

Chemical Structure and Properties of Plasma-Polymerized Maleic Anhydride Films

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Plasma-assisted polymerization of maleic anhydride has been investigated under different experimental conditions. Significant variations in the film chemical structure and the film properties were obtained using pulsed plasma depositions operated at different duty cycles. The film chemical structures were obtained using X-ray photoelectron spectroscopy (XPS) and Fourier transform infra red spectroscopy (FT-IR). Surface derivatization reactions using decylamine and benzylamine were used to demonstrate their surface reactivity toward nucleophilic moieties and to change the surface free energy of the plasma polymer films, all of which are of particular interest for future applications in the attachment of biological molecules and cells. A method of substrate pretreatment was developed to ensure reliable binding between the substrate and the plasma polymer film in aqueous solution. Impedance spectroscopy was used to monitor polymer film changes in aqueous media. The hydrated films showed some resemblance to polyelectrolyte films and a clear correlation could be observed between the density of anhydride groups and the behavior of the films in solution.

Introduction

Plasma polymerization can be used to deposit thin polymeric films showing a variety of chemical structures and properties, which are dependent on the experimental conditions (such as the input power, gas composition, monomer pressure, and substrate position) employed during the process. The various species present within the plasma influence the reaction pathways and thus the structure of the polymer film. A certain degree of control over the types and numbers of species present in a plasma is possible by careful control over the energy input during the deposition. The energy input can be varied either by minimizing the peak power¹ P_{peak} , moving substrates into the afterglow zone^{2,3} or by pulsing the applied power.^{4–8}

Pulsed plasma-polymerization processes have received increased attention over the past 10 years and monomers containing amines,⁹ halogens,^{10–13} and even

metal atoms^{14,15} to name but a few, have been successfully polymerized with a high retention of the labile bonds. It has previously been shown that the ratio of the plasma on-phase to the plasma off-phase (i.e., the duty cycle = $t_{\text{on}}/t_{\text{on}} + t_{\text{off}}$) largely determines which reaction mechanisms predominate to form a plasma polymer film.^{4,5} Another reason for the observed specificity of the pulsed plasma process is the fact that pulsing allows the energy input into the process to be reduced below that possible with the continuous process. This is because the equivalent power in the pulsed experiment (P_{eq}) is a product of the input power and the duty cycle employed ($P_{\text{peak}}t_{\text{on}}/(t_{\text{on}} + t_{\text{off}})$). Thus, by careful choice of deposition parameters, it is possible to achieve P_{eq} less than those generally employed during the continuous wave processes.

Maleic anhydride is of particular interest for the synthesis of functional organic thin films because of the double bond and the reactive anhydride group. It is widely used as an organic reagent and can participate in a variety of chemical reactions occurring at the double bond by photochemical reactions,^{16,17} conventional po-

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lymerization,^{18,19} copolymerization,^{20–22} and graft polymerization^{23,24} or at the anhydride group as, for example, discussed by Kalguthar et al.²⁵ and Evenson et al.^{26,27} Plasma assisted polymerization of maleic anhydride is, however, difficult, since even at relatively low input energies the anhydride group is lost and the deposited films contain mostly dissociation products rather than the desired anhydride group. Ryan et al.⁴ showed that under pulsed plasma conditions maleic anhydride could be plasma-polymerized by what was suggested to be a radical polymerization reaction initiated at the double bond, which led to a relatively high retention of the anhydride functionality with decreasing duty cycle.

The present paper describes the homopolymerization of maleic anhydride using RF plasma processes and aims to gain an understanding of the film characteristics in solvents and solvent reactions after deposition using different duty cycles. This involves a study of the swelling characteristics of different films and it can be demonstrated that the use of electrochemical impedance measurements offer a viable route to characterize reactive plasma polymers films when they are immersed in aqueous solution. The reactivity of the anhydride groups within the plasma films was studied in wet chemical reactions with different amine-terminated reagents. The high conversion levels found in the present work are in agreement with comparable previous work^{26,27} describing the gas-phase reactions of reagents such as trifluoroethylamine and Jeffamine with surface anhydride groups. The films studied in this work were required to fulfill criteria such as a high density of anhydride groups, reliable binding to the substrate, durability, and nonsolubility in aqueous solution, which are vital prerequisites for biological applications of plasma polymer films.

Experimental Section

Materials. All chemicals used in this work were obtained from Sigma-Aldrich, Germany, and not purified further.

Substrate Preparation. The plasma films for FT-IR or XPS analysis were deposited on 1 mm thick silicon substrates, which were cleaned in ethanol and dried in dry nitrogen prior to the plasma treatment. For electrochemical measurements, the films were deposited on gold electrodes of size 8 mm². The gold (120 nm thickness) was thermally evaporated onto clean microscope slides using a thin chromium layer to assist adhesion. It was then pretreated by cleaning it in freshly made Piranha solution (30% H₂O₂:70% H₂SO₄), and then rinsed and immersed in 5 mM allylmercaptan/ethanol solution for 4 h, to form a self-assembled monolayer. The resultant film was dried

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and stored in dry N₂ until plasma polymerization. The plasma deposition on these substrates was always carried out within 2 h of substrate preparation.

Plasma Polymer Preparation. Plasma polymerization was carried out in a home-built, cylindrical, 30 cm long Pyrex reactor described in detail elsewhere.⁹ The 13.56 MHz rf power was delivered to the reactor by two concentric external electrodes separated by a distance of 12 cm. Approximately 10 g of maleic anhydride, in a flask, was attached directly to the system. The substrates were placed on a glass platform halfway between the electrodes in the center of the plasma glow. Before introduction of the substrate, the chamber was cleaned in a continuous wave O₂/Ar (1:1) plasma for approximately 1 h at a power 100 W. The monomer vapor was introduced into the chamber at a pressure of 0.1 mbar. The plasma was ignited and run at peak powers of 100 W during the pulsed plasma depositions. The duty cycles studied were 1/40, 5/40 and 10/40 (ms on/ms off). At a peak power of 100 W, the *P*_{eq} used during the pulsed processes were thus 2.4, 11, and 20 W respectively. The freshly prepared plasma samples were stored in a desiccator and used in subsequent experiments within 2 h. Some comparison studies were made with continuous wave plasma polymerized maleic anhydride films using a peak power of 5 and 40 W.

Chemical Structure Analysis. A Tencor Alphastep 200 was used to determine film thickness. The films analyzed by FT-IR had typical thicknesses between 50 and 100 nm, while all films used for electrochemical measurements (dry film thickness before extraction or hydrolysis) had a thickness between 40 and 55 nm. Contact angles were measured using the sessile drop method. A 10 μ L drop of Milli-Q water was placed on the sample, the syringe needle was removed from the drop, and the angle between the surface of the drop and the sample surface was measured. This was repeated five times, and the values were averaged.

A Nicolet 850 Spectrometer was used for Fourier Transform infra red spectroscopy (FT-IR). FT-IR is particularly suitable for the analysis of plasma polymerized maleic anhydride films, since it allows the unique identification of the anhydride group by the characteristic doublet at 1760 and 1830 cm^{−1}, which is generally well separated from the carbonyl absorption band (1730 cm^{−1}) and the amide absorption band (1680 cm^{−1}). By careful comparison of the relative intensities of the various absorption bands some conclusions can be made with respect to the relative abundance of groups throughout the depth of the films.

X-ray photoelectron spectroscopy (XPS) was performed approximately 1 day after sample preparation using a VG-Sigmaprobe²⁸ and 7 days after treatment using a Perkin-Elmer PSI 5000 series instrument. Both instruments were equipped with an X-ray source monochromator and an Al K α (1486.6 eV) X-ray source. For the PSI 5000 instrument the pass energy used was 17.9 eV giving a resolution of 0.6 eV for Ag(3d_{5/2}). For the VG-Sigmaprobe a pass energy of 100 and 20 eV were used for the survey and the high-resolution scans, respectively. The samples were stored under dry Ar until analysis. An electron flood gun was used to compensate surface charging. XPS is a powerful tool to study the surface chemistry of polymers. It enables a quantification of the elements present within the film to a depth of approximately 50–80 Å. Furthermore, high-resolution scans of the individual elemental peaks provide a certain degree of chemical bond information. The XPS C(1s) peak profiles can be used to provide some quantitative information about individual functional groups and have been employed to illustrate overall changes in film compositions when subjected to a derivatization process.

Surface Derivatization. Surface derivatization was carried out by covering the surface of the freshly prepared plasma polymerized maleic anhydride films with a few drops of pure

- (28) The VG Sigmaprobe is equipped with a zoom microscope and color CCD camera allowing the analysis area (400 μ m to 4 mm) to be viewed. The monochromator system allows X-ray spot sizes ranging from <15 to >600 μ m to be selected. A power range of 1–200 W was used over the spot setting.

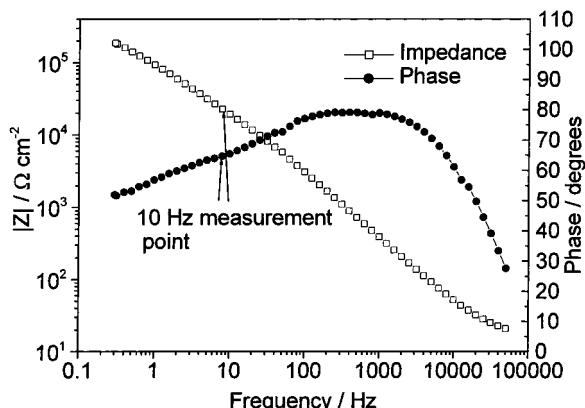


Figure 1. Typical spectra showing the changes in impedance $|Z|$ and phase angle ϕ for a hydrated CW plasma polymer.

decylamine or benzylamine. These were left in a covered Petri dish for 40 min and then rinsed for several minutes with dichloromethane to remove unreacted amine. Surface coverage of the amine compound on the anhydride film was determined using XPS, FT-IR, and contact angle measurements.

Electrochemistry. Impedance measurements were used to study the hydrolysis and the swelling behavior of the pulsed plasma polymerized maleic anhydride films. The change in impedance of the films was measured by immersing the films in 0.1M KCl and immediately following the change in impedance at 10 Hz, with respect to time. This technique was used as it gives the fastest response to the change in the film properties. The impedance $|Z|$ at 10 Hz appears to be most sensitive to the change in resistance of the film, and thus indicative of the formation of conducting pathways through the film. Impedance measurements were made on a Solatron 1260 frequency response analyzer in combination with an EG&G 273A potentiostat. The technique of single frequency impedance analysis has been described by Ho et al, who used this method to follow the pH dependence of the capacitance of a polymer coated electrode for biosensing applications.²⁹ Ho et al chose a high frequency (20 kHz) for their measurements, as this is most sensitive to film capacitance. Since, however, in the work presented here the resistance is likely to be most sensitive to the processes of swelling and hydrolysis, a lower frequency impedance point at 10 Hz was chosen.

The correct interpretation of the single frequency impedance results needs to be undertaken with some care, since $|Z|$ contains information not only on the films resistance, but also its capacitance. Figure 1 shows a typical multifrequency impedance spectrum for a hydrated CW plasma polymer and indicates the 10 Hz impedance point used to follow the swelling of the polymers. The total impedance $|Z|$ at any particular frequency is related to the resistive part of the impedance Z and the capacitive part of the impedance Z' ³⁰ by

$$|Z| = Z - jZ' \quad \text{where } j = \sqrt{-1}$$

When the maleic anhydride polymer hydrolyses and swells in water, it can be expected that both its resistance and its capacitance will change. The formation of conducting pathways through the polymer, caused by the formation of hydrated acid groups in the polymer will have a strong effect on the film resistance. The capacitance of the polymer will also change on hydrolysis/swelling. As water is adsorbed into the film, the dielectric constant (ϵ_r) of the film will increase, thus increasing the capacitance of the film. Furthermore, the underlying gold will become wetted, adding a gold double layer capacitance many times larger than the polymer capacitance (per unit dielectric area) into the total measured capacitance.

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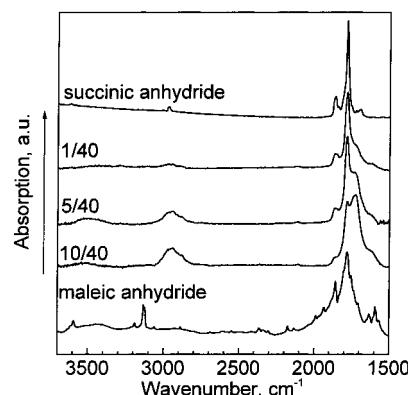


Figure 2. FT-IR spectra of unreacted maleic anhydride, succinic anhydride and pulsed plasma-polymerized maleic anhydride.

The phase angle ϕ is the phase difference between the current and the potential and is indicative of the relative capacitive or resistive nature of the measured impedance at a particular frequency. A phase angle of 90° would be found for a pure capacitive impedance and likewise, a phase angle of 0° would be found for a pure resistive impedance. At 45° there would thus be an equal contribution to the total impedance from a resistor and capacitor in parallel. Measuring the phase for the simultaneous swelling/hydrolysis of the maleic anhydride plasma polymer film therefore gives additional information on the origin of the measured impedance $|Z|$ at a particular time. Hence, the measurement of the change in the impedance properties and phase of such reactive films are well suited for measuring the kinetics of the film hydrolysis/swelling.

Results and Discussion

SAM Adhesion Layer. Plasma-polymerized maleic anhydride films initially showed very poor adhesion to the gold surface of the electrodes. When submersed in aqueous solution, the plasma film was observed to separate from the substrate surface making it impossible to study their electrochemical behavior in aqueous solution. To overcome this problem, a monolayer of allylmercaptan was self-assembled on the metal surfaces prior to the polymerization. The immense improvement in substrate/plasma film adhesion observed suggests that the self-assembled monolayer (SAM) forms covalent bonds not only with the gold, but also with the plasma polymer. It is assumed that the SAM is not destroyed by the plasma, or at least that enough of it remains to be activated in the plasma and participate in the polymerization of the maleic anhydride at the SAM/plasma polymer film interface. This would lead to an interface consisting of a network containing allylmercaptan and anhydride components. This could, however, not be verified spectroscopically in this work. The combination of a thiol self-assembled monolayer and the plasma polymer led to sufficiently adhesive plasma films for subsequent reproducible tests in aqueous solution.

Chemical Structure Analysis. The FT-IR spectrum of the monomer shows typical peaks for the anhydride ring structure at wavenumbers of 1780 and 1860 cm^{-1} , Figure 2. The spectrum of pulsed plasma polymerized maleic anhydride using a plasma ON/OFF ratio of 10/40 (ms/ms) shows the film to contain both the anhydride structures around 1780 and 1860 cm^{-1} , as well as structures representative of carboxyl groups around

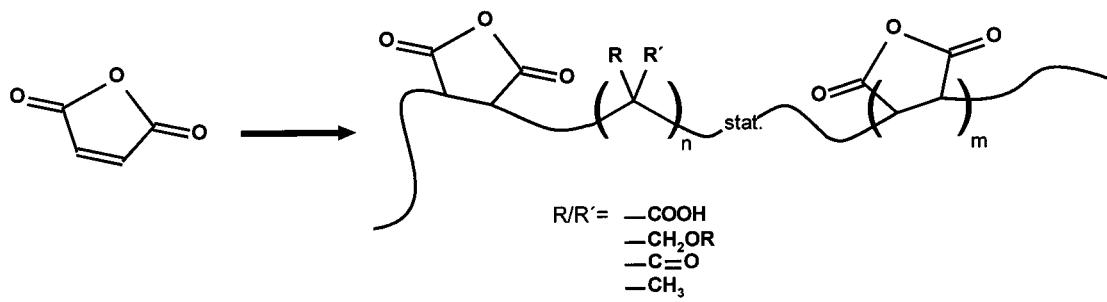


Figure 3. Simplified reaction schematic of plasma-polymerized maleic anhydride.

1730 cm^{-1} . As the duty cycle was decreased, the intensity of this latter component was consistently reduced and the anhydride structure became more prominent. Thus, the polymerization reactions were seen to become more selective leading to improved retention of the anhydride structure. These results are in accord with the prior work by Ryan et al.⁴ It appears that with decreasing energy flux (or lower duty cycle) the film chemical structure becomes increasingly similar to succinic anhydride, Figure 2a, implying that polymerization mechanisms involve primarily the double bond of the monomer, creating chains of a poly-maleic anhydride (Figure 3) with a repeating unit resembling succinic anhydride. In this context we note the C–H vibrations from saturated carbons at frequencies ~ 3000 cm^{-1} in the IR spectra of the plasma films, Figure 2.

The low-duty cycle films were found to be very stable to extraction in dry acetone for 24 h. No changes could be observed in the IR spectra and only a negligible decrease (5%) in the film thickness occurred, underlining the excellent bonding of the plasma polymer to the substrate and the low amount of unbonded (unreacted) material within the polymer network.

X-ray photoelectron spectroscopy (XPS) shows that after plasma polymerization at 1/40, 100W, the total oxygen concentration is reduced from O/C = 0.43 in the monomer molecule to O/C = 0.33 in the polymerized films. Other plasma conditions lead to O/C ratios ranging between 0.27 and 0.35 ± 0.01 , but no particular trend could be observed with respect to the plasma conditions used. C(1s) XPS spectra of 1 day old polymers deposited under different duty cycle conditions are shown in Figure 4.

These spectra are arranged in order of increasing plasma duty cycles top to bottom. A distinctive feature among these spectra is the progressive increase in the relative importance of the highest binding energy peak (~ 289 eV) with decreasing average power input during plasma polymerization. This high binding energy peak correlates with increased presence of anhydride (and/or ester) groups in the polymer films.³¹ The film variations with plasma duty cycle changes shown in Figure 4 are in accord with the aforementioned IR results and with the results obtained by Ryan et al.⁴

The more detailed analysis of a polymeric maleic anhydride film deposited at low plasma duty cycle is

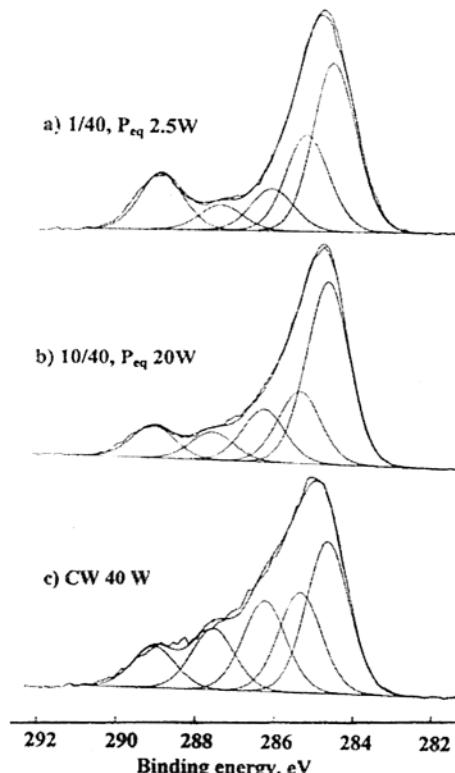


Figure 4. XPS C(1s) spectra of plasma-polymerized maleic anhydride using (a) a $t_{\text{on}}/t_{\text{off}}$ ratio of 1/40, (b) a $t_{\text{on}}/t_{\text{off}}$ ratio of 10/40, and (c) 40 W continuous wave.

shown in Figure 5a with the corresponding peak assignment provided in Table 1. Here a higher resolution C(1s) XPS spectrum of a film deposited at a 1/40 ms plasma on/off ratio and 100W peak power is resolved into contributions from various functional groups. In this analysis, five different functionalities, corresponding to C–C, C–C–O, C–O, C=O, and C(O)O, were employed. The binding energies assigned to each of these peaks are in accord with accepted values for these functionalities.³¹ The peak representative of the α -carbons (i.e., 285.5 eV) is assumed to include contributions from C–C–O, C–C=O, and C–C(O)O groups, thus accounting for the somewhat broader peak width assigned for this component.

The C(O)O high-energy binding peak would include anhydride as well as ester and even carbonate groups, if present. The relative areas from each of these peaks are also provided in Table 1. One notes that the sum of the areas of these highest binding energy peaks (23.8)

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Table 1. Relative Functional Groups Contributions Observed in the XPS C(1s) Profiles (Figure 5) of Maleic Anhydride Films Deposited at a Duty Cycle of 1/40 before and after Reaction with Decylamine

Functional Group	?	C-C	C-C-O	C-O	C=O	C(O)N	C(O)O
binding energy (eV)	282.8	284.6	285.5	286.7	287.5	288.1	288.9
Relative peak areas							
before reaction	-	52.3	23.9	5.9	4.1	-	13.8
after reaction	5.9	53	18.0	7.7	4.6	4.9	5.9

is in close agreement with the α -carbons peaks areas (23.9), as anticipated for these peak assignments. This C(1s) spectrum is of particular interest in terms of subsequent derivitizations of the maleic anhydride films, as described in part c below.

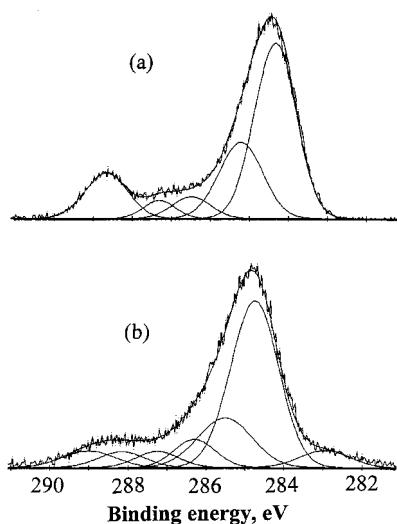


Figure 5. Resolved high-resolution C(1s) XPS spectra of polymeric maleic anhydride films produced at a plasma on/off ratio of 1/40 (ms) at 100 W peak power. (a) As deposited. (b) After reaction with decylamine.

Functional Group Reactivity. (a) *In Air.* Maleic anhydride is a frequently used chemical because of the reactivity of the anhydride group. Its lifetime under standard room temperature and pressure is therefore considerably short. As such, it is to be expected that the anhydride groups within the plasma polymer film will be reactive toward many reagents, leading to what could be considered a rapid aging process. Under normal temperature (18–25 °C), pressure (760 mmHg) and humidity (75%) maleic anhydride plasma polymer films

were found to react readily with water vapor leading to an opening of the anhydride ring to form carboxylic acid groups. This could be readily observed by FT-IR via a relative intensity increase of the carboxylic acid spectral contribution at a wavenumber of 1730 cm⁻¹. Within approximately 1 week a considerable loss of the anhydride structure could be observed, Figure 6, for samples prepared at 1/40, 100 W. An uptake of oxygen with time was also observed in the XPS data of plasma polymerized maleic anhydride samples prepared using the same deposition conditions. The elemental analysis 1 day after preparation showed an O/C ratio of 0.33, which increased to 0.39 after 1 week.

Analysis of films prepared under higher duty cycle (10/40) and continuous wave plasma treatment (5 and 40 W) indicates that hydrolysis of these films occurs to a much less extend. This was observed when comparing the FT-IR spectra of a 1/40 (100 W) pulsed and a 5 W CW plasma-deposited film, Figure 6b. Immediately after plasma deposition, the spectra appeared very similar for these two particular plasma polymers. However, after 1 week under ambient temperature, pressure and humidity the hydrolysis was seen to be far more advanced in the 1/40 pulsed plasma film, as revealed by the reduced relative intensity of the anhydride peaks (1780 and 1860 cm⁻¹). It would seem that the lower duty cycle plasma deposited films are less cross-linked, such that water molecules are able to penetrate into the polymer network more readily.

(b) *In Aqueous Solution.* Given that the plasma film is covalently bonded to the substrate surface, two processes are expected to occur when plasma polymerized maleic anhydride is submersed in aqueous solution: (a) hydrolysis reaction of the maleic anhydride leading to acid groups and (b) a swelling of the polymeric network as the solvent molecules penetrate into the film. The conversion reactions could be monitored in the FT-IR spectra of films when submersed in aqueous

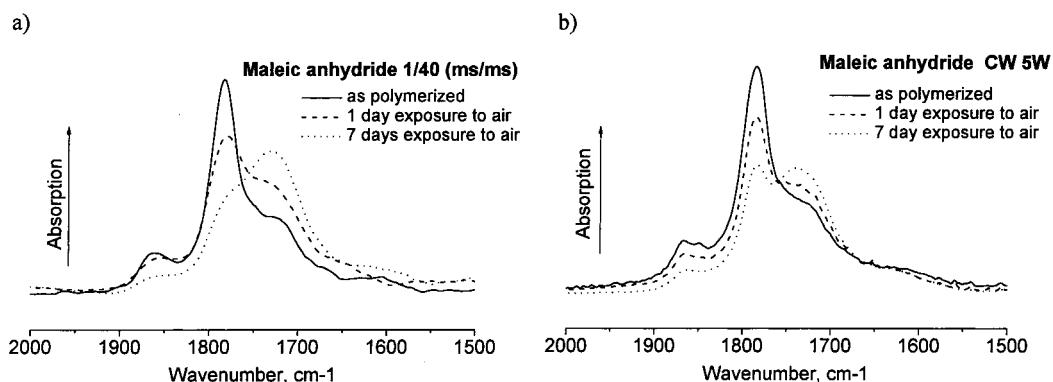


Figure 6. FT-IR spectra of the hydrolysis of plasma-polymerized maleic anhydride films generated using (a) pulsed 1/40 ms on/off, 100W, and (b) 5W CW plasma.

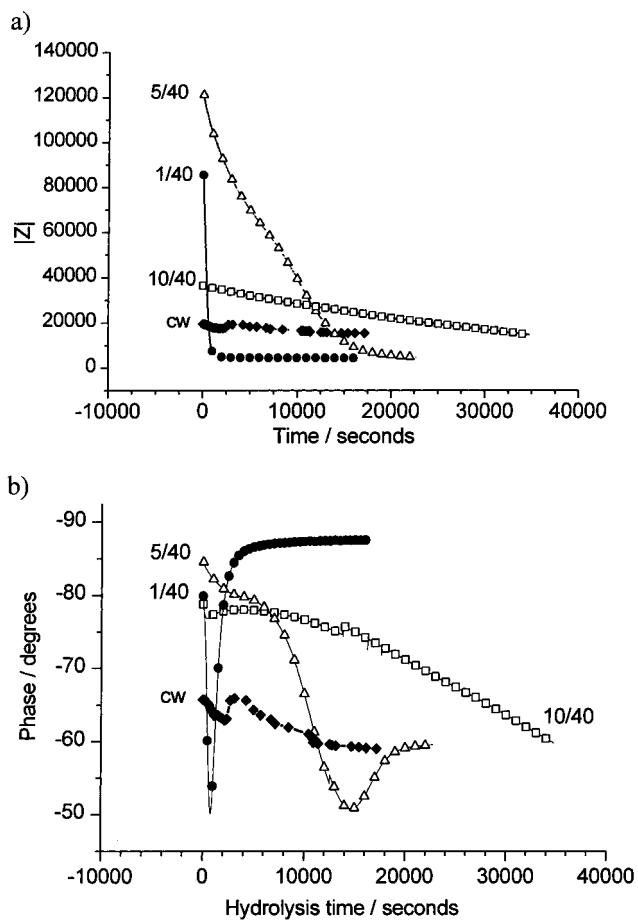


Figure 7. Change in (a) the total impedance $|Z|$ and (b) the phase ϕ of the plasma-polymerized maleic anhydride polymers with immersion in 0.1 M KCl.

solution. Again, the data suggests the transformation of the FT-IR anhydride peaks (1780 and 1860 cm^{-1}) to the carboxylic acid peak (1730 cm^{-1}) to be faster for the low duty cycle film ($P_{\text{eq}} = 2.5\text{ W}$) than for high duty cycle films (data not shown). Similar results were observed for films deposited at the same duty cycle but increasing input power P_{peak} . This suggests that with increasing $P_{\text{eq}} (=P_{\text{peak}}(t_{\text{on}}/t_{\text{on}}+t_{\text{off}}))$ the plasma polymer layers are more cross-linked resulting in a reduced rate of penetration of water molecules into the polymer network.

The change in impedance $|Z|$ of the films (measured at 10 Hz) when submersed in aqueous solution is plotted vs immersion time in Figure 7a. The graphs of the hydrolysis of the $1/40$ and $5/40$ films showed two very distinct parts, a very fast initial change followed by a slower change. To make an approximate comparison of the change in impedance of the different polymers, a linear fit was made to the early linear regions of the different plots. The results are given in Table 2.

It would appear reasonable to relate the early linear part of the graphs in Figure 7a to the hydrolysis of surface maleic anhydride groups; therefore, the gradient of the slopes represents the rate of hydrolysis of the films. In this case, the values given in Table 2 and the data shown in Figure 7 appear to correlate with the relative abundance of surface anhydride groups as measured by FT-IR and XPS for the different polymer films (*vida supra*). Clearly the $1/40$ system, with the highest abundance of surface anhydride groups, under-

Table 2. Summary of Electrochemical Measurements, Showing Rate of Change of Impedance and Final Multifrequency Impedance Measurements on Polymers after Swelling/Hydrolysis

system	gradient of linear region	time to reach plateau/s	total plasma power
$1/40$	-87	1700	2.5 W
$5/40$	-9	20000	5 W
$10/40$	-0.6	>35000	20 W

goes the most rapid rate of hydrolysis, followed sequentially by the $5/40$ and $10/40$ systems.

Figure 7b shows the change in the phase angle ϕ of the plasma polymers with immersion in 0.1 M KCl . This is of interest as it gives information on what part of the system, i.e., gold or polymer, is dominating the measured impedance at a particular time. The 40 W CW system shows only a small change in phase with immersion time, suggesting that the polymer film always dominates the measured impedance. The $10/40$ system shows a small decrease in phase angle showing that the resistive contribution to the total impedance increases a little with time. The phase angle behavior of the $5/40$ and $1/40$ systems are quite different. Both show a local minimum after a certain hydration time, Figure 7b. In the case of the $1/40$ system this can be explained by the rapid hydrolysis of the polymer and a change of origin of the impedance. At very short hydration times the impedance is still dominated by the polymer, but as the maleic anhydride plasma polymer hydrolyses, the impedance becomes effectively dominated by the double layer capacitance of the gold, since the polymer becomes so hydrated it cannot be measured separately from the gold. The local phase minima correspond to this transition from the impedance response being dominated by the polymer to being dominated by the gold double layer. A similar explanation can be made for the $5/40$ system, which also shows a local minimum, but after a longer time. This suggests a slower hydrolysis, which can be correlated to fewer maleic anhydride groups and possibly a higher degree of cross-linking in the polymer compared to the $1/40$ system.

(c) *Surface Derivatization.* The excellent adhesion of the plasma film to the substrate together with the presence of the anhydride groups offers a number of interesting possibilities for further molecular tailoring via simple wet chemical derivatization reactions. In the present case, this possibility has been demonstrated by addition of an amine (e.g., decyl- or benzylamine) to the film surface of the maleic anhydride polymer. With both amines, dramatic changes in film compositions were observed. For example, XPS analysis of $1/40$, 100 W pulsed plasma-polymerized films treated with benzylamine or decylamine showed an N/C ratio of 0.065 ± 0.005 and O/C ratio of 0.25 ± 0.01 . A high resolution $\text{C}(1s)$ XPS spectrum of the maleic anhydride polymer film after reaction with the decylamine is shown in Figure 5b. Clearly, the comparison of the spectra in Figure 5a,b reveals a decrease in intensity, accompanied by a shift to somewhat lower binding energies, for the highest energy peaks after reaction with the amine. This is precisely the result one would anticipate from conversion of anhydride groups to amides and carboxylates, as illustrated in Figure 8, in that the two higher binding

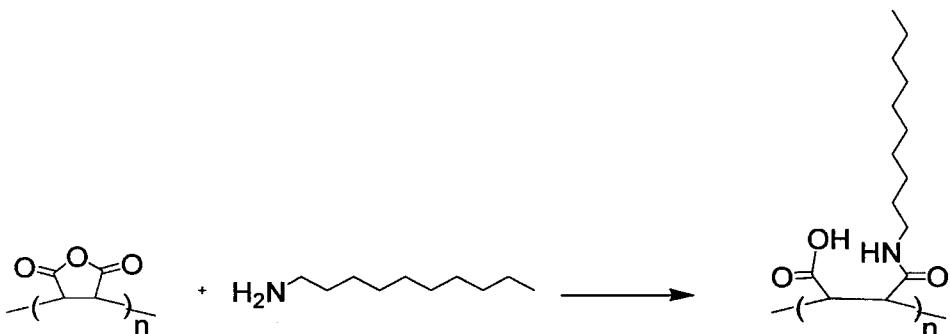


Figure 8. Simplified reaction schematic of plasma-polymerized maleic anhydride films with decylamine.

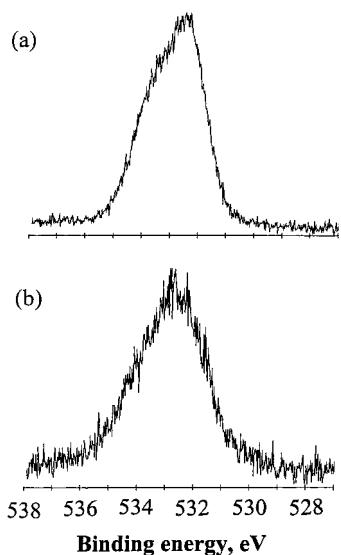


Figure 9. O(1s) XPS spectra of the same films as shown in Figure 5 before (a) and after (b) reaction with decylamine.

energy anhydride group carbons (~ 289 eV) are replaced by a lower binding energy amide carbon (~ 287.6 eV) and one carboxylate (~ 289 eV).³¹

A similar XPS C(1s) spectral change was observed previously in conversion of acid chloride groups to amides.¹¹ Peak data for the resolved C(1s) spectrum, after reaction with the amine, are also included in Table 1. It is of interest to note the appearance of a very low C(1s) binding energy peak (at 282.8 eV) after reaction. This low binding energy peak indicates the bonding of a more electropositive group to a carbon atom. In the present case this peak may signify the presence of $-\text{COO}^- \text{NH}_3^+$ (or $-\text{NH}_3^+$) groups formed from interaction of the decylamine with carboxylic acid groups generated during the anhydride reaction. The fact that the area of the 288.1 and 282.8 eV peaks are approximately equal would suggest that the $-\text{COO}^- \text{NH}_3^+$ groups arise primarily from the conversion reaction of the anhydride, while the higher binding energy C atoms (288.9 eV) in Figure 5b represent ester groups originating from the plasma-polymerization reaction and which are not reactive toward the amine. High-resolution O(1s) XPS spectra of the as deposited polymer film along with a decylamine derivatized film are shown in Figure 9 a,b, respectively.

In view of the relative insensitivity of O(1s) binding energies to functional group variations, coupled with the obviously complex oxygen–carbon bonding in these

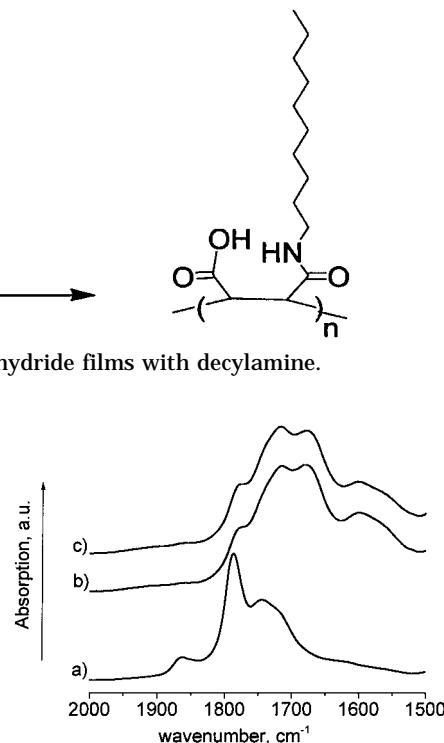


Figure 10. FT-IR spectra of (a) 1/40 (150 W) pulsed plasma-polymerized maleic anhydride, (b) after treatment with benzylamine, and (c) after treatment with decylamine.

films, resolution of these spectra into the different components were not carried out. However, these spectra are presented as they provide strong additional qualitative support for the film analysis presented above. In particular, a shift toward lower O(1s) binding energies, in Figure 9b, coupled with a broadening of the overall peak envelope, is in accord with conversion of anhydride groups to amides in which the central oxygen atoms in anhydrides (\sim 534 eV) are replaced with an amide oxygen at \sim 531.5 eV.³¹

FT-IR absorption spectra of films treated with benzyl and decylamine also reveal substantial chemical changes. In Figure 10 absorption spectra of the as deposited 1/40, 100W film (a) is compared to those obtained after reaction with benzyl and decylamine (b,c respectively).

These spectra reveal a clear relative intensity increase at a wavenumber of 1730 cm^{-1} , representing the carboxyl groups, and at 1680 cm^{-1} , representing the amide I bonds formed. The carboxyl and amide peaks appear with approximately equal relative intensity, in correlation with the chemical equation in Figure 8. The peak appearing $\sim 1600\text{ cm}^{-1}$ is representative of the amide II bond observed for many solid-state amide groups. It is interesting to note that after 40 min of reaction there is still significant evidence of anhydride functional groups within the films (1780 and 1860 cm^{-1}). Since transmission FT-IR probes the complete thickness of the film (ca. 40 nm) it appears that the reaction of the amine with the anhydride group is restricted to only the upper part of the film, suggesting that the amine has not been able to penetrate the film completely during the 40 min reaction period.

The reaction of the amines with the anhydride groups of the plasma polymer was also monitored using contact angle goniometry. Freshly prepared films using pulsed

plasma conditions of 1/40, 100 W for 4 min showed an average contact angle of 57°. Even though these films are known to hydrolyze fairly rapidly, the process of hydrolysis is still slow enough to enable a reasonably accurate determination of the contact angle, which is generally carried out in less than 1 min. After 24 h of hydrolysis in Milli-Q water the contact angle was found to have decreased to 31°. Surface reactions with the less hydrophilic benzylamine and decylamine led to significant changes in the angles measured; surface contact angles of 77° and 89° were measured for plasma-polymerized maleic anhydride film reacted with benzylamine and decylamine, respectively.

Conclusions

The data presented here confirm that pulsed plasma polymerization of maleic anhydride offers possibilities to synthesis unique polymeric films. The combined information from FT-IR, XPS, electrochemistry, and contact angle measurements demonstrate that with decreasing duty cycle (or average power input) a polymer network is formed with an increasing abundance of anhydride groups which is accompanied by decreased cross-linking. The films were found to be stable in aqueous solution due to an improved method of covalent binding of the plasma polymer to the substrate. The anhydride groups present reacted readily with water (vapor or liquid), and the conversion rate to the acid group increased with decreasing duty cycle. Wet chemical derivatization of the anhydride group in low duty cycle films using decylamine and benzylamine suggested the major portion of the oxygen to be associated with anhydride groups. When in solution, the 1/40 films are believed to be of almost a gel type nature and are thus nontypical of conventional plasma polymer films.

The film compositional differences with plasma duty cycles were further confirmed by impedance spectroscopy measurements. A correlation was observed between the impedance of the films in buffer solution and their chemical structures as determined by XPS and FT-IR. For films having a high abundance of anhydride groups a very rapid change in impedance upon immersion was observed. Similarly, the phase observed for these low duty cycle generated polymers rapidly reached a minimum, suggesting a very rapid hydrolysis of the anhydride groups. The lower the abundance of anhydride groups, the longer was the time required to reach this phase minimum. A similar minimum in the impedance and the phase could not be obtained within a reasonable time period for films deposited at the higher duty cycle of 10/40 and under continuous wave, 40 W, plasma conditions. Thus, it can be concluded that the greater the concentration of anhydrides, the greater will be the reactivity of the film. These highly reactive films appear to swell considerably converting into a polyelectrolyte-type gel making them particularly interesting in light of the growing interest of plasma modified surfaces in various solution applications. The present work suggests that impedance measurements represent a viable route to characterize film properties intended for use in applications, such as those involving biomaterials in aqueous solutions.

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