

# Quantitative Attenuated Total Reflectance Fourier Transform Infrared Analysis of Microwave Plasma Reacted Silicone Elastomer Surfaces

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Quantitative analysis of acrylamide and maleic anhydride solid monomers reacted to the surface of PDMS elastomers by a recently developed microwave plasma shows that, for 5–35 s plasma reaction times, the maximum surface concentration for acrylamide is 4–5 pmol/cm<sup>2</sup> and for maleic anhydride is 1–2 pmol/cm<sup>2</sup>. Reactions of the amide and anhydride functionalities to carboxylic acid salt groups are accomplished by base hydrolysis. Attenuated total reflectance Fourier transform infrared quantitative analysis reveals a 66% conversion for acrylamide and 48% for maleic anhydride.

## Introduction

Due to desirable physical properties and chemical inertness, silicone elastomers are used in countless applications, but their surfaces are often modified to achieve necessary properties. Among many surface reactions, gas plasma treatments of silicone surfaces are widely used because they alter properties such as surface friction,<sup>1</sup> bondability to other surfaces,<sup>2,3</sup> and biocompatibility.<sup>4,5</sup> Successful plasma reactions resulted in the formation of amine, alcohol,<sup>6</sup> and Si–H groups,<sup>7</sup> and the primary advantage of gas plasma modifications of polymers is the ability to rapidly alter surface chemistry without degradation of the bulk polymer.

In the plasma processes producing a desired functionality, determination of functionality content is particularly important if postplasma reactions are to be performed. For this reason, attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy is a useful surface analysis technique because it provides adequate sensitivity, and frequency group analysis allows determination of molecular and macromolecular arrays. However, until recently, quantitative aspects were not successfully resolved.<sup>8</sup> A modified Kramers–Kronig transformation (KKT) has been successfully applied to ATR FT-IR spectra in order to quantify the amount of Si–H functionality produced as a result of nitrogen or argon microwave plasma reactions on poly(dimethylsiloxane) (PDMS) elastomers.<sup>9</sup> By use of this approach, a single superimposable calibration plot for all angles of incidence was obtained, allowing determination of the concentration of the Si–H groups as a function of penetration depth and as a function of silica content in PDMS.

In this study, we will further explore the use of quantitative analysis and expand the scope of the previous

studies which showed that acrylamide and maleic anhydride can be microwave plasma reacted on PDMS surfaces.<sup>10</sup> The use of ATR FT-IR spectroscopy will again focus on the analysis of these plasma reactions, and KKT correction of the spectra will allow determination of the monomer quantity chemically reacted to the PDMS surface. The extent to which hydrolysis of the plasma reacted surfaces produces new acid salt groups will be also quantitatively evaluated.

## Experimental Section

**Substrate Preparation.** Poly(dimethylsiloxane) (PDMS) films were prepared from a linear dimethyl–vinylmethylsiloxane copolymer ( $M_n = 28\,000$ , Huls America, Inc.). The reaction between vinyl groups forming the cross-linked PDMS network was initiated by addition of 0.5% (w/w) *tert*-butyl perbenzoate (Aldrich Chemical) to the linear PDMS. The films contained 20% (w/w) Aerosil 200 SiO<sub>2</sub> filler (Degussa Corp.). The linear PDMS resin and initiator were first premixed for 24 h to ensure complete dissolution of the initiator. The oligomer–initiator solution was combined with SiO<sub>2</sub> and mixed for an additional 24-h period in a rolling ball mill. The cross-linking reaction was accomplished by pressure molding the oligomer mixture for 15 min at 149 °C, and postcuring it for 4 h at 210 °C. In an effort to eliminate surface contaminants and residual low molecular weight species before plasma treatment, the postcured PDMS films were stirred in methylene chloride for 5 h. Methylene chloride was removed from the PDMS substrate by vacuum desiccating the sample for 24 h. The PDMS substrate was stored in a desiccator until use.

**Plasma Surface Treatments.** The plasma reactor designed for the plasma experiments employed in these studies was discussed in the recent publication.<sup>10</sup> Prior to plasma deposition of solid monomers, the reactor was washed with water, oven dried, and argon plasma cleaned for 10 s. Solid-state monomers, acrylamide, propionamide, maleic anhydride, and succinic anhydride (Aldrich Chemical) were utilized in the microwave plasma reactions. In a typical microwave plasma reaction, 50 mg of a solid monomer and a PDMS sample with approximate dimensions of 50 × 20 × 2 mm were placed in the reactor. The reactor was evacuated to approximately 250 mTorr for 10 min to allow time for the PDMS to degas, followed by two argon flushes, reevacuation to the desired operating pressure (250, 100, or 50 mTorr), and exposure to microwave radiation. The microwave source, KMC Model KMO-24G, used in these experiments delivered a maximum of approximately 600 W of power with an output frequency of 2.45 GHz. During the plasma experiment, continuous vacuum was applied in order to maintain the plasma glow during longer reaction times. Unless otherwise specified, plasma reaction times varied from 5 to 35 s. After

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(1) Cho, D. L.; Yasuda, H. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1988**, *42*, 139.

(2) DeLollis, N. J.; Montoya, O. *J. Adhes.* **1971**, *3*, 57.

(3) Liston, E. M.; Rose, P. W. *Int. Symp. Plasma Chem., 7th* **1985**, *1*, 219.

(4) Yasuda, H.; Gazicki, M. *Biomaterials* **1982**, *3*, 68.

(5) Gombotz, W. R.; Hoffman, A. S. *Crit. Rev. Biocompat.* **1987**, *4* (1), 1.

(6) Gombotz, W. R.; Hoffman, A. S. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1984**, *38*, 65.

(7) Gaboury, S. R.; Urban, M. W. *Polym. Commun.* **1991**, *32* (13), 390.

(8) Huang, J. B.; Urban, M. W. *Appl. Spectrosc.* **1992**, *46* (11), 1666.

(9) Gaboury, S. R.; Urban, M. W. *Polymer* **1992**, *33* (23), 5085.

(10) Gaboury, S. R.; Urban, M. W. *Langmuir* **1993**, *9*, 3225.

plasma reactions, the reactor was allowed to cool down for 5 min before removal of the PDMS specimen. All plasma-treated samples were stored in a desiccator under ambient conditions.

**Surface Hydrolysis.** After acrylamide plasma reactions on PDMS, surface amide groups were hydrolyzed to carboxylic acid salt groups with a solution of 1 M NaOH/NaHCO<sub>3</sub>. Each sample was placed in a round-bottom flask containing 125 mL of a 1 M NaOH/NaHCO<sub>3</sub> solution. The samples were refluxed for 30 min, rinsed twice with distilled water, and vacuum dried for 24 h. The same procedure for hydrolysis of maleic anhydride treated PDMS was employed; except it was carried out at room temperature.

**Spectroscopic Measurements.** ATR FT-IR spectra of all PDMS samples were collected on a Digilab FTS-14B equipped with a liquid nitrogen cooled MCT detector. A resolution of 4 cm<sup>-1</sup> and a mirror speed of 0.3 cm/s were used. An ATR cell (Spectra Tech Inc.) was aligned at a 60° angle of incidence with a 45° end parallelogram KRS-5 crystal. For the quantitative analysis, all spectra were collected with a perpendicular polarization using an aluminum wire grid polarizer with a 0.4-μm grid spacing (Specac Ltd.). Each spectrum represents 400 coadded scans ratioed against a reference spectrum obtained by coaddition of 400 scans of an ATR crystal. In order to quantify the amount of surface functionality, a Kramers-Kronig (KK) transformation along with Fresnel's equations were utilized, allowing the use of a Beer's law type relationship which is independent of the sample refractive index, crystal coverage, and the angle of incidence.

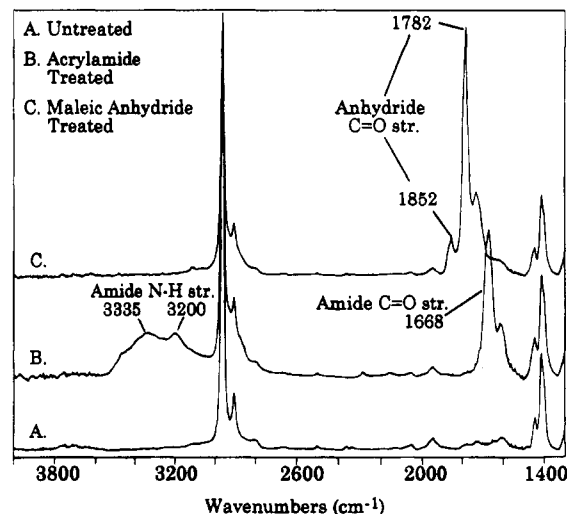
For determination of extinction coefficients of amide, anhydride, and carboxylic acid salt carbonyl bands, various concentration standards of acrylamide, maleic anhydride, and sodium propionate were prepared, and transmission spectra were obtained. Transmission spectra were collected on a Mattson Cygnus 25 single beam spectrometer (Sirius 100) at a resolution of 4 cm<sup>-1</sup>, and with a mirror speed of 0.316 cm/s. Through the use of a liquid transmission cell with a known path length, Beer-Lambert's law was used to obtain extinction coefficients.

Both spectrometers and the cell compartments were continuously purged with purified air (Balston Filter Products). All spectral manipulations were performed using Spectra Calc software (Galactic Industries).

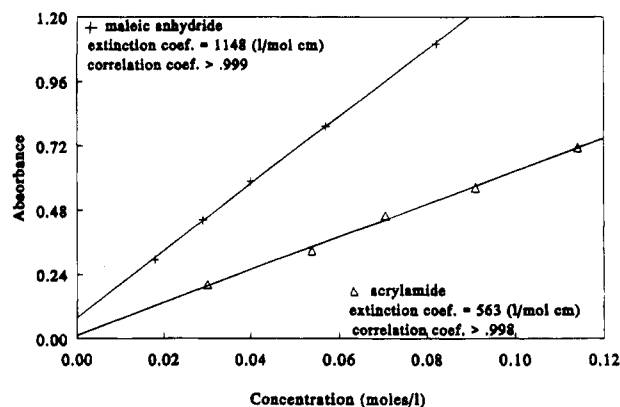
## Results and Discussion

In the previous study,<sup>10</sup> we demonstrated the ability of microwave energy to generate plasmas which allowed reactions of acrylamide and maleic anhydride solid phase monomers onto the surface of PDMS elastomers. It was found that, among studied species, solid phase monomers not containing a C=C bond, such as propionamide or succinic anhydride, could not be reacted to the surface. However, monomers with C=C bonds, such as acrylamide or maleic anhydride, were bonded through the C=C bond using a microwave plasma source, and the reaction times did not exceed 15 s. As an example, Figure 1 illustrates these results for 5-s microwave reaction times of acrylamide (trace B) and maleic anhydride (trace C). For reference purposes, trace A is an ATR spectrum of untreated PDMS. A fraction of amide or anhydride functionalities remaining after the plasma reaction is reactive, as was demonstrated by further base hydrolysis reactions.

Before we undertake a task of quantifying ATR FT-IR data, it should be realized that there are optical effects that may obscure quantitative analysis. To account for these effects, several theoretical approaches for quantifying ATR FT-IR spectral data based on the Kramers-Kronig transformation (KKT) algorithms have been developed.<sup>11-14</sup> Unfortunately, the theories are generally applicable to either strong bands, or weak bands, but not



**Figure 1.** ATR FT-IR spectra in the 4000–1300-cm<sup>-1</sup> region of (A) untreated PDMS, (B) acrylamide plasma treated PDMS, and (C) maleic anhydride plasma treated PDMS.



**Figure 2.** Plots of C=O stretching band absorbances for maleic anhydride and acrylamide as a function of concentration.

both. In a recent study,<sup>8</sup> a new algorithm has been developed, and this approach allows quantitative assessments of a wide range of band intensities. For this reason, it will be used to determine the amounts of acrylamide and maleic anhydride microwave plasma reacted PDMS surfaces.

### Analysis of Acrylamide Plasma Reacted PDMS.

As shown in Figure 1, solid phase microwave plasma treatments with acrylamide or maleic anhydride can be utilized to obtain amide or anhydride surface groups. In order to quantify the amount of the functional groups, it is first necessary to obtain the extinction coefficient for a particular absorption band; in our case, the amide C=O stretching band. For this reason, a series of acrylamide solutions with known concentrations were prepared. By use of a transmission FT-IR cell, the absorbance spectra of each solution in a liquid IR cell with a known path length were recorded. Figure 2 shows the plot of absorbance for the corresponding C=O stretching band as a function of concentration. The plot is linear, with a correlation coefficient of greater than 0.998, and its slope and the path length of the transmission cell were used to obtain the extinction coefficient. The value for the acrylamide carbonyl band was calculated to be 563 (L/(mol cm)). In the next step, ATR FT-IR spectra must be corrected using the KKT algorithm,<sup>8</sup> to allow calculations of concentrations from the Beer-Lambert equation

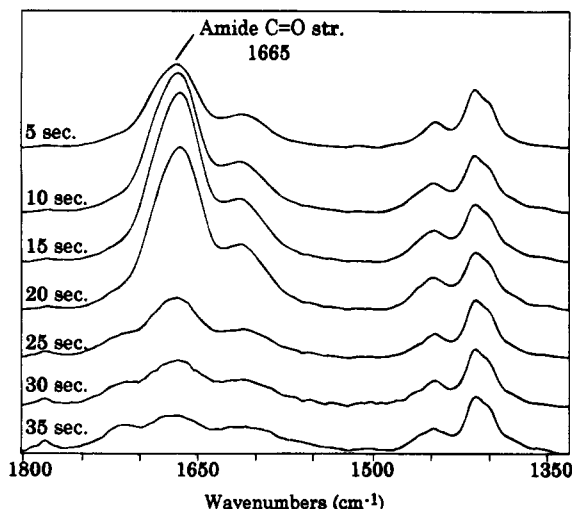
$$\beta = \epsilon c \quad (1)$$

(11) Tshmel, A. E.; Vetteoren, V. I. *Spectrochim. Acta* **1973**, *29A*, 1681.

(12) Dignam, M. J.; Mamiche-Afara, S. *Spectrochim. Acta* **1988**, *44A*, 1435.

(13) Bertie, J. E.; Eysel, H. H. *Appl. Spectrosc.* **1985**, *39*, 392.

(14) Plaskett, J. S.; Schatz, P. N. *J. Chem. Phys.* **1963**, *38*, 612.



**Figure 3.** ATR FT-IR spectra in the 1800–1350-cm<sup>-1</sup> region of PDMS which has been acrylamide plasma reacted for various reaction times.

**Table 1.** Average  $\beta$  Values, Volume Concentrations, and Surface Concentrations for Acrylamide Plasma Reacted PDMS

reaction time (s)	av $\beta$ at 1665 cm <sup>-1</sup> (cm <sup>-1</sup> )	volume concn (mol/cm <sup>3</sup> × 10 <sup>-8</sup> )	surface concn (mol/cm <sup>2</sup> × 10 <sup>-12</sup> )
5	0.0204 ± 0.0071	3.61 ± 1.26	2.86 ± 1.00
10	0.0312 ± 0.0058	5.53 ± 1.03	4.38 ± 0.82
15	0.0286 ± 0.0052	5.07 ± 0.93	4.02 ± 0.73
20	0.0246 ± 0.0054	4.36 ± 0.97	3.45 ± 0.76
25	0.0096 ± 0.0018	1.70 ± 0.32	1.35 ± 0.26
30	0.0085 ± 0.0037	1.51 ± 0.66	1.19 ± 0.53
35	0.0049 ± 0.0010	0.88 ± 0.18	0.69 ± 0.14

where  $\epsilon$  is the extinction coefficient,  $c$  is the concentration, and  $\beta$  is the linear absorptivity, which are values obtained from the KKT corrected spectra.

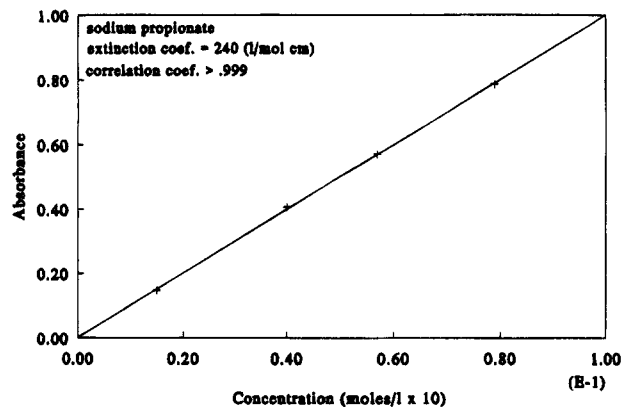
In the previous study,<sup>10</sup> it was determined that the microwave plasma energy input of 600 W and a 50 mTorr gas pressure yielded the greatest deposition of solid monomer onto PDMS surfaces. In addition, the amount of deposited monomer was greatest at reaction times of less than 15 s but decreased beyond 15 s. For this reason PDMS samples were acrylamide microwave plasma treated with 600 W and 50 mTorr, at reaction times of 5 to 35 s, in 5-s intervals. A representative set of spectra in the amide carbonyl region are shown in Figure 3, and Table 1 lists the resulting average  $\beta$  values with the standard deviation for the KKT corrected amide band intensities.

By use of eq 1, and the extinction coefficient for the acrylamide C=O stretching band at 1665 cm<sup>-1</sup> calculated from the data shown in Figure 2, volume concentrations can be calculated from the  $\beta$  values given in Table 1. These results are also tabulated in Table 1. This concentration is an average volume concentration for the depth to which the light penetrates into the sample. Therefore, by taking into account the depth of penetration at 1665 cm<sup>-1</sup>, an average surface concentration can be obtained for the surface thickness which is analyzed by the ATR experiment. The depth of penetration can be calculated by<sup>15</sup>

$$d_p = \frac{\lambda/n_c}{2\pi(\sin^2 \theta_i - (n_s/n_c)^2)^{1/2}} \quad (2)$$

where  $d_p$  is the depth of penetration,  $\lambda$  is the wavelength

(15) Harrick, N. J. *Internal Reflection Spectroscopy*; Wiley: New York, 1967.



**Figure 4.** Plots of COO<sup>-</sup> antisymmetric stretch band absorbances for sodium propionate as a function of concentration.

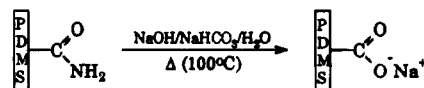
**Table 2.** Average Surface Concentrations of Acid Salt Groups, Residual Amide Groups, and the (Acid Salt + Residual Amide) Sum for Hydrolyzed Acrylamide Plasma Treated PDMS

reaction time (s)	surface concentration (mol/cm <sup>2</sup> × 10 <sup>-12</sup> )		
	acid salt	amide	acid salt + amide
5	1.44	0.74	2.19
10	2.87	1.11	3.98
15	2.55	1.10	3.65
20	2.92	1.02	3.94
25	1.37	0.54	1.91
30	1.48	0.56	2.04
35	1.08	0.39	1.46

of light,  $n_c$  is the refractive index of the crystal,  $n_s$  is the refractive index of the sample, and  $\theta_i$  is the effective angle of incidence. For infrared light at 1665 cm<sup>-1</sup>, the average depth of penetration is estimated to be 0.792  $\mu$ m. The surface concentrations calculated from the volume concentrations are shown in Table 1.

The maximum average surface amide concentration is in the 4–5 pmol/cm<sup>2</sup> range and occurs at plasma reaction times of approximately 10–15 s. The remaining concentrations will be also expressed in pmol/cm<sup>2</sup> units, but it should be noted that these surface concentrations take into account the volume from the surface to the estimated depth of penetration from eq 2, for example, 0.792  $\mu$ m. Thus, they do not account for the fact that the concentration of the surface functional groups is nonhomogeneous.

In order to examine the reactivity of the surface reacted acrylamide, the base hydrolysis reaction shown below was used to convert the amide groups to carboxylic acid salt groups. This method can successfully produce a

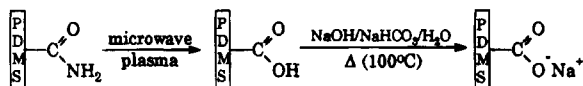


significant amount of carboxylic acid salt groups,<sup>10</sup> and in order to obtain the amount of this group formed, the same procedures will be applied. For quantifying the acid salt content, the C=O stretching band at 1582 cm<sup>-1</sup> will be used again. The extinction coefficient for this band was found to be 240 L/(mol cm) and was determined using sodium propionate solutions. Figure 4 illustrates the calibration curve. From the KKT corrected spectra, not only the  $\beta$  values for the acid salt C=O stretching band at 1582 cm<sup>-1</sup> can be used to calculate the acid salt formation but also the residual amide content can be determined. Table 2 shows the resulting average surface concentration values for the acid salt groups, residual amide groups, and the sum of the two concentrations.

The sum concentrations of acid salt and amide groups is tabulated in Table 2 because it reveals the total functional group concentration on the surface. If the hydrolysis reaction of the amide groups occurs exclusively, the average sum of the acid salt and amide concentration values in column 4 of Table 2 would have similar values to the average amide concentrations originally reacted on the PDMS surface for a given reaction time which are listed in Table 1. While the concentrations are similar, the differences are too large to be considered a random error.

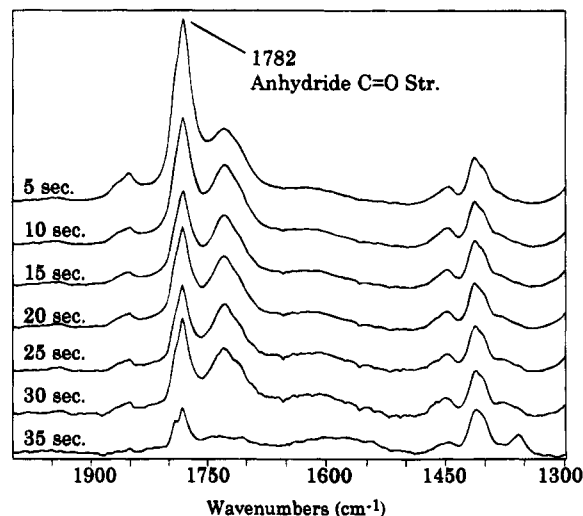
At this point, let us closer examine these concentration differences. It appears that there are two distinct groups of specimens: One group consists of the samples where the total acid and residual amide concentrations after hydrolysis are smaller than the amide concentration before hydrolysis. This is observed for the reaction times varying from 5 to 15 s, and these values are listed in Tables 1 and 2. In this case, the concentration difference is most likely due to the loss of nonbonded amide species during base hydrolysis, making it impossible for total concentrations after hydrolysis to be as large as before hydrolysis.

The second group consists of specimens in which the total acid and residual amide concentrations after hydrolysis are greater than the amide concentration before hydrolysis and occur for reaction times varying from 20 to 35 s. Furthermore, a trend in the concentration difference would also indicate that there are more acid and amide functionalities after hydrolysis than the total amount of amide originally reacted on the PDMS. One possibility explaining this difference is that a species, other than amide groups, reacts during the base hydrolysis forming acid salt groups. Carboxylic acid would be one source of such additional acid salt groups. Indeed, upon examination of the acrylamide plasma reacted PDMS spectra which are shown in Figure 3, a shoulder at approximately  $1710\text{ cm}^{-1}$  is detected in the 20-s reaction spectrum. Its intensity becomes very pronounced in the 25–35-s spectra. The increasing trend of the  $1710\text{-cm}^{-1}$  band at extended reaction times also parallels the increase in concentration discrepancy that occurs with increased reaction times. Thus, these data provide evidence that some of the surface reacted amide groups, at extended reaction times, are additionally reacted to form carboxylic acid. These groups are converted to acid salt groups along with the amide functionality and are shown below.



**Analysis of Maleic Anhydride Plasma Reacted PDMS.** For quantitative analysis of maleic anhydride functionality on PDMS surfaces resulting from the microwave plasma reactions, the same approach will be used. Again, it is necessary to obtain the extinction coefficient for the band to be analyzed, and for maleic anhydride the  $1782\text{-cm}^{-1}$  band assigned to symmetric C=O stretching will be used. Figure 2 shows the plot of absorbance of the C=O stretching band as a function of the concentration for the standard solutions. The plot is linear, and a correlation coefficient greater than 0.999 is determined. The extinction coefficient for the  $1782\text{-cm}^{-1}$  carbonyl band was calculated to be  $1148\text{ L}/(\text{mol cm})$ .

Similar to acrylamide, maleic anhydride microwave plasma reactions on PDMS were performed in 5-s increments, from 5 to 35 s. A set of representative spectra are shown in Figure 5. Volume and surface concentrations were also calculated by the method described earlier for acrylamide plasma reacted PDMS. The  $\beta$  values and



**Figure 5.** ATR FT-IR spectra in the  $2000\text{--}1300\text{-cm}^{-1}$  region of PDMS which has been maleic anhydride plasma reacted for various reaction times.

**Table 3.** Average  $\beta$  Values, Volume Concentrations, and Surface Concentrations for Maleic Anhydride Plasma Reacted PDMS

reaction time (s)	av $\beta$ at $1782\text{ cm}^{-1}$ ( $\text{cm}^{-1}$ )	volume concn ( $\text{mol}/\text{cm}^3 \times 10^{-8}$ )	surface concn ( $\text{mol}/\text{cm}^2 \times 10^{-12}$ )
5	$0.0265 \pm 0.0070$	$2.31 \pm 0.61$	$1.71 \pm 0.45$
10	$0.0256 \pm 0.0086$	$2.23 \pm 0.75$	$1.65 \pm 0.55$
15	$0.0195 \pm 0.0073$	$1.70 \pm 0.64$	$1.25 \pm 0.47$
20	$0.0183 \pm 0.0049$	$1.59 \pm 0.42$	$1.18 \pm 0.31$
25	$0.0183 \pm 0.0087$	$1.60 \pm 0.76$	$1.18 \pm 0.56$
30	$0.0161 \pm 0.0016$	$1.41 \pm 0.14$	$1.04 \pm 0.10$
35	$0.0076 \pm 0.0005$	$0.66 \pm 0.04$	$0.49 \pm 0.03$

**Table 4.** Average Surface Concentrations of Acid Salt Groups, Residual Anhydride Groups, and the ((Acid Salt)/2 + Residual Anhydride) Sum for Hydrolyzed Maleic Anhydride Plasma Treated PDMS

reaction time (s)	surface concentration ( $\text{mol}/\text{cm}^2 \times 10^{-12}$ )		
	acid salt	anhydride	(acid salt)/2 + anhydride
5	1.65	0.43	1.25
10	0.50	0.74	0.99
15	0.23	0.60	0.74
20	0.14	0.64	0.71
25	0.14	0.53	0.60
30	0.21	0.56	0.66
35	0.17	0.27	0.36

concentrations for respective reaction times are given in Table 3. It should be noted that the  $1725\text{-cm}^{-1}$  band does not change for the surface reactions ranging from 5 to 30 s, but it disappears when reaction is conducted for 35 s. This band is due to symmetric stretching vibrations of the secondary carbonyl fragments of the anhydride groups and most likely is being destroyed at the reaction times exceeding 35 s.

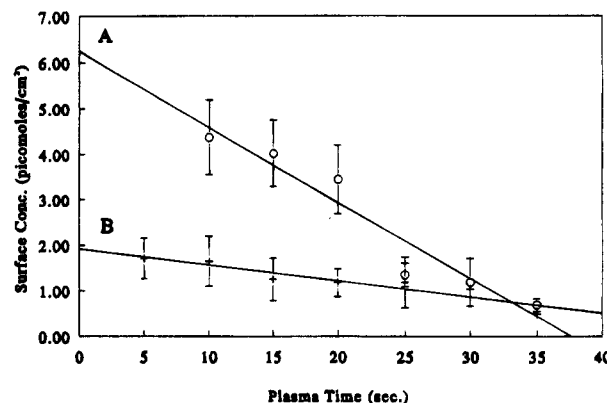
As was illustrated for the acrylamide plasma reacted PDMS, plasma reacted maleic anhydride was further reacted through the use of base hydrolysis. ATR FT-IR spectra were obtained after the hydrolysis, and quantitative analysis of the surface changes was carried out. The resulting acid salt, residual anhydride, and ((acid salt)/2 + residual anhydride) concentrations are reported in Table 4.

It appears that 5 s maleic anhydride plasma reaction time produces the greatest quantity of acid salt groups after hydrolysis. The percent conversion of the original anhydride groups to acid salt groups is also the highest for the 5-s plasma reaction (48%). On the other hand, all other reaction times give conversions of less than 20%.

However, it should be noted that when comparing concentrations of acid salt groups to original anhydride groups, the acid salt concentrations must be divided by 2 since, as a result of hydrolysis, each anhydride group will produce two acid salt groups. For this reason, summed up surface concentrations given in Table 4 were divided by 2 so that the data can be directly compared to the original anhydride surface concentration values given in Table 3. Comparison of the sum surface concentrations in Table 4 to the surface concentrations in Table 3 shows that less than 100% of the originally deposited anhydride is accounted for after hydrolysis. Similar to the acrylamide, this observation can be attributed to the loss of anhydride functionality from the PDMS surface during the hydrolysis reaction.

**Rates of Amide and Anhydride Removal.** The surface concentration values given in Tables 1 and 3 show that the majority of acrylamide or maleic anhydride monomers are reacted onto the PDMS surface during the first 5 to 10 s of reaction time. Extended times; however, result in a decrease of the amide and anhydride concentrations which, according to the previous chapter, is primarily attributed to two factors. First, the starting monomers are being chemically modified by the plasma into the species that no longer react onto the PDMS surface, and second, while the plasma induces the reactions of monomers onto the PDMS surface, it also causes the removal of surface species already produced on the surface.

Based on the decreasing surface concentrations shown in Tables 1 and 3, it is useful to calculate the rate at which the species reacted to the surface is being removed. Since both reactions which lead to bonding of the monomer species to the PDMS surface and removing the reacted monomer from the surface may occur simultaneously, exact determination of the reaction rate is difficult. However, assuming that the predominant reaction upon extended reaction times is the removal of surface reacted monomer species, approximate rates can be calculated. Using the single component reaction rate equations, zero-, first-, and second-order reaction plots were constructed. The plot for a zero-order reaction, shown in Figure 6, appears to give linear correlations closest to 1 (0.96 for maleic anhydride and 0.94 for acrylamide). Although the deviation from linearity is expected, especially considering that the previous assumption does not take into account formation of new functionality, this plot allows calculations of the approximate rate at which the surface species are removed. For acrylamide, the rate of removal is estimated



**Figure 6.** Plots of surface concentrations as a function of plasma time for (A) acrylamide and (B) maleic anhydride.

at  $0.17 \text{ pmol}/(\text{cm}^2 \text{ s})$ , whereas for maleic anhydride it is  $0.04 \text{ pmol}/(\text{cm}^2 \text{ s})$ .

### Conclusions

Quantitative analysis of solid monomer microwave plasma reactions on PDMS reveals that the amount of acrylamide or maleic anhydride reacted onto the surface is of the order of 1 to  $5 \text{ pmol}/\text{cm}^2$ . Furthermore, it is found that for the reaction times yielding the maximum monomer content on the PDMS surface, conversion to the acid salt is 66% for acrylamide and 48% for maleic anhydride. For extended exposure times, the rate of functional group removal is estimated through the use of a zero-order reaction plot.

Finally, it should be kept in mind that, although a common jargon used in any quantitative surface studies is that "concentration of surface species is such and such ...," it is often forgotten that the "depth" of surface reactions will change with the surface morphology. For polymeric surfaces, the surface morphology will be influenced by so-called free volume which is reflected by the polymer glass transition temperature. In the case of PDMS surfaces, free volume is fairly accessible due to relatively low glass transition temperature. Therefore, the data presented in this paper should be understood as an average concentration of species across a few micrometer top surface. As a matter of fact, when reflection theory for stepwise stratified media<sup>16</sup> is utilized to the ATR depth profiling experiments for modified PDMS, approximately 80% of the newly created surface species are present in the  $1\text{-}\mu\text{m}$  layer.

(16) Hueng, J. B.; Urban, M. W. *Appl. Spectrosc.* **1993**, *47* (7), 973.