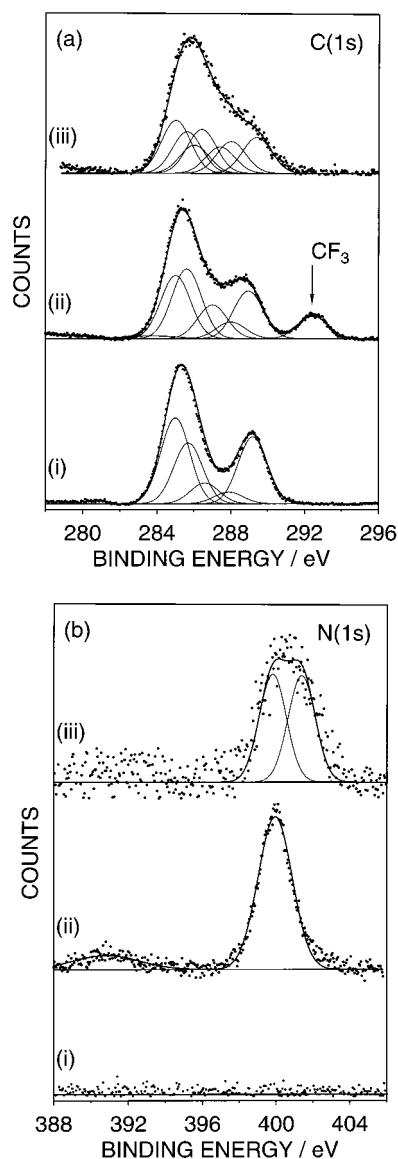
Figure 2. (a) C(1s) and (b) N(1s) XPS spectra of (i) the untreated maleic anhydride pulsed plasma polymer layer, (ii) the plasma polymer functionalized with trifluoroethylamine, and (iii) the plasma polymer functionalized with Jeffamine.

puter program with Gaussian components having equal full width at half-maximum (this is an approximation since the peaks will also possess some Lorentzian character).[24] Instrumental sensitivity factors determined using chemical standards were taken as C(1s):O(1s):F(1s):N(1s) equals 1.00:0.36:0.23:0.72, respectively.

For the adhesion measurements, two strips of polypropylene film (ICI, Capacitor Grade, 25 μm thickness) were coated with pulsed maleic anhydride plasma polymer and exposed to Jeffamine vapor. They were then sandwiched together and cured overnight at 120 °C. Subsequently, single lap adhesion tests were carried out using an Instron 5543 tensilometer operating at a crosshead speed of 1 mm min^{-1}.

3. Results

(a) Pulsed Plasma Polymerization of Maleic Anhydride. High structural retention in the maleic anhydride pulsed plasma polymer layers was confirmed by infrared analysis, and the following characteristic

Scheme 1. Mechanism for the Uncatalyzed Reaction between Anhydrides and Amines To Form Amic Acids[41,42]
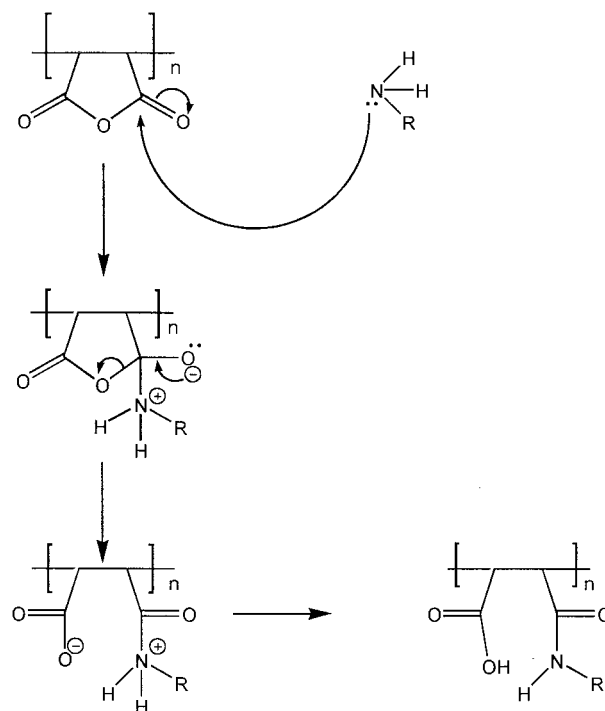
cyclic anhydride absorbances were detected:[15,25] asymmetric and symmetric C=O stretching, anhydride group stretching, and C−O stretch vibrations, Figure 1 and Table 1.

XPS analysis indicated the presence of five types of C(1s) environments:[26] hydrocarbon ($\underline{C}H_x \sim 285.0$ eV): carbon singly bonded to an anhydride group ($\underline{C}-C(O)-O- \sim 285.7$ eV), carbon singly bonded to oxygen ($-\underline{C}-O \sim 286.6$ eV), carbon doubly bonded to oxygen ($O-\underline{C}-O/-\underline{C}=O \sim 287.9$ eV), and anhydride groups ($O=\underline{C}-O-\underline{C}=O \sim 289.4$ eV), Figure 2. Complete coverage of the underlying glass substrate was confirmed by the absence of any Si(2p) signal showing through. Pulsing the electrical discharge on the microsecond to millisecond time scale allowed the coating composition to be controlled (i.e., the concentration of anhydride functionalities).[15] Optimum anhydride group retention ($t_{off} = 1200$ μs, $t_{on} = 20$ μs, $P_p = 5$ W, and 24 nm thickness) corresponds to 58% of the surface carbon atoms belonging to cyclic anhydride repeat units.

(b) Functionalization Reactions with Trifluoroethylamine. A key reaction between anhydride groups and primary amines is aminolysis, Scheme 1.[27] The deposited maleic anhydride pulsed plasma polymer layer was exposed to trifluoroethylamine vapor, with the aim of producing half-amide linkages at the surface with adjacent carboxylic acid groups in a 1:1 surface ratio,[12] as depicted in Scheme 1. Infrared spectroscopy con-

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Scheme 2. Ring Closure of Amic Acid during Heating To Form Cyclic Imides[14]
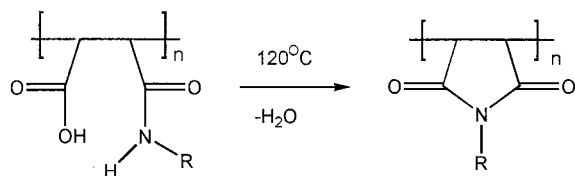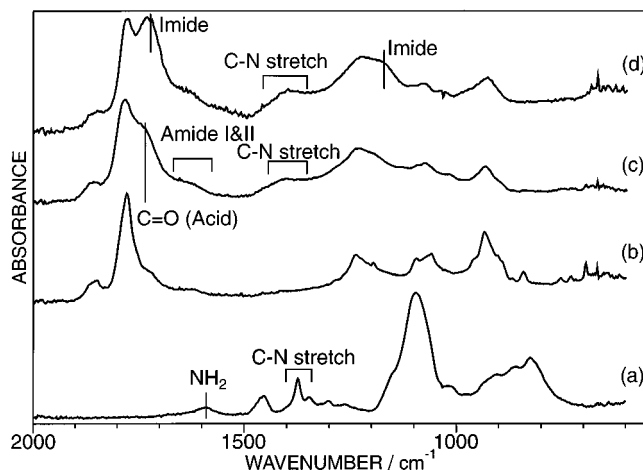
firmed that ring opening of the cyclic anhydride centers had occurred to yield amide and carboxylic acid bands associated with amic acid groups, as seen by the appearance of the following new features superimposed on the background maleic anhydride plasma polymer infrared spectrum: overlapping amide I and amide II bands, carboxylic acid stretching, and C−NH monosubstituted amide stretching, Figure 1 and Table 1. Furthermore, infrared spectroscopy indicated that heating at 120 °C gave rise to ring closure and the formation of cyclic imides,[14] Scheme 2. The presence of background spectral features from the underlying maleic anhydride plasma polymer layer was consistent with functionalization occurring just at the surface (ATR-FTIR sampling depth is approximately 100 nm[28]).

The reaction efficiency within the outer region of the surface was investigated by XPS. The C(1s) spectra following exposure to trifluoroethylamine vapor could be fitted to six different types of carbon functionality:[26] hydrocarbon ($\underline{C}H_x \sim 285.0$ eV), carbon singly bonded to an amide/carboxylic acid group ($\underline{C}H_2C(O)NHR/\underline{C}H_2C$-(O)OH) ~ 285.7 eV), carbon singly bonded to both nitrogen and a trifluoromethyl carbon (N−$\underline{C}$−CF$_3$ $\sim$ 287.0 eV), amide group (RHN−$\underline{C}$=O $\sim$ 287.9 eV), anhydride/carboxylic acid groups ($\overline{O}$=$\underline{C}$−O−$\underline{C}$=O/$\underline{C}$(O)-OH ~ 289.4 eV), and trifluoromethyl carbon (−$\underline{C}$F$_3$ $\sim$ 292.5 eV), with a corresponding Mg K$\alpha_{3,4}$ satellite $\sim$ 283.7 eV), Figure 2. The unambiguous assignment of the trifluoromethyl C(1s) peak, as well as the contribution from the three trifluoromethyl fluorine atoms (−C$\underline{F}_3$ ~ 687.7 eV)[26] to the F(1s) region, confirmed that surface functionalization had indeed taken place. The N(1s) peak was assigned to amide groups (RH$\underline{N}$−C=O $\sim$ 399.8 eV),[12,26] and the peak areas were used to calculate the overall aminolysis efficiency,[27,29] Figure 2. Nitrogen incorporation at the surface reached a limiting value after approximately 30 min exposure to trifluoroethylamine vapor, which corresponds to an overall conversion factor of 0.93 ± 0.01 in the outermost 2−3 nm region (the XPS sampling depth[26]). This was confirmed by the complete disappearance of the characteristic XPS features associated with surface aminolysis following a 5 s exposure of the functionalized surface to a 1 keV Ar$^+$ ion beam. Heating at 120 °C gave rise to no change in the N(1s) XPS spectrum. This was to be expected since the N(1s) binding energy values of amide and imide linkages are very similar ($\approx$400 eV).[26]

(c) Functionalization Reaction with Jeffamine. Jeffamine was also found to readily undergo reaction with the maleic anhydride pulsed plasma polymer layer, Scheme 3. This was confirmed by infrared spectros-

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Figure 3. Infrared absorbance spectra of (a) Jeffamine liquid, (b) untreated maleic anhydride pulsed plasma polymer layer, (c) plasma polymer functionalized with Jeffamine, and (d) heating of (c) to 120 °C.

Scheme 3. Reaction between the Maleic Anhydride Pulsed Plasma Polymer Layer and Jeffamine (Looping Around of the Polypropylene Glycol (PPG) Backbone of Jeffamine Need Not Necessarily Occur to the Adjacent Acid Site)
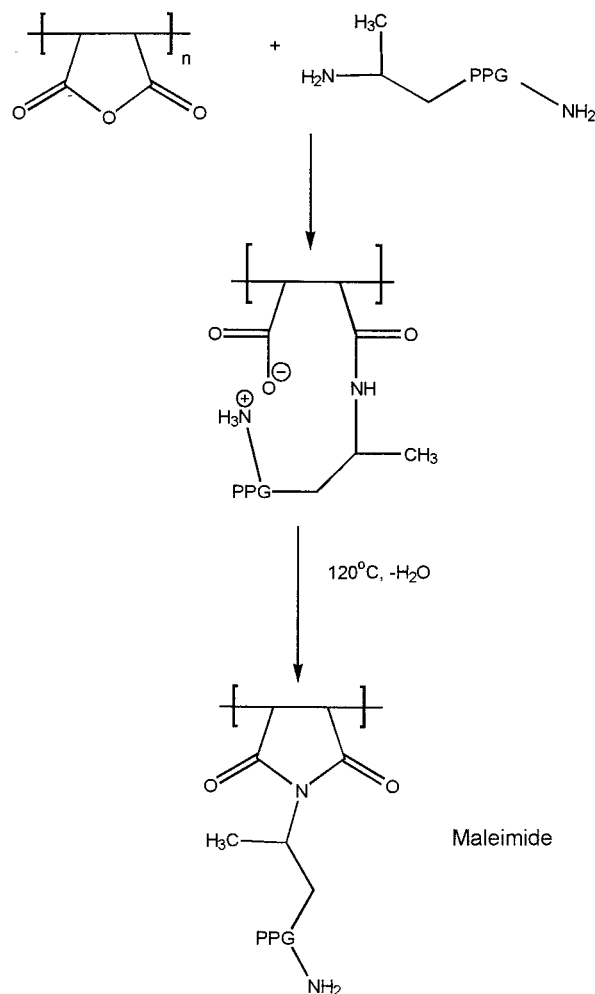
copy: overlapping amide I and amide II bands, carboxylic acid stretch, and C−NH monosubstituted amide stretching, Figure 3 and Table 1. Once again, heating at 120 °C indicated ring closure and the formation of cyclic imides, Scheme 3.

Table 2. Influence of Heating at 120 °C upon Amide/Amine (400 eV) versus Ammonium Salt (402 eV) N(1s) Peak Area Ratios for Functionalized Maleic Anhydride Plasma Polymer and Poly(acrylic acid) Surfaces

	maleic anhydride plasma polymer		poly(acrylic acid)	
nucleophile	unheated	heated	unheated	heated
trifluoroethylamine	1 peak at 400 eV	1 peak at 400 eV	1 peak at 402 eV	1 peak at 402 eV
Jeffamine	$\approx$1:1	1 peak at 400 eV	1 peak at 402 eV	1 peak at 402 eV
ammonia	$\approx$2.9:1	1 peak at 400 eV	1 peak at 402 eV	1 peak at 402 eV
diethylamine	$\approx$3.6:1	$\approx$3.6:1		

On this basis, the following carbon functionalities were fitted to the C(1s) XPS envelope of Jeffamine functionalized maleic anhydride pulsed plasma polymer:[26] hydrocarbon ($\underline{C}H_x \sim 285.0$ eV), carbon singly bonded to amide/carboxylic acid groups ($\underline{C}H_2C(O)NHR/\underline{C}H_2C$-(O)OH ~ 285.7 eV), amine groups ($\underline{C}-NH_2 \sim 286.0$ eV), carbon singly bonded to oxygen ($\underline{C}-O \sim 286.4$ eV), carbon singly bonded to nitrogen in the Jeffamine end groups (HN$-\underline{C}H(CH_3)-O \sim 287.4$ eV), amide groups ($\underline{C}(O)NHR \sim 287.9$ eV), and anhydride/carboxylic acid groups (O=$\underline{C}$-O-$\underline{C}$=O/$\underline{C}(O)OH \sim 289.4$ eV)), Figure 2. Interestingly, the N(1s) XPS region indicated the presence of two different types of nitrogen environment in approximately equal concentrations, Table 2. The higher binding energy peak (402 eV) can be assigned to ammonium salt formation following protonation of terminal amine groups on the Jeffamine chain by surface carboxylic acid centers generated during aminolysis of the cyclic anhydride groups. This was confirmed by reacting a series of amines with poly(acrylic acid), Table 2. The other N(1s) feature at approximately 400 eV can be attributed to either amine environment (a free end of Jeffamine) or amide linkages.[26] Since the N(1s) peak area ratio of amide/amine to ammonium salt is approximately 1:1, then each Jeffamine chain must be bonded via an amide linkage at one end and looped around to form an ammonium salt complex at its other end (if additional Jeffamine chains from the vapor phase had reacted with the carboxylic acid centers generated during aminolysis of the cyclic anhydride groups, then the ratio of amide/amine to ammonium salt N(1s) environments should have been greater than 1:1, i.e., much closer to 3:1). This assignment was confirmed by heating at 120 °C, which gave rise to the disappearance of the ammonium salt feature at 402 eV to produce the cyclic imide linkage in conjunction with detachment of the other end of the Jeffamine chain from the surface, Scheme 3. Corresponding heating experiments conducted with ammonium salts of poly(acrylic acid) confirmed that amide formation via dehydration of the ammonium salt was not a possibility at 120 °C, Table 2. Furthermore, the inability of a secondary amine (diethylamine) to undergo the imide cyclization reaction to form the maleimide (i.e., retention of the ammonium salt) is consistent with this explanation (secondary amines are prevented from reacting beyond the amide because of the lack any additional N–H bonds), Scheme 2 and Table 2. On this basis, the extent of Jeffamine attachment to the surface was calculated to be 0.95 $\pm$ 0.02 from the N(1s) peak areas after 30 min reaction time. Once again, exposure to a 1 keV Ar$^+$ ion beam for very short periods confirmed that aminolysis had only occurred at the plasma polymer surface.

(d) Adhesion. Jeffamine was used as a coupling agent for adhering two pieces of polypropylene together (each of which had been coated with maleic anhydride

Table 3. Lap Joint Adhesion Test Measurements

substrate	maximum recorded load/N cm^2
polypropylene (PP) substrate failure	24.9 $\pm$ 0.3
plasma polymer deposited onto PP, and then heating the joint at 120 °C	did not adhere
plasma polymer deposited onto PP followed by exposure to Jeffamine (no heating of joint)	did not adhere
plasma polymer deposited onto PP followed by exposure to Jeffamine, and then heating the joint at 120 °C	18.9 $\pm$ 1.0

plasma polymer and then exposed to Jeffamine vapor). It was found that heating at 120 °C (imide formation) gave rise to good adhesion, Table 3.

4. Discussion

In the past it has been demonstrated that radiation grafting of monomers onto inert polymeric supports can produce materials that combine the desirable surface properties of the graft with the good mechanical properties of the underlying substrate.[30] However, the total number of grafting sites can be limited as well as uncontrollable, depending on the nature of the polymer backbone. Continuous wave plasma deposition of reactive monomers has also been utilized in this context with limited success,[31] since the selective incorporation of desired functional groups onto the plasma polymer layer tends to be poor owing to extensive molecular fragmentation processes within the electrical discharge.[31] In the case of pulsed plasma polymerization of maleic anhydride, the large and controllable concentration of surface anhydride groups[15] is ideally suited for subsequent derivatization chemistry (e.g., vapor-phase aminolysis). This approach alleviates many of the drawbacks associated with conventional solution-based and extrusion techniques (e.g., reorientation of surface functional groups and solvent extraction of low molecular weight species).[32] In fact the overall reaction yields measured for 2,2,2-trifluoroethylamine and Jeffamine-D230 correlate well with previously reported model studies comprising the vapor-phase aminolysis of poly-(ethylene-alt-maleic anhydride) copolymer surfaces.[33]

It is interesting to note that in contrast to the other amines examined, trifluoroethylamine does not yield the additional ammonium salt during amide formation at each cyclic anhydride center, Table 2. This can be accounted for on the basis of acid dissociation constants (K_a). Trifluoroethyleneamine has a K_a value of 2.5 $\times$

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10^{-6}, whereas ammonia and diethylamine have values of 5.6×10^{-10} and 1×10^{-11}, respectively.[34,35] Hence ammonia and diethylamine are much more basic compared to trifluoroethylamine, and therefore far more likely to accept a proton from the carboxylic acid group belonging to the amic acid center during cyclic anhydride ring opening, Scheme 1. Furthermore, the second dissociation constant for maleic acid is 8.57×10^{-7};[35] this can be attributed to the proximity of the carboxyl groups in the cis configuration giving energetically unfavorable electrostatic effects.[18] Poly(acrylic acid) is a stronger acid[35] ($K_a = 5.6 \times 10^{-4}$) compared to the carboxylic acid group formed adjacent to the amide linkage, and therefore poly(acrylic acid) is more capable of donating a proton to a weaker acid such as trifluoroethylamine (K_a value of 2.5×10^{-6}), Table 2.

Tailoring solid surfaces using the combination of pulsed plasma deposition of anhydride groups and the subsequent aminolysis reaction is attractive for a variety of applications; these include the control of hydrophilicity, biocompatability[20] (e.g., attachment of heparin[37]), modification of polymer adsorption characteristics,[9] microcontact printing,[36] ion conducting membranes,[37] patterned polymer multilayers,[38] thin film electrodes,[39] catalysis, and adhesion.

5. Conclusions

Amine-terminated nucleophiles can be chemically fixed onto any shaped solid substrate via reaction with a well-adhered maleic anhydride pulsed plasma polymer layer. The intermolecular spacing and concentration of amine-containing moieties attached to the surface can be finely tuned by controlling the level of anhydride group incorporation during pulsed plasma deposition.

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