# The Effect of Chloro-Functional Molecules on the Ammonia Plasma Treatment of Silicone Elastomers

SCOTT R. GABOURY and MAREK W. URBAN*

Department of Polymers and Coatings, North Dakota State University, Fargo, North Dakota 58105

**SYNOPSIS**

Attenuated total reflectance (ATR) FTIR spectroscopy was utilized for surface studies of ammonia/plasma-modified poly(dimethylsiloxane) (PDMS) elastomer networks containing residual chloro-functional molecules. Ammonia/plasma modification of PDMS containing chloro-functional molecules causes the formation of surface amide groups, but due to the parallel formation of surface ammonium chloride, amide groups are not chemically bonded to the PDMS surface. The two primary sources of chlorine-containing species are residual traces of freon and cross-linking initiators present in the network. In the absence of chloro-functional molecules, ammonia/plasma surface modifications of PDMS leads to the formation of stable surface amide groups.

## INTRODUCTION

Although plasma-surface modifications of polymers are of great importance for the improvement of polymer biocompatibility,[1-3] such surface treatments are complex and inadequately understood.[4] In spite of these drawbacks, the advantage of plasma-surface modification lies in its ability to alter a small surface layer without adversely affecting the bulk properties of the polymer. However, these surface changes can be affected by the presence of impurities, oxygen being among the most common ones.

It is well known that the presence of gas within an energetic plasma environment leads to fragmentation of the gaseous species into a number of highly reactive fragments with various lifetimes.[5] For example, when ammonia is introduced into the plasma chamber, species such as $NH_3$, $NH_2$, NH, $N_2$, $H_2$, and H are believed to exist.[6] Ammonia/plasma treatments have been shown to form bonded NH functional groups on the surface of several polymers.[7] Furthermore, if nonbonded molecules are present within the substrate networks, they may significantly affect the gas plasma treatments. The latter issue is the focus of this study in which poly(dimethylsiloxane) (PDMS) elastomers with and without chloro-functional species will be ammonia/plasma-modified. The chlorine-containing species will be purposely introduced by the use of a chlorine-containing initiator or by a cleaning process during which freon is introduced. Attenuated total reflectance (ATR) FTIR spectroscopy will be used to monitor the structures that develop upon surface modifications. ATR FTIR spectroscopy has two main advantages for this study: It is a surface-sensitive technique and it does not require high vacuum conditions that might disturb weakly bonded or absorbed species.

## EXPERIMENTAL

### Substrate Preparation

Two different types of PDMS were used. The first PDMS substrate, later referred to as substrate A, was prepared in our laboratory using a linear dimethyl–vinylmethylsiloxane copolymer (MW = 28,000, Huls America Inc.) cross-linked with *t*-butyl perbenzoate (Aldrich Chemical). Before cross-linking, Aerosil 200 $SiO_2$ filler (Degussa Corp.) was added in the amount of 37.5 w/w % to attain processability and to improve the mechanical properties of the cross-linked films. The resin was pressure-

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 44, 401–407 (1992)
© 1992 John Wiley & Sons, Inc. CCC 0021-8995/92/030401-07$04.00

molded for 15 min at 149°C and postcured for 4 h at 210°C.

The second PDMS substrate, later on referred to as substrate B, was commercially obtained. The commercial process utilizes a linear PDMS resin (General Electric SE-477OU) containing pendant vinyl groups necessary for further cross-linking. It also contains 37.5 w/w % of fumed $SiO_2$ filler. A chloro-functional initiator, Cadox TS-50 (Akzo Company), which contains 2,4-dichlorobenzoyl peroxide, was used to initiate cross-linking. The substrate was cross-linked by pressure molding of the premixed chemicals for 10 min at 116°C and postcured for 4 h at 204°C.

### Gas/Plasma Surface Treatments

The substrate samples were cut to an approximate size of 50 × 75 × 2 mm and plasma-treated using the previously described bell jar plasma chamber and the procedures outlined elsewhere.[8] An ultrapurity grade ammonia gas (Linde) was used.

In an effort to optimize the surface treatment, several combinations of parameters, summarized in Table I, were used. Later on, these treatments will be referred to by the number in the far left column of Table I. The gas/plasma treatment (3), except for exposure time, was used to prepare a series of samples with the exposure times ranging from 200 s to 15 min. Since the plasma chamber contains different energy zones between the two electrodes,[4] two different positions between the electrodes were used. They are labeled as ON or OFF the electrode in Table I. The ON and OFF sample positioning, with respect to the electrodes, are schematically depicted in Figure 1.

### Sample Washing

Selected samples exhibiting strong ammonium chloride bands were rinsed with distilled deionized (DDI) water for 15 min and placed in a vacuum desiccator for 2 days to remove residual traces of water followed by ATR FTIR spectral analysis. In an effort to determine the nature of the species washed from the surface, transmission FTIR spectra of the material washed from the surface were collected.

### Freon Cleaning

For the samples that were freon-cleaned, the PDMS substrates were placed in an ultrasonic bath of Freon-TS for 30 min. After removal from the bath, the freon-cleaned samples were allowed to dry for 1 week prior to ammonia/plasma treatment.

**Table I Optimized Parameters of Ammonia/Plasma Treatment**

| | Power (watts) | Pressure (mTorr) | Time (s) | Position in Camber (ON or OFF Electrode) |
|---|---|---|---|---|
| (1) | 10 | 30 | 200 | ON |
| (2) | 100 | 30 | 200 | OFF |
| (3) | 10 | 300 | 200 | OFF |
| (4) | 100 | 300 | 200 | ON |

### Spectroscopic Measurements

ATR FTIR spectra were collected on a Digilab FTS-14B. The instrument was equipped with a liquid nitrogen-cooled MCT detector and continuously purged with purified air (Balston Filter Products). Spectra were collected at a resolution of 4 $cm^{-1}$ and a mirror speed of 0.3 cm/s. In a typical experiment, the ATR cell (Spectra Tech) was aligned at 45° with a 45° end parallelogram KRS-5 crystal. Each spectrum was obtained by coadding 400 scans to increase the signal-to-noise ratio.

Transmission FTIR spectra were collected on a Mattson Cygnus 25 single-beam spectrometer (Sirus 100), also continuously purged with purified air (Balston Filter Products). A resolution of 4 $cm^{-1}$ and a mirror speed of 0.316 cm/s were used. A background of two clamped KBr salt plates was first collected and ratioed against the sample spectra, collected with the sample placed between the same KBr salt plates. All spectra represent 100 coadded scans. All spectral manipulations were performed using Spectra Calc software (Galactic Industries).

## RESULTS AND DISCUSSION

In an effort to establish optimum parameters of plasma treatment conditions, a series of substrate A samples were treated with the parameters listed in Table I. In all four treatments [(1)–(4)], samples were exposed for 200 s, but pressure, wattage, and sample position were changed. Figure 2 illustrates that the spectra of the 200 s-treated samples (traces B–E) exhibit the intensity increase of two bands at 1726 and 1653 $cm^{-1}$. The 1726 $cm^{-1}$ band is assigned

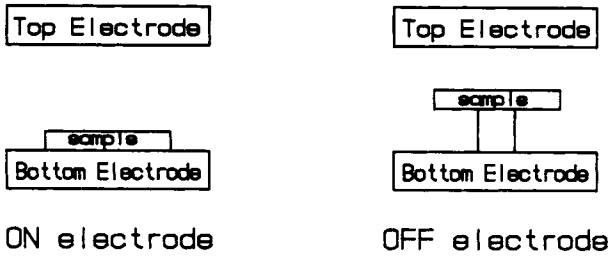


**Figure 1** Two sample positions in the plasma chamber, relative to the electrodes.

to the normal stretching vibrations of carbonyl groups that result from surface oxidation. Apparently, oxygen from an unknown source is being incorporated into newly forming carbonyl surface groups as well as into other oxygen-containing functional species. Although oxygen was not intentionally introduced into the plasma chamber, oxidation is a common occurrence in many plasma reactors. Sources of oxygen may include residual oxygen or water vapor trapped in the silicone network, silica dissociation from the chamber wall or the silicone network, and atmospheric oxygen that reacts upon the silicone surface when it is first removed from the plasma chamber.

The 1653 $cm^{-1}$ band was assigned to the normal vibrations of amide carbonyl groups (Fig. 2). This band indicates that the ammonia/plasma treatment leads to surface reactions that incorporate ammonia onto the PDMS surface in the form of amide functionality. Among the four 200 s treatments, the chamber conditions referred to as (3) in Table I appear to introduce the largest amount of surface amide groups. These functional groups are highly desirable for enhancement of surface biocompatibility. The increased amide formation is demonstrated by comparing the 1653 $cm^{-1}$ band in Figure 2, traces B, C, and E, to trace D. As will be seen later on, this finding leads to the use of conditions (3) for plasma treating samples with longer exposure times.

In an effort to increase the amount of amide functionality on the PDMS surface, substrate A was treated with conditions (3) for 15 min. Figure 3 shows the ATR FTIR spectrum of the untreated surface (trace A) and the 15 min ammonia/plasma-treated PDMS (trace B). In contrast to the 200 s exposure (Fig. 2, trace D), there is a substantial intensity increase in the 1653 $cm^{-1}$ amide band. Furthermore, the N—H stretching vibrations in the 3500–3100 $cm^{-1}$ region also increase, although this increase is likely attributed to a combination of N—H and O—H stretching vibrations, making individual N—H stretching assignments troublesome.

It is well known that during plasma-surface modification a thin surface layer of the substrate is often etched or ablated away. After plasma treatment, a fraction of the ablated material often remains on the substrate in the form of a nonbonded surface layer. In view of the above considerations, at this point, it is appropriate to determine whether the observed amide functionality is actually bonded to the PDMS surface or if it is a part of the nonbonded ablated surface layer. Since the environment in which biopolymers should function and exhibit desirable stability is aqueous, the ammonia/plasma-treated PDMS films were washed in distilled deionized (DDI) water and the spectrum was collected (Fig. 3, trace C). Our premise was that such an approach would remove any nonbonded species that might have remained on the PDMS surface. With the exception of a slight intensity decrease in the 1800–1600 $cm^{-1}$ region, the spectrum of the ammonia/plasma-treated PDMS appears almost identical to the spectrum of the same sample before washing (Fig. 3, trace B). The small intensity decrease in the 1800–1600 $cm^{-1}$ region is most likely due to the removal of a small amount of ablated

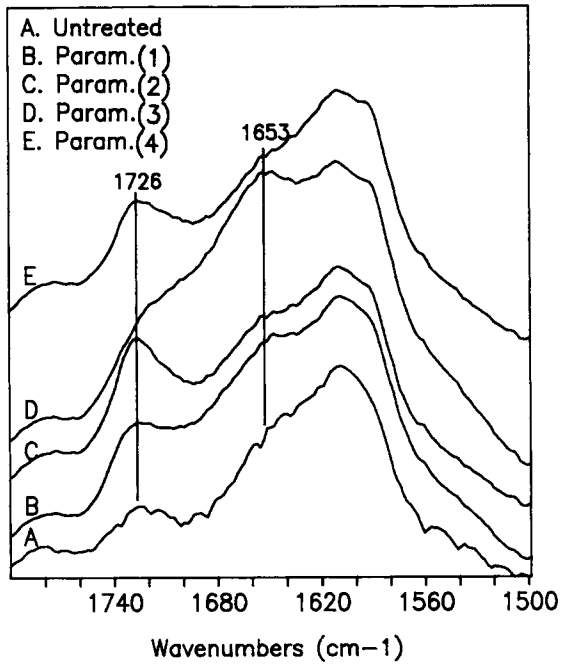


**Figure 2** ATR FTIR spectra in the 1800–1500 $cm^{-1}$ region of 200 s ammonia/plasma-treated PDMS using various treatment parameters: (A) untreated, (B) parameter 1, (C) parameter 2, (D) parameter 3, (E) parameter 4.

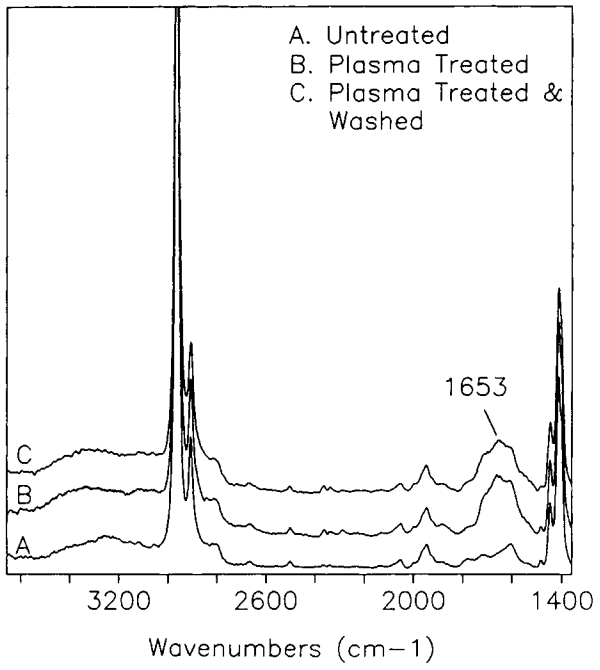


**Figure 3** ATR FTIR spectra in the 3600–1400 $cm^{-1}$ region of PDMS containing no chloro-functional molecules: (A) untreated, (B) ammonia/plasma-treated, (C) ammonia/plasma-treated and washed.

material from the surface. This observation indicates that the amide functionality formed on the PDMS surface is bonded to the PDMS network.

Knowing that the ammonia/plasma treatment of substrate A, which is free of chloro-functional molecules, generates bonded amide surface functionality, let us examine the same ammonia/plasma treatment of substrate B. This network consists of the same basic components as substrate A, but it is cross-linked with a chloro-functional peroxide. Substrate B was ammonia/plasma-treated using conditions (3) with a 15 min exposure time. ATR FTIR spectra are illustrated in Figure 4. Trace A of Figure 4 shows the spectrum of the untreated substrate B, whereas trace B is the spectrum of the ammonia/plasma-treated surface. As evident by the 1653 $cm^{-1}$ band in trace B, the spectrum of the ammonia/plasma-treated PDMS does indicate the formation of amide functionality. In addition, two strong bands at 3150 and 3053 $cm^{-1}$ are observed.

Postponing temporarily the discussion of the origin of the 3150 and 3053 $cm^{-1}$ bands, let us focus on the surface changes detected in substrate B. Similarly, the ammonia/plasma-treated substrate B was washed with water and the resulting ATR FTIR spectrum was recorded. The spectrum is shown in Figure 4, trace C, and illustrates two important features. First, the species responsible for the two new bands at 3150 and 3053 $cm^{-1}$ (trace B) is removed from the surface as these bands are absent in trace C. Second, the intensity of the amide band at 1653 $cm^{-1}$ after water washing is reduced by almost one-half, indicating the removal of a substantial amount of the amide groups. The removal of the amide functionality was not observed upon washing the ammonia/plasma-treated PDMS that does not contain chloro-functional molecules (substrate A).

At this point, it is important to determine the nature of the species responsible for the 3150 and 3053 $cm^{-1}$ bands. With the chemical compositions of ammonia gas and the PDMS substrate in mind, one would expect that the species, giving rise to absorptions in the N—H stretching region, might be organic amide or amine groups. However, vibrational frequencies and shapes of the 3150 and 3053 $cm^{-1}$ bands vary significantly from those reported for amides and amines.[9,10] Therefore, it becomes apparent that the presence of chloro-functional molecules in the PDMS network may contribute to the formation of the yet to be determined surface species.

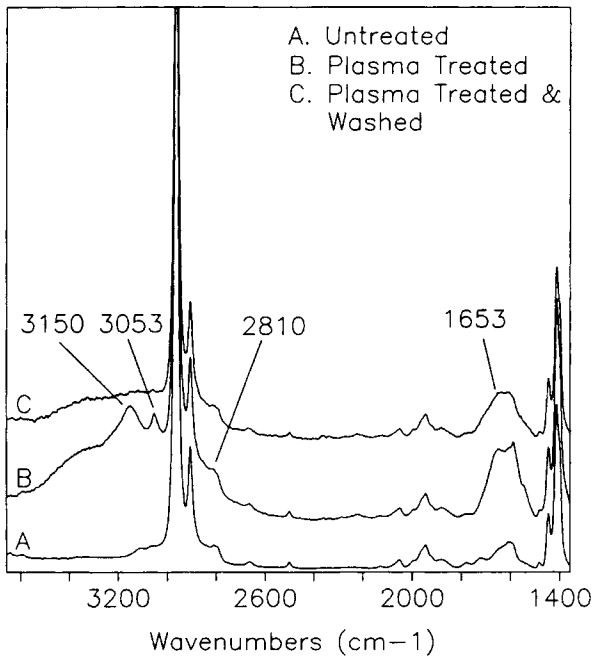


**Figure 4** ATR FTIR spectra in the 3600–1400 $cm^{-1}$ region of PDMS containing a chloro-functional initiator: (A) untreated, (B) ammonia/plasma-treated, (C) ammonia/plasma-treated and washed.

Folman[11] reported that when ammonia gas is adsorbed on a chlorinated silica surface three characteristic bands are detected. Two intense bands at 3150 and 3053 $cm^{-1}$ along with a relatively weak band at 2805 $cm^{-1}$ are attributed to the formation of ammonium chloride adsorbed on the silica surface. A closer examination of the spectrum of ammonia/plasma-treated substrate B (Fig. 4, trace B) indeed reveals a broad PDMS band at approximately 2810 $cm^{-1}$ that increases in intensity due to the appearance of a second underlying band. Furthermore, upon water washing, the 2810 $cm^{-1}$ band is reduced, as are the 3150 and 3053 $cm^{-1}$ bands (Fig. 4, trace C).

To confirm the presence of ammonium chloride, the species washed from the PDMS surface were analyzed by transmission FTIR spectroscopy (Fig. 5, trace B). A comparison of this spectrum with that of ammonium chloride (Fig. 5, trace A) indicates that the three main bands in the ammonium chloride spectrum at 3118, 3032, and 1407 $cm^{-1}$ appear at the same frequencies as in the spectrum of the removed surface material. In both cases, the N—H stretching frequencies are shifted from 3150 and 3053 $cm^{-1}$ for the ammonium chloride on the PDMS surface to 3118 and 3032 $cm^{-1}$ for ammonium chloride washed from the PDMS surface. This shift is attributed to adsorption of the ammonium chloride $NH_4^+$ ion to the substrate.[11]

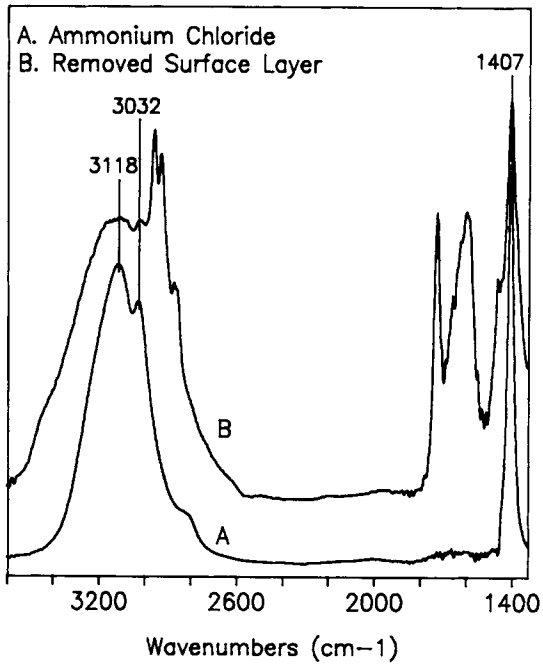


**Figure 5** Transmission FTIR spectra in the 3600–1400 $cm^{-1}$ region of (A) ammonium chloride and (B) material washed from ammonia/plasma-treated PDMS.

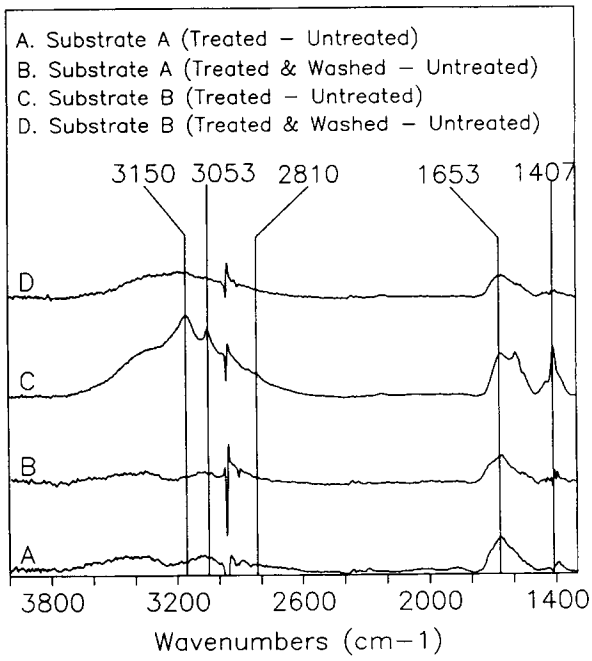


**Figure 6** ATR FTIR subtraction spectra in the 4000–1300 $cm^{-1}$ region of (A) (plasma-treated substrate A) − (untreated substrate A); (B) (plasma-treated and washed substrate A) − (untreated substrate A); (C) (plasma-treated substrate B) − (untreated substrate B); (D) (plasma-treated and washed substrate B) − (untreated substrate B).

Figure 5 also indicates that the band at 1407 $cm^{-1}$ is characteristic of ammonium chloride. This region of the PDMS spectrum also contains an absorption due to the PDMS network that interferes with the identification of the 1407 $cm^{-1}$ band. However, the use of spectral subtractions allows us to reveal the presence of this band in all ATR FTIR spectra of the samples where 3150 and 3053 $cm^{-1}$ bands are detected. Figure 6 shows several subtractions to illustrate this point. Since substrate A contains no chloro-functional molecules, subtractions of the untreated substrate A spectrum from the spectra of ammonia/plasma-treated and treated followed by surface washing exhibit no significant changes except for the amide formation at 1653 $cm^{-1}$. This is illustrated by traces A and B of Figure 6. As we recall, substrate B contains a chloro-functional initiator. Consequently, subtraction of the untreated substrate B spectrum from the spectrum of treated substrate B (Fig. 6, trace C) show not only the amide band at 1653 $cm^{-1}$, but also the three most intense ammonium chloride bands at 3150, 3053, and 1407

$cm^{-1}$ along with the weak ammonium chloride band at 2810 $cm^{-1}$. The subtraction of the substrate B spectrum from the spectrum of substrate B after ammonia/plasma treatment and surface washing (Fig. 6, trace D) clearly reveals the removal of ammonium chloride. This is evident by the absence of all four characteristic ammonium chloride bands present in Figure 6, trace C.

It is well known that various processing agents or small molecule residues are often introduced during polymer fabrication. Consequently, freon cleaning of polymers is often used to remove processing agents, because, in addition to good solvating power, freons exhibit high volatility.[12] To determine the effect of freon on ammonia/plasma treatment of PDMS, substrate B was cleaned with Freon-TS (1,1,2-trichloro-1,2,2-trifluoroethane).

Prior to the ammonia/plasma treatment, freon was allowed to diffuse out of the PDMS network for 1 week. Such pretreated substrates were exposed to ammonia/plasma using conditions (3) with a 15 min exposure time, followed by ATR FTIR analysis. After spectral collection, the substrate was washed with water and the spectrum was again collected. The resulting spectra are shown in Figure 7. As illustrated in trace C, plasma-treated PDMS shows very intense ammonium chloride bands, indicating that

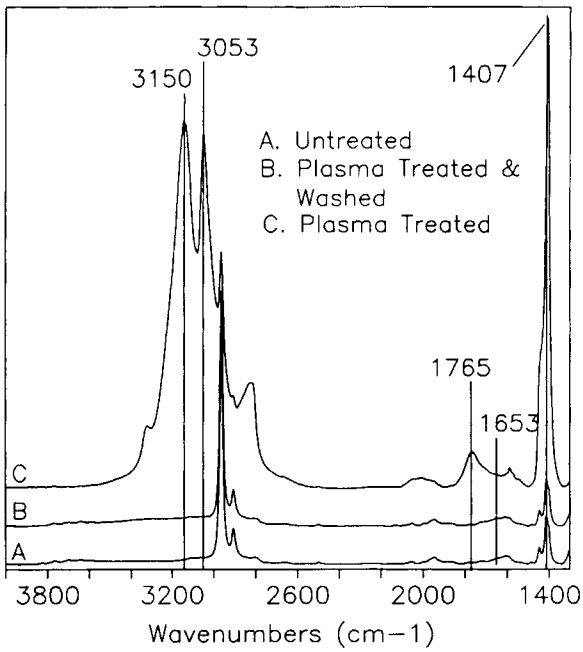


**Figure 7** ATR FTIR spectra in the 4000–1300 $cm^{-1}$ region of substrate B cleaned with freon: (A) untreated, (B) ammonia/plasma-treated and washed, (C) ammonia/plasma-treated.

freon trapped within the polymer network contributes chlorine to the formation of ammonium chloride. Furthermore, the amide carbonyl band at 1653 $cm^{-1}$ is absent and instead a new carbonyl band at 1765 $cm^{-1}$ is detected. Apparently, the formation of amide groups is inhibited by the development of ammonium chloride, and because of this, residual oxygen that might have been involved in the formation of amide groups, as previously indicated, it is being used to form a different type of carbonyl group at 1765 $cm^{-1}$. However, all surface species that are being formed parallel to the ammonium chloride formation are removable by water washing. This is shown by the ATR FTIR spectrum of the ammonia/plasma-treated PDMS after washing with water (Fig. 7, trace B). The spectrum appears to be virtually identical to that of the untreated substrate (trace A). Apparently, the ammonium chloride formation prevents not only generation of surface amide groups but other bonded functionalities as well.

## CONCLUSIONS

This study shows that PDMS substrates free of chloro-functional molecules can be amide-functionalized utilizing ammonia/plasma modification. It appears that the amide groups are bonded to the PDMS surface, but the presence of a chloro-functional molecule, such as an initiator or residual freon from the cleaning process, will lead to the formation of surface ammonium chloride. More importantly, the formation of an ammonium chloride surface layer inhibits the development of surface-bonded amide groups. The inhibition of amide formation in the PDMS containing a chloro-functional initiator is only partial because a relatively small amount of surface ammonium chloride is formed. However, a larger amount of chloro-functional species in the PDMS network, such as is the case of freon cleaning, may lead to a relatively large amount of ammonium chloride formation upon ammonia/plasma treatment. In addition, a significant amount of surface ammonium chloride completely inhibits surface amide group formation as well as other surface functional groups.

## REFERENCES

1. A. S. Hoffman, *Adv. Polym. Sci.* **57,** 141 (1984).
2. D. Cohn, in *Polymers in Medicine III,* Migliaresi, C., Ed., Elsevier Science, Amsterdam, 1988, p. 43.

3. A. S. Hoffman, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **42,** 251 (1988).
4. H. Yasuda, *Plasma Polymerization,* Academic Press, Orlando, FL, 1985.
5. H. V. Boening, in *Encyclopedia of Polymer Science and Engineering,* 2nd ed., Wiley-Interscience, New York, 1988, Vol. 11, p. 248.
6. R. d'Agostino, F. Gramarossa, S. De Benedictis, and G. Ferraro, *Plasma Chem. Plasma Process,* **1,** 19 (1981).
7. J. R. Hollahan, B. B. Stafford, R. D. Falb, and S. T. Payne, *J. Appl. Polym. Sci.*, **13,** 807 (1969).
8. M. W. Urban and M. T. Stewart, *J. Appl. Polym. Sci.*, **39,** 265 (1990).
9. G. Socrates, *Infrared Characteristic Group Frequencies,* Wiley, New York, 1980.
10. L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* 3rd ed., Chapman and Hall, London, 1975.
11. M. Folman, *Trans. Faraday Soc.* **57,** 2000 (1961).
12. H. R. Scheffer, *Metall,* **27,** 596 (1973).

*Received November 8, 1990*
*Accepted March 15, 1991*