Microwave Plasma Reactions of Imidazole on Polyurethane Elastomer Surfaces: A Spectroscopic Study

Heung Kim and Marek W. Urban*

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

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Recently initiated studies concerning surface modifications of poly(dimethylsiloxanes) using microwave plasmas were extended to polyurethane (PU) surfaces. However, when the same experimental conditions used in the closed and open flow microwave plasma reactors were applied, no chemical bonding of imidazole molecules to PU surfaces was detected. In order to facilitate the imidazole–urethane surface reactions, PU specimens were immersed in an imidazole-containing methylene chloride solution and exposed to Ar microwave plasmas. This approach appears to be successful in creating chemically stable imidazole species attached to PU surfaces. Imidazole molecules are bonded to PU surfaces through the C=N bond opening of imidazole, to create C–O–C surface bonds. Analysis of the imidazole–urethane linkages was accomplished using attenuated total reflectance Fourier transform infrared spectroscopy and revealed that the same surface structures on PU surfaces, but different concentration levels of imidazole at various depths from the surface, can be generated under closed and open flow reactor conditions. Quantitative assessments of the surface reactions at various depths are also presented.

Introduction

Due to various desirable chemical and physical properties, polyurethane (PU) elastomers are often used in countless applications. However, in order to achieve necessary surface properties, their surfaces may require modifications. This is particularly important in biomedical applications where surface biocompatibility and stability may require specific modifications. Among many surface reactions, gas plasma reactions are widely used due to their ability to alter surface properties, such as surface friction,1 adherence,2,3 and biocompatibility,4,5 while maintaining bulk properties. This approach opens numerous opportunities for not only modifying surface properties but also creating reactive sites for further surface and interfacial reactions.

Recently,6,7 we utilized microwave energy to generate plasmas allowing us to attach imidazole to cross-linked poly(dimethylsiloxane) (PDMS) elastomer surfaces under closed and open flow microwave plasma reactor conditions. Analysis of the imidazole molecules chemically attached to the PDMS surfaces and their reactive sites resulting from Ar microwave plasma reactions was conducted using attenuated total reflectance (ATR) FT-IR spectroscopy. These studies showed that imidazole radicals resulting from the hydrogen abstraction of the N–H bonds react with the SiCH₂ radicals, to form Si–CH₂imidazole entities in Ar microwave plasma reactions under closed reactor conditions. On the other hand, under open flow reactor conditions, imidazole molecules react to the PDMS surface through ring opening, resulting in the C≡C surface group formation.

Although we used the same experimental setup of closed and open flow reactor conditions to react imidazole on PU surfaces, it became evident that no species resulting from the Ar microwave plasma reactions between PU and imidazole were detected. For that reason imidazole molecules were deposited on a PU surface prior to Ar microwave plasma energy exposure. The scope of this paper is to report the results of these reactions, particularly focusing on the formation of surface imidazole molecules on PU, and the effect of microwave plasma parameters on surface reactivity of PU. Furthermore, we will attempt to quantify imidazole molecules chemically attached to the PU surfaces at various surface depths.

Experimental Section

Sample Preparation. Imidazole was absorbed into the PU by swelling its soft segments in methylene chloride. In a typical experiment, 0.015 mol of imidazole (Aldrich Chemical Co.) was dissolved in 50 mL of methylene chloride (Aldrich Chemical Co.), and PU (EN-20, Conap Co.) was immersed in such a solution for 15 min at room temperature. After removal, in order to clean the PU surface, PU was washed with methanol. Prepared in such a way PU specimens were evacuated and stored in a vacuum desiccator. Microwave plasma reactions were conducted using the experimental setup reported earlier.6 In a typical experiment, discharge times used in these experiments were 30 s.

Spectroscopic Measurements. ATR FT-IR spectra were collected on a Mattson Sirius 100 single beam spectrometer. A resolution of 4 cm⁻¹ and a mirror speed of 0.3 cm s⁻¹ were used. The ATR cell was aligned at various angles of incidence using a 30° angle parallelogram Ge crystal and a 45° angle parallelogram KRS-5 crystal. Each spectrum represents 300 coadded scans ratioed against a reference spectrum obtained from 200 coadded scans of an empty ATR cell. All spectra were corrected for spectral distortion using Q-ATR software.8

Results and Discussions

Before we analyze PU surfaces and determine potential reactions with imidazole, let us realize that, although the urethane linkage shown in Figure 1 is a primary component of the PU structure, there are “soft” and “hard” segments in a PU network which may have a different affinity for reactions with other species. This is why, in spite of our efforts to react imidazole to PU, surfaces using a traditional experimental setup, so successfully utilized for the PDMS/imidazole reactions,1 appeared to create a...
problem. In essence, several attempts resulted in unsuccessful reactions. For that reason, imidazole was incorporated into the surface of PU by immersing it in an imidazole-containing methylene chloride solution. Details concerning procedures involved are described in the Experimental Section. After PU specimens were immersed into the solution, they were exposed to microwave radiation in order to facilitate reactions of imidazole and PU linkages.

Trace A in Figure 2 illustrates the ATR FT-IR spectrum in the 4000–2000 cm\(^{-1}\) region of imidazole-absorbed PU in the presence of Ar microwave plasma under 26.6 Pa in a closed reactor: A, unreacted PU; B, imidazole–PU; C, imidazole–PU under 26.6 Pa/10 s. With these data in mind, and our previous studies on PDMS,\(^6\) let us consider how discharge pressures affect the efficiency of reactions. Figure 3 illustrates ATR FT-IR spectra of imidazole-absorbed PU in the presence of Ar plasma under various discharge pressure conditions. As discharge pressures decrease from 106.7 Pa (trace B) to 26.6 Pa (trace E), the intensity of the C–H stretching bands due to the C=C entities in imidazole at 3143 cm\(^{-1}\) increases. As the pressure decreases from 53.3 Pa (trace D), a new band at 3397 cm\(^{-1}\) attributed to the N–H stretching modes in imidazole develops, and its intensity becomes pronounced when 26.6 Pa pressure is used (trace E). At the same time, the intensity of the band at 2639 cm\(^{-1}\) due to the NH\(_\ldots\)H ionic interactions between imidazole and PU increases when compared to results at higher pressures. This is illustrated in traces D and E. On the basis of these findings, it appears that the imidazole molecules are attached to the PU surface when microwave plasmas are employed. Furthermore, the amount of imidazole molecules detected at the PU surface increases, when lower discharge pressures are employed.

Although these data provide some evidence for the imidazole–PU reactions, at this point, it would be highly speculative to assess if imidazole is indeed chemically bonded to the PU surface. For that reason, we conducted a series of experiments in which the effect of discharge pressures of Ar plasma on imidazole–PU was examined. While trace A of Figure 4 illustrates the spectrum of unreacted PU, traces B and C of Figure 4 illustrate ATR FT-IR spectra of imidazole–PU reacted in the presence of Ar plasma under 106.7 and 79.8 Pa/30 s; D, imidazole–PU under 79.8 Pa/30 s; E, imidazole–PU under 26.6 Pa/30 s.

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pressures decrease to 26.6 Pa (trace E), an increase of the band intensity at 1441 cm\(^{-1}\) is detected and decreases of the amide I band intensity of the C=O stretching at 1731 cm\(^{-1}\) and the amide II band intensity of N–H deformation at 1532 cm\(^{-1}\) due to amide groups in PU are observed. On the other hand, the C=N stretching band due to imidazole is not detected in this spectral region. On the basis of the analysis of these results, it appears that imidazole reacts to PU surface under Ar plasma pressures lower than 79.8 Pa, and the reaction sites are the C=N bond of imidazole and the amide groups on PU.

Although the results presented in Figure 4 identify reaction sites on PU and imidazole entities, in order to establish a detailed mechanism responsible for these reactions, different spectral ranges need to be analyzed. For that reason, traces B and C of Figure 5 illustrate the 1300–1000 cm\(^{-1}\) region. It appears that the characteristic features detected in traces B and C are similar to that detected in trace A. As the discharge pressures of Ar plasma decrease from 53.3 Pa (trace D) to 26.6 Pa (trace E), the intensity of the amide IV band of the (C=O)–N stretching band at 1222 cm\(^{-1}\) of PU decreases. On the other hand, the intensity of the C–O–C stretching band at 1063 cm\(^{-1}\) increases.

Based on these data, one can deduce how the C–O–C linkages between imidazole and PU are being formed. As illustrated in Figure 5, traces D and E exhibit appearance of a new band at 1095 cm\(^{-1}\) attributed to the C–N stretching modes. This band results from the reactions of imidazole through C=N bond opening to the PU surface. The reaction mechanism responsible for imidazole–PU in the presence of Ar plasma is proposed in Figure 6. The C=N bond of imidazole and the amide C=O bond of PU open up to create the C–O–C linkage. As we recall, this reaction occurs in the presence of Ar microwave generated plasmas. Furthermore, hydrogen abstraction of the N–H bonds in PU results in the formation of the C–N linkage through the C=N bond opening of imidazole. The interactions of the NH–N molecules between the PU linkages and chemically attached imidazole molecules were already discussed in conjunction with Figure 3 (traces D and E).
So far, we determined that a 26.6 Pa Ar pressure and 30 s discharge times in Ar microwave plasma result in high surface yields of imidazole reactions on the PU surface. If this is the case, we would like to establish the amount of imidazole reacted to the PU surface, including quantitative analysis as a function of the depth of penetration. Although this can be accomplished by changing an angle of incidence in an ATR setup or using ATR crystal with various refractive indices, the band distortions resulting from optical effects should be also taken into account. Figure 7 illustrates ATR FT-IR spectra, corrected using the Q-ATR algorithm, of imidazole reacted to PU recorded at various incidence angles. The reactions were conducted under 26.6 Pa and 30 s discharge time conditions in Ar microwave plasma. As the angle of incidence of infrared light entering into the ATR crystal changes from 40° (KRS-5, trace A) to 60° (Ge, trace F), the intensities of the C–C stretching band at 1581 cm\(^{-1}\) and the C–H stretching band due to C=C bond at 1447 cm\(^{-1}\) increase. On the other hand, the intensities of the amide C=O stretching band at 1732 cm\(^{-1}\) and N–H deformation band of PU at 1533 cm\(^{-1}\) decrease. These results indicate that the amount of imidazole reacted to the PU surface decreases with increasing depth of penetration.

Although at this point we are in a position to quantify the results shown in Figure 7, let us temporarily postpone this analysis and realize that the experiments described above were conducted using a closed reactor system. As our previous studies indicated, reaction mechanisms of imidazole to poly(dimethylsiloxane) (PDMS) can vary, depending upon whether open and closed reaction chamber conditions were used. For that reason, we analyzed the effect of an open flow microwave plasma reactor to the imidazole reactions with PU surfaces. Figure 8 illustrates ATR FT-IR spectra of imidazole reacted to PU using open flow microwave plasma reactor. In contrast to the PDMS studies, the reaction mechanisms of imidazole for the open and closed microwave plasma reactors result in the appearance of the C=C bond stretching band of imidazole at 1588 cm\(^{-1}\) and the disappearance of amide C=O stretching band of PU at 1732 cm\(^{-1}\).

With the objective of many surface studies is determination of the chemical makeup of the surface species, today's applications require quantitative knowledge. However, one of the drawbacks of infrared analysis is the necessity of obtaining a calibration curve. Typically, such a curve represents a band intensity plotted as a function of concentration, and its slope is equal to an extinction coefficient. In our case, the C=C bond stretching band will be used as a measure of surface reactions on PU. Figure 9 shows the plot of absorbance of the C=C stretching band of imidazole, plotted as a function of imidazole concentrations in KBr powder. On the basis of this plot, the extinction coefficient of the C=C bond of imidazole was determined to be 86.49 L/mol-cm. Since the next step of analysis requires volume concentrations,

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the volume concentration of imidazole reacted to polyurethane can be obtained using the Beer–Lambert law

\[ \beta = \epsilon c \]

where \( \beta \) is the extinction coefficient, \( c \) is the concentration, the \( \beta \) is the linear absorbivity. While these quantities are necessary to quantify the data, one issue that should be also mentioned is that in order to use ATR FT-IR spectra for quantitative purposes, they should be corrected for optical effects. For that reason, we developed an algorithm which we utilize in all ATR studies. In this algorithm, the absorption index spectrum is refined by an iterative process that minimizes the difference between the true and calculated reflectivity resulting from optical effects. This iterative process was used in conjunction with the numerical Kramers–Kronig transformation (KKT) method to obtain ATR spectra suitable for quantitative analysis using the Beer–Lambert law. Further details involved in this algorithm have been published elsewhere.

The volume concentration of imidazole reacted to polyurethane is plotted in Figure 10 and changes with depth of penetration. Under the closed reactor conditions, the volume concentration of imidazole decreases from 7.51 \( \times \) 10\(^{-3} \) to 0.30 \( \times \) 10\(^{-3} \) mol/L. On the other hand, the volume concentration of the imidazole reacted to polyurethane under the open flow reactor conditions decreases from 2.54 \( \times \) 10\(^{-3} \) to 1.51 \( \times \) 10\(^{-3} \) mol/L. On the basis of the results illustrated in Figure 10, it is apparent that the amount of imidazole reacted to the PU surface varies with the surface depth and the conditions of the surface reactions. Furthermore, as the depth of the penetration changes, reactions under closed conditions lead to a significant change while going from 0.3 to 1.25 \( \mu \)m. In contrast, only small concentration changes are detected for the open system.

The major differences between open and closed microwave plasma reactors are the lifetime of gas phase monomeric molecules and pressure changes during the plasma reactions. In a closed microwave plasma reactor, the lifetimes of the gas phase are longer, compared to that in the open flow reactor. This phenomenon is responsible for larger quantities of imidazole reacted to the PU surface in the open flow reactor. As the depth of penetration into the PU increases in a closed microwave plasma reactor, the concentration of gas phase imidazole molecules decreases due to an increase of pressure during plasma discharge, which results in a lower plasma energy and subsequent decrease of the volume concentration of imidazole reacted to the PU surface. However, for the open flow reactor, the pressure is constant during the plasma discharge, and therefore, the concentration of the gas phase imidazole molecules remains constant. As a result, relatively uniform volume concentrations of imidazole at various depths are detected.

**Conclusions**

In an effort to facilitate the imidazole–PU reactions, PU specimens were immersed in a methylene chloride–imidazole solution, followed by an exposure to the microwave radiation using closed and open flow microwave plasma conditions. Physisorbed imidazole molecules incorporated into PU elastomer networks react with PU surfaces in the presence of Ar plasma, which creates chemically bonded imidazole entities to the PU surfaces through the C=N opening of imidazole and C=O opening of PU, resulting in the C−O−C linkages between PU and imidazole. Although in this particular study the highest concentration of chemically bonded imidazole was obtained at 26.6 Pa Ar pressure and 30 s discharge times, it should be kept in mind that other factors may also influence the extent of surface reactions. They may include a soft/hard segment ratio, their free volumes, and glass transition temperatures as well as other factors.

Analysis of microwave plasma reactions conducted under closed and open flow reactor conditions reveals the same structures, but concentrations of imidazole reacted to PU surfaces vary with depth. Under closed reactor conditions, as the depth of penetration increases, the volume concentration of imidazole entities reacted to PU surfaces decreases. On the other hand, the volume concentration of imidazole entities reacted to PU surfaces under open flow reactor conditions remains constant with depth penetration. The decrease of imidazole concentration reacted to PU surfaces with depth of penetration under closed reactor conditions results from a decrease of the gas phase imidazole molecules due to increase of the pressure during microwave plasma discharge. For the open flow reactor, the pressure remains constant during Ar microwave discharge, which results in the uniform concentration of imidazole entities reacted to the PU surfaces.