Analysis of Gas–Plasma-Modified Poly(dimethylsiloxane) Elastomer Surfaces

Attenuated-Total-Reflectance–Fourier Transform Infrared Spectroscopy

Scott R. Gaboury and Marek W. Urban*

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

*Corresponding author.

Gas–plasma surface modifications of polymer systems have been widely studied and used to enhance adhesion or biocompatibility as well as other properties. The scope of adhesion studies of plasma-modified polymers typically deal with the enhancement of surface adhesion (1–3), improvement...
of bonding between polymers and fillers (4–6), or increased composite strength (7). One of the areas that recently received increased attention is the enhancement of polymer biocompatibility. This compatibility is usually accomplished by gas–plasma surface treatments (8–11) of polymers that have good mechanical properties, but poor surface biocompatibility. One of the most widely used biopolymers is cross-linked siloxane rubber, which, despite its inertness, needs to be surface-modified to function in biologically active environments. Although several studies (12–15) have utilized gas–plasma surface modifications, the issue of surface structure–property relationships remains questionable. The advantage of gas–plasma modification lies in its ability to favorably alter surface properties without adversely affecting the bulk mechanical properties of the polymer. Energy in the radio and microwave frequency ranges is often used as a means for either surface plasma polymerization or surface plasma modification. For surface plasma modifications of polymer surfaces, cold plasmas are in a thermal nonequilibrium reaching electron temperatures of 20,000–30,000 °C, whereas the bulk gas temperatures remain below 200–300 °C (16). Consequently, the electrons as well as other gas particles have sufficient energy to cleave common organic bonds, but thermal degradation of bulk polymer is marginal because of the low bulk gas temperature. Although the types of plasmas generated by radio and microwave frequencies are in general similar, there are differences in equipment. Due to the nature of radiation, the use of radio frequency plasma chambers allows a greater degree of flexibility in terms of geometry and the size of plasma chambers and electrodes. Microwave plasmas, however, generate a more uniform distribution of energy and, therefore, more homogeneous surface treatments (17).

To understand the chemical changes that occur as a result of plasma modifications, it is essential to characterize the molecular level changes and, on that basis, to further advance the understanding of surface chemistry and structure–property relationships on surfaces. Because vibrational spectroscopy has proven to be a sensitive technique, the primary focus of this study will be on spectroscopic monitoring of the structures that develop on silicone elastomer surfaces as a result of gas–plasma modifications.

Characterization of Plasma-Treated Polymers

The changes that occur on polymeric surfaces as a result of gas–plasma exposure have a fundamental significance on surface properties. Therefore, it is important to use surface characterization methods that are selective and sensitive to the structural changes resulting from the treatments. A list of several other surface techniques utilized in the study of plasma-modified surfaces is given in Table I. Although X-ray photoelectron spectroscopy (XPS), secondary-ion mass spectrometry (SIMS), and ion-scattering spectroscopy (ISS) are well-established methods for analyzing the chemical composition of a polymers, the use of high-vacuum conditions and careful surface preparation is required. Transmission electron microscopy (TEM), surface potential difference, contact angle, and adhesion measurements yield important information about material properties that are altered by plasma modification, but do not provide molecular level information about the species formed on the surface. Because of instrumental advancements in Fourier transform infrared (FTIR) spectroscopy, ATR–FTIR spectroscopy has become a highly sensitive technique. Due to good crystal–sample contact in polymers with low glass-transition temperatures, such as silicone elastomers, ATR–FTIR is particularly suited. Because this technique requires no high-vacuum environment, which can often disrupt weakly bonded surface species, and no special sample preparation, it is very attractive and useful in the studies of polymer surfaces.

In the ATR–FTIR experiment, the sample is placed in intimate contact with an infrared transparent crystal. When infrared light is passed through the crystal at an angle above the critical angle, the light is internally reflected except for a small portion of the light that is absorbed by the sample surface. The light reflected from the crystal–sample interface carries information about the vibrational energy of chemical bonds present on the sample surface. Typically, ATR–FTIR spectroscopy allows the detection of vibrational spectra for surface layers in the range of 0.1 to 10 μm in thickness. For quantitative analysis of surfaces, it is necessary to consider the depth of penetration that depends upon the refractive index of the crystal and incident angle of the light. Furthermore, to account for optical effects during the measurements, Kramers–Kronig transformations must be utilized (18–20). The effect of band separation and intensity changes on the ATR analysis and spectroscopic interpretation has been described recently (21). Because this chapter focuses on the actual use of ATR–FTIR spectroscopy for surface analysis, readers interested in theoretical principles should refer to the original literature.

Inert Gas–Plasma Modifications

The use of inert gases in the presence of plasma environments can substantially affect surface properties of polymers. Unlike other gas treatments, inert
gases are not incorporated into the polymer surface, but surface reactions result from rearrangements caused by interactions with the highly energetic gas particles (23).

**Argon Treatment.** ATR-FTIR spectroscopy and dynamic mechanical thermal analysis (DMTA) were used to study the effects of argon-, carbon dioxide-, and ammonia-plasma modifications on poly(dimethylsiloxane) (PDMS) (24). A radio frequency (rf) plasma chamber with a steady gas flow configuration was used for the plasma treatments. The extent of the surface changes was characterized by the relative increase of the carbonyl band at 1725 cm\(^{-1}\) ratioed to the PDMS bulk band at 1412 cm\(^{-1}\) as shown in Figure 1. In the power range from 10 to 200 W, the surface carbonyl concentration increases steadily until a power of 50 W is reached. Beyond 50 W, the carbonyl band decreases, which is attributed to two competing processes: surface modification and surface ablation. Below 50 W there is a faster increase in the rate of surface modification than in surface ablation, whereas above 50 W the surface ablation becomes more rapid than the surface modification. Even though argon gas was used, such inert gas-plasma surface treatments lead to the formation of two carbonyl bands at 1725 and 1720 cm\(^{-1}\). Although the origin of the oxygen that yields carbonyl formation is unknown, there are various possible sources: (1) When the chamber is vented to the air, atmospheric oxygen may react with radicals formed on the PDMS surface during the plasma treatment or (2) oxygen may come from residual air in the plasma chamber or air trapped in the PDMS network. In addition, the network contains oxygen in the polymer backbone and on the surface that may dissociate and contribute to surface oxidation. DMTA shows that argon-plasma treatment of the PDMS reduces the storage modulus. Because the storage modulus is directly related to cross-link density (25), these studies also show that the decrease of storage modulus as a result of argon-plasma modification leads to the decrease of PDMS cross-link density.

In the most recent studies (26), microwave argon- and nitrogen-plasma treatments of PDMS have formed Si-H functionality on the surface of PDMS. ATR-FTIR surface spectra in the 2300-1500 cm\(^{-1}\) region of the untreated and nitrogen- and argon-plasma-treated PDMS samples that contain SiO\(_2\) filler are shown in Figure 2, traces A, B, and C, respectively. The striking appearance of bands at 2158 cm\(^{-1}\) upon plasma treatment indicates the formation of new surface species. The band at 1726 cm\(^{-1}\) (Figure 2, traces B and C) is due to carbonyl species and results from surface oxidation, whereas the band at 2158 cm\(^{-1}\) is attributed to the Si-H stretching mode (27). As illustrated in Figure 3, the Si-H stretching mode at 2158 cm\(^{-1}\) is accompanied by the Si-H bending mode observed at 912 cm\(^{-1}\). In an effort to further confirm the Si-H formation, a series of PDMS samples with various nitrogen-plasma exposure times were analyzed. With increasing nitrogen-plasma exposure time, the 2158- and 912-cm\(^{-1}\) bands increase at approximately the same rate, which provides further evidence that both bands are due to the formation of the same species, namely, Si-H. At this point, however, the mechanism for the Si-H formation is not fully understood. The bond energies of the methyl silicones shown in Table II (28) suggest that due to the lower carbon-silicon and carbon-hydrogen bond
energies, these bonds are preferentially cleaved by the excited gas particles. This process yields reactive silicon sites on the polymer backbone as well as reactive carbon and hydrogen fragments in the gas phase. If the bonds are cleaved, the reactive silicon sites may recombine with the reactive hydrogen-containing species. The primary reason for the foregoing assessment is that the silicon-hydrogen bond energy is higher than the silicon-carbon bond energy. Therefore, more stable species are formed when silicon bonds to hydrogen. Furthermore, because the fragments cleaved from the polymer are primarily CH₃ groups that can further dissociate in the gas phase, there is an optimum hydrogen:carbon ratio of 3:1 in the gas phases. This excess of hydrogen species compared to carbon species leads to a statistically higher chance of hydrogen reacting with the silicon. Finally, the hydrogen:carbon ratio in the gas phase may be further increased by the cleavage of hydrogen species from carbon atoms that remain attached to the polymer chain. A schematic representation of the process is shown in Chart I.

**Chemically Active Gas–Plasma Modification**

**Carbon Dioxide.** Carbon dioxide–plasma treatments of PDMS surfaces lead to the formation of multiple carbonyl as well as alkene groups (24). This change is demonstrated by the appearance of carbonyl bands at 1725, 1700, and 1675 cm⁻¹ and an alkene band at 1596 cm⁻¹ in the ATR-FTIR spectra. The 1700-cm⁻¹ band is assigned to hydrogen-bonded carbonyl groups, most likely to the Si–OH functional groups that are formed as a result of the gas–plasma treatment. The Si–OH formation is demonstrated by a broad band centered at 3400 cm⁻¹. The band at 1596 cm⁻¹ is attributed to the formation of vinyl groups.

**Oxygen.** Oxygen–plasma modification of PDMS generates a substantial amount of surface hydroxyl functionalities (29, 30). However, the nature of the species to which the hydroxyl groups are bonded is not agreed upon. For example, it was observed that the formation of two broad hydroxyl bands
Although the conclusions drawn from the recent study (30) about the nature of the hydroxyl bonding on the PDMS surface appear to be accurate, the assessment that this study disproves previous work (29) seems unfounded. It is well known that the changes of plasma parameters, such as chamber geometry, vacuum conditions, substrate preparation, and others, can drastically affect the surface treatment and, therefore, the structures that develop as a result of such surface modifications (31). In view of the experimental procedures employed and a comparison of the experimental parameters used in each study, it is quite apparent that the exposure time, plasma power, and pressure substantially vary between the two studies. Therefore, although a comparison between the two studies is of little use, each study contains useful information.

Ammonia. Numerous studies have been conducted on the ammonia-plasma modification of polymer surfaces. The primary driving force was the desire to form reactive N–H species for future surface-grafting reactions. Indeed, studies have shown that the use of ammonia-plasma treatment leads to amine- or amide-functionalized surfaces (32–34).

Recently, we studied the effects of ammonia-plasma on PDMS and PDMS-containing chlorofunctional impurities (35). During the ammonia-plasma treatment of PDMS that contained nonbonded chlorofunctional impurities, ammonia was incorporated into the polymer surface in the form of amide functionality. The incorporation was demonstrated by the appearance of an amide carbonyl band at 1653 cm⁻¹. As is well known, during gas-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 nonbonded surface layers. For that reason, ammonia-plasma-pretreated PDMS films were washed in distilled-deionized (DDI) water to remove any residues of nonbonded material. ATR–FTIR spectra, shown in Figure 4 were collected before (trace B) and after washing (trace C). 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. This observation was attributed to the removal of a fraction of ablated material from the surface. The presence of the 1653-cm⁻¹ band after washing indicates that the amide functionality formed as a result of ammonia-plasma exposure was chemically bonded to the PDMS surface.

When a chlorofunctional impurity such as the chlorofunctional radical initiator 2,4-dichlorobenzoyl peroxide is used, the effect of ammonia-plasma surface modifications is significantly different (35). Similarly to the previous experiments, PDMS cross-linked with this initiator was ammonia-plasma-treated and ATR–FTIR spectra were collected before and after water washing. The resulting spectra are shown in Figure 5. The spectrum of the unwashed PDMS shows the formation of the amide carbonyl groups with a
Figure 4. ATR-FTIR spectra in the 3600–1400 cm⁻¹ region of PDMS with no chlorine-containing molecules: A, untreated; B, ammonia-plasma treated; C, ammonia-plasma treated and washed.

Figure 5. ATR-FTIR spectra in the 3600–1400 cm⁻¹ region of PDMS with a chlorine-containing initiator: A, untreated; B, ammonia-plasma treated; C, ammonia-plasma treated and washed.

As the previous section illustrated, even small quantities of chlorine-containing species may generate undesirable surface properties. Therefore, the presence of nonbonded molecules, such as processing agents or small molecule residues, may further enhance problems associated with gas-plasma surface modifications. Freon is a well-known cleaning agent that is used to remove processing agents because it exhibits good solvating power and high volatility (37). In an effort to establish the effect of such cleaning practices, residual 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113, DuPont) in the PDMS network was examined as another chlorine-containing impurity (35). ATR-FTIR spectra of the gas-plasma-treated PDMS before surface washing again showed intense ammonium chloride bands, which indicates that freon trapped within the polymer network contributes chlorine to the formation of ammonium chloride (Figure 6, trace C). Furthermore, the amide carbonyl band at 1653 cm⁻¹ is absent and a new carbonyl band at 1765 cm⁻¹ is detected. After the surface was washed with water, the spectra indicate that all surface species that were formed concurrently with the ammonium chloride formation were water-soluble and removable. ATR-FTIR spectra of the plasma-treated and washed PDMS surfaces appear to be virtually identical to the spectra of the substrate before plasma treatment (Figure 6, traces A and B). Apparently, ammonium chloride completely inhibits the generation of bonded...
surface amide functionality as well as the formation of other surface-bonded species.

The conclusion based on these studies is that PDMS substrates free of chlorine-containing molecules can be amide-functionalized by ammonium-plasma modification. However, the presence of chlorine-containing molecules, such as a radical initiator or residual chlorinated cleaning solvents, leads to the formation of surface ammonium chloride. The ammonium chloride layers inhibit the development of surface-bonded amide groups. Our preliminary experiments indicate that the degree of amide formation is inversely proportional to the amount of ammonium chloride formed on the surface (S. R. Gaboury and M. W. Urban, unpublished work in progress).

Summary

Although, in general, only limited surface spectroscopic data are available for the gas-plasma-modified PDMS substrates, ATR-FTIR spectroscopy apparently provides a means for analysis of the structures that develop as a result of energetic plasmons. In this chapter, the most recent advances, which use rf and microwave (MW) gas-plasma treatments, were reviewed. Ar–rf plasma leads to the formation of oxidized layers, whereas Ar–MW plasma generates useful Si–H surface groups. Although NH$_3$–rf plasma can be used to introduce surface amide functionality, it should be kept in mind that even residues of nonbonded chlorine-containing species may generate water-soluble layers of ammonium chloride. Apparently, these layers inhibit the amide group formation of PDMS surfaces.

References


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