Effect of Discharge Gases on Microwave Plasma Reactions of Imidazole on Poly(dimethylsiloxane) Surfaces: Quantitative ATR FT-IR Spectroscopic Analysis

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Although our recent studies revealed that under Ar microwave plasma conditions reactions of imidazole with poly(dimethylsiloxane) (PDMS) result in the formation of Si–CH2–imidazole species, the issue of the discharge gas effect on microwave plasma reactions remain unanswered. This study examines how these reactions in the presence of Ar, O2, and CO2 gases under microwave plasma conditions will affect surface reactions on PDMS in the presence of imidazole vapors. When Ar microwave plasma reaction conditions are employed, imidazole molecules react to the PDMS surface through hydrogen abstraction of the N–H bonds to form Si–CH2–imidazole and Si–CH2–CH3 linkages. When O2 microwave plasma reactions are conducted for 20 s or less discharge times, Si–O–imidazole and Si–O–CH3 species on the PDMS surface are formed. On the other hand, for discharge times above 20 s, the Si–O–CH3 linkages are converted to Si–O–CH2–imidazole entities as a result of hydrogen abstraction. The CO2 microwave plasma reactions in the presence of imidazole vapors result in the formation of Si–O–imidazole–CH3 species on the PDMS surface, followed by hydrogen abstraction, resulting in the formation of Si–O–imidazole–CH2 radicals, which react with subsequent imidazole molecules through the formation of CH2–N linkages. Similarly to the previous studies, quantitative ATR FT-IR surface analysis showed that the highest yields of imidazole reactions occur under O2 microwave plasma conditions. All experiments utilized in this study allowed surface analysis at 1.3 μm from the surface.

Introduction

There are numerous forms of energy available for conducting surface and interfacial reactions.1–4 Among them, microwave-energy-generated plasma appears to be an effective source for reacting monomeric molecules to elastomeric surfaces.5–8 In particular, the opportunity of controlling surface reactions by changing reaction conditions is quite appealing methodologies.9–11 In the previous studies,12–15 we developed closed- and open-flow plasma reactors which allowed us to chemically bond imidazole molecules to cross-linked poly(dimethylsiloxane) (PDMS) surfaces when Ar microwave plasma was employed. Using attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy,16,17 quantitative analysis of imidazole reactions under open and closed reactor conditions was performed. When the reactions were conducted under the open-flow plasma reactor conditions, imidazole molecules were reacted to the PDMS surface by ring opening to form C=≡N surface species. CH2=CH2 radicals resulting from the imidazole ring opening are grafted to form the –(CH=CH)n– linkages on the PDMS surface, and the generated –C≡N radicals acted as terminal groups in the grafting process.15 In contrast, when closed reactor conditions were utilized, multilayers of imidazole rings were reacted to the PDMS surface through hydrogen abstraction of the N–H entities of imidazole, followed by hydrogen abstraction of H–C-C–H18.

Although previous studies12,15 showed that by changing reaction conditions one can significantly alter surface products, it became apparent that one of the deficiencies of these studies was a lack of understanding of the effect of discharge gases on microwave plasma reactions. For example, reactions conducted under Ar, O2, or CO2 microwave plasma are expected to yield significant differences in surface reactions. For that reason, this study will focus on addressing the issue of how reaction mechanisms of imidazole on the PDMS surface will be affected by the presence of these gases. As with the previous studies,14 we will attempt to quantify the surface reactions between imidazole and PDMS at surface depths of 1.3 μm, when different microwave plasma conditions are utilized.

Experimental Section

**Substrate Preparation.** Poly(dimethylsiloxane) (PDMS) was prepared from a linear, vinyl-terminated dimethylvinylmethylsiloxane polymer (Mn = 28 000; Huls American Inc.). Reactions

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between vinyl groups forming cross-linked PDMS networks were initiated by the addition of 0.5% w/w of tert-butyl perbenzoate (Aldrich Chemical Co.) to PDMS. The PDMS oligomer and the initiator were first premixed for 24 h to ensure complete dissolution of initiator in PDMS. Films of cross-linked PDMS were prepared by pressure molding the oligomer-initiator mixture for 15 min at 149 °C, and postcross-linking for an additional 4 h at 100 °C. Cross-linked PDMS films containing SiO₂ were prepared in a similar way by the addition of 5% w/w of Aerosil 200 (Degussa Corp.) SiO₂. Prior to cross-linking, specimens were mixed in a rolling ball mill for 24 h and cross-linking was accomplished by a pressure molding under approximately 330 psi for 15 min at 149 °C using a Carver Lab. press (model C) and post-crosslinking for an additional 4 h at 100 °C. Surface contaminants and residual low-molecular-weight species were removed by stirring PDMS films in methylene chloride for 5 h. In an effort to remove any residual methylene chloride from PDMS specimens, each specimen was vacuum-desiccated in 1.3 Pa for 24 h at room temperature.

**Surface Reactions.** Plasma reactions were conducted using closed reactor conditions which was disclosed elsewhere. Cross-linked PDMS substrate, with approximate dimensions of 50 × 25 × 2 mm, and approximately 50 mg of solid imidazole were placed into the reactor, which was evacuated to 1.3 Pa, and brought back to atmospheric pressure by introducing a desired discharge gas. The reactor was evacuated again, followed by purging it with the discharge gas to a specific pressure. For all gases, the pressure was 26.6 Pa. At this point, a microwave radiation of 600 W of power with an output frequency of 2.45 GHz (KMC Model KMO-24G) was turned on to induce plasma reactions. In these cases, gas plasma reactions on PDMS surface were carried out using imidazole that, at 1.3 Pa, exhibits partial vapor pressure of 2.6 × 10⁻⁶ Pa. Under these conditions, the reaction-chamber pressure increases continuously during microwave plasma discharge. Under the same pressure conditions, the pressure in the reaction chamber remains constant, and no sorption of imidazole into the PDMS network is detected without microwave plasma discharge.

**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 60° angle of incidence using a 45° parallelogram KRS-5 crystal. Such an experimental setup allows surface analysis at 1.3 μm from the surface. Each spectrum represents 200 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.

**Results and Discussion**

**Ar Microwave Plasma Reactions.** Figure 1 a–d, illustrates a series of ATR FT-IR spectra for imidazole reacted to the PDMS surface in the presence of Ar microwave plasma. Although each part of this figure represents a spectrum of the same specimen in a different spectral region, each trace is the spectrum of the PDMS surface conducted using various microwave plasma conditions. Whereas trace A in Figure 1 a–d, illustrates the spectrum of unreacted PDMS in different spectral regions, trace B is the spectrum of imidazole reacted to PDMS at 10 s discharge time. Appearance of a new band at 3149 cm⁻¹ is detected in trace B of Figure 1a, which is attributed to the C–H stretching modes of the H–C=Si–H entities of imidazole. When discharge times increase from 10 s (trace B) to 30 s (trace D), the band intensities due to the
H–C=C–H groups increase. However, no N–H stretching bands due to imidazole molecules are detected. These observations indicate that imidazole reacts to the PDMS surface, most likely by hydrogen abstraction of the N–H bonds. Trace B of Figure 1b illustrates the same ATR FT-IR spectrum as in Figure 1a, that is, the spectrum of imidazole reacted to the PDMS surface at 10 s discharge times, but in the 1800–1300 cm⁻¹ region. New bands appear at 1603 and 1556 cm⁻¹, which are attributed to the C=C and C=N stretching modes of imidazole, and their intensities become stronger when discharge times increase from 10 s (trace B) to 30 s (trace D). Analysis of the spectral regions illustrated in Figure 1c for the same reactions shows that a new band at 1393 cm⁻¹ attributed to the C–H deformation modes of the H–C=C–H entities in imidazole is detected. These results indicate that imidazole reacts to the PDMS surface through the hydrogen abstraction of the N–H bonds but without the C=C cleavage and subsequent ring opening.

To further substantiate these conclusions, the spectral region between 1200 and 950 cm⁻¹ was analyzed. This is illustrated in Figure 1d, which exhibits the appearance of two new bands at 1069 and 1042 cm⁻¹ resulting from imidazole reactions. The new band detected at 1042 cm⁻¹ comes from the formation of the Si–CH₂CH₃ species on the PDMS surface. On the other hand, the band at 1073 cm⁻¹ is attributed to the Si–C vibrational modes of the –Si–CH₂–N= groups. Based on this analysis, we are in a position to identify imidazole and PDMS sites that are responsible for the –Si–CH₂–N= formation. The Si–CH₂ free radicals formed on the PDMS surface react with the methyl radicals abstracted from PDMS, followed by abstraction of imidazole radicals from imidazole to form Si–CH₂=CH₂ and Si–CH₂=imidazole linkages. Figure 2 illustrates the proposed reaction mechanisms responsible for the formation of these species on the PDMS surface.

While one of the objectives of many surface studies is the determination of the chemical makeup of a surface, another objective is to be able to quantify newly formed species. For this reason, we performed quantitative analysis of imidazole reactions on the PDMS surface at different discharge time conditions. The imidazole I band of the ring stretching vibration at 1663 cm⁻¹ will be used to measure the extent of the surface reactions. Because quantitative infrared analysis requires a calibration curve, Figure 3 illustrates the absorbance of the imidazole I band plotted as a function of known imidazole concentrations. The spectra that allow us to determine this calibration curve were recorded using a transmission mode of detection. Based on this plot, the extinction coefficient of the imidazole I band was determined to be 67.80 L/mol cm. The next step requires the use of the Beer–Lambert law, but to accomplish quantitative surface analysis, it is necessary to correct all ATR spectra for optical effects. For that reason, we employed well-established algorithm which allows an absorption index spectrum to be refined by an iterative process that minimizes the difference between the true and calculated reflectivity resulting from optical effects. At the same time, the Kramers–Kronig relation between absorption (k) and refractive (n) indices is maintained. This iterative process is used in conjunction with numerical double Kramers–Kronig transformation (KKT) method to obtain ATR spectra suitable for quantitative analysis. On the basis of the KKT-corrected spectra, linear absorptivity is obtained to allow calculations of surface concentrations from the Beer–Lambert law (β = cλ), where β is the extinction coefficient, c is the surface concentration, and λ is the linear absorptivity. Further details involved in applications and the use of this algorithm, which accounts for distortions of strong and weak bands as well as quantitative ATR measurements, are documented in the literature.

Using these approaches, surface concentrations of imidazole reacted to the PDMS surface under Ar microwave plasma conditions are plotted in Figure 4. As the discharge times increase from 5 to 20 s, the surface concentration of imidazole increases from 0.23 × 10⁻⁷ to 4.64 × 10⁻⁷ mol/L. On the other hand, it decreases from
4.64 × 10⁻⁷ to 4.32 × 10⁻⁷ mol/L when discharge times increase from 20 to 30 s. Based on these data, it is apparent that the discharge times exceeding 20 s result in diminished imidazole surface concentrations because of an increase of the inner pressure to 228.7 Pa under closed reactor conditions. As a result, solid monomer imidazole cannot be supplied to a gas phase, thus not allowing a continuation of the surface reactions.

**O₂ Microwave Plasma Reactions.** Figure 5a–d, illustrates a series of ATR FT-IR spectra for imidazole reacted to the PDMS surface in the presence of O₂ microwave plasma. Again, for reference purposes, trace A in Figure 5a–d illustrates the spectrum of unreacted PDMS surface recorded in different regions. The bands detected at 2963 and 2905 cm⁻¹ of trace A in Figure 5a are assigned to antisymmetric and symmetric C–H stretching modes, respectively, of the Si–CH₃ groups on PDMS. Trace B in all parts of this figure is the spectrum of imidazole reacted to PDMS at 10 s discharge times showing different spectral regions. In contrast to the Ar microwave plasma experiments, no N–H and C–H stretching bands due to imidazole molecules are detected. When discharge times increase up to 20 s (trace C), new bands at 2925 and 2854 cm⁻¹ are detected, and their intensities increase for 30 s discharge times (trace D). These bands are attributed to the C–H stretching region resulting from the formation of newly formed CH₂ linkages on the PDMS surface.

A spectral region from 1800 to 1300 cm⁻¹ of the same reactions is shown in Figure 5b. As seen here, new bands at 1603 and 1558 cm⁻¹ (trace B) are detected that are attributed to the C=C and C=N stretching modes of imidazole molecules. In addition, an imidazole band due to imidazole ring stretching vibrations is detected at 1661 cm⁻¹, but no N–H deformation bands due to imidazole molecules are present. Based on these data, it appears that imidazole molecules react with the PDMS surface through hydrogen abstraction of the N–H bonds of imidazole and the formation of the CH₂ linkages but without the C=C cleavage and imidazole ring opening.

These observations suggest that when O₂ microwave plasma conditions are employed formation of the CH₂ linkages on PDMS should occur; if this is indeed the case, analysis of the C–H deformation region should allow us to confirm these findings. Trace A of Figure 5c, which represents the spectral region from 1500 to 1350 cm⁻¹ for the same reactions, exhibits the band at 1415 cm⁻¹ in unreacted PDMS. This band is attributed to the C–H deformation modes of the Si–CH₃ groups in PDMS. Another band of interest is the band at 1448 cm⁻¹, which is attributed to the C–H deformation modes of the Si–CH₂ groups on PDMS, resulting from the cross-linking reactions of the vinyl groups in PDMS. For the imidazole reactions conducted on PDMS at 10 s discharge times, the spectrum shown in trace B indicates the presence of a new band at 1382 cm⁻¹. This band, which increases at extended reaction times, is attributed to the C–H deformation modes of the H–C=CH₂ entities in imidazole. When discharge times increase up to 20 s (trace C), another band at 1457 cm⁻¹ is detected, and its intensity increases with extended discharge times up to 30 s. This is illustrated in trace D in Figure 5c. Since this band is attributed to the formation of the Si–O–CH₂ species, it is reasonable to expect that these linkages result from the O₂ microwave plasma reactions of imidazole on the PDMS surface. This
Conclusion is supported by the fact that, at the same time, the intensity of the C–H deformation modes detected at 1415 cm\(^{-1}\) due to Si–CH\(_3\) groups on the PDMS surface decreases with the increased discharge times. Based on these findings, for discharge times below 20 s, imidazole molecules react with the PDMS surface through methyl group abstraction of the Si–CH\(_3\) species to form Si–O bonds. On the other hand, above 20 s discharge times, formation of the Si–O–CH\(_3\) linkages is detected and their concentrations increase with extended discharge times.

If this is indeed the case, let us analyze the Si–O stretching region of the imidazole reacted to the PDMS surface. This is presented in trace A in Figure 5d which shows a series of ATR FT-IR spectra for imidazole reacted to the PDMS surface in the presence of O\(_2\) microwave plasma under various discharge time conditions. The band intensity of the Si–O–CH\(_3\) species for discharge times below 20 s increases with extended discharge times. Based on these data, it appears that when discharge times do not exceed 10 s, microwave plasma reactions result in the formation of the Si–O–imidazole species on the PDMS surface. On the other hand, up to 20 s, the CH\(_3\) and Si–O radicals are rearranged to form Si–O–CH\(_3\) linkages. Therefore, no increase of the imidazole concentration is detected. Above 20 s discharge times, hydrogen abstraction of the newly formed Si–O–CH\(_3\) species occurs to form the Si–O–CH\(_2\) radicals, which are capable of further reactions with imidazole to form Si–O–CH\(_2\) imidazole entities on the PDMS surface. Proposed reaction mechanisms for various discharge times are depicted in Figure 7.

**CO\(_2\) Microwave Plasma Reactions.** Figure 8a–d illustrates a series of ATR FT-IR spectra for imidazole reacted to the PDMS surface in the presence of CO\(_2\) microwave plasma. For reference purposes, trace A and B illustrate the spectra of imidazole reacted to the PDMS surface under 30 s discharge times when Ar and O\(_2\) microwave plasma are employed. In trace A of Figure 8a, the band detected at 3152 cm\(^{-1}\) is attributed to the Si–O–C=C–H stretching modes of the Si–CH\(_2\)-imidazole species on the PDMS surface. The band at 2856 cm\(^{-1}\) shown in trace B is attributed to the H–C=C–H stretching modes of the Si–O–CH\(_2\)-imidazole entities on the PDMS surface. When CO\(_2\) is employed in the microwave plasma reactions from 10 (trace C) to 30 s discharge times (trace E), no bands due to the H–C=C–H and N–H entities of imidazole are detected. These observations indicate that imidazole reactions in the presence of the CO\(_2\) microwave plasma environment occur not by a hydrogen abstraction of the N–H bonds but by the hydrogen abstraction of the H–C=C–H entities on imidazole.

With these findings in mind, let us now examine the C=C and C=N stretching regions for imidazole reacted to the PDMS surface. This is illustrated in Figure 8b. Trace B of Figure 8b illustrates the ATR FT-IR spectrum of imidazole reacted to the PDMS surface at 10 s discharge times. This spectrum exhibits the appearance of new bands at 1600 and 1555 cm\(^{-1}\) which are attributed to the C=C and C=N stretching modes of imidazole. When discharge times increase up to 30 s, the intensities of these bands increase. However, similarly to the O\(_2\) microwave plasma conditions (Figure 5b), no N–H deformation bands due to imidazole are detected. In traces A and B of Figure 8b, the band at 1381 cm\(^{-1}\) is detected, and it is attributed to the C–H deformation modes of the H–C=C–H entities of imidazole molecules. However, when CO\(_2\) microwave plasma is employed for 10 (trace C) to 30 s (trace E), no
bands due to the $\text{H-C=C-H}$ entities of imidazole are detected. On the other hand, the band at 1401 cm$^{-1}$ is detected. This is shown in trace C, and this band is attributed to the $\text{C-H}$ deformation modes of newly formed $\text{CH}_3\text{-CdC}$ entities of imidazole on the PDMS surface. These observations indicate that imidazole reactions occur through hydrogen abstraction of the $\text{N-H}$ and $\text{H-C=C-H}$ entities of imidazole, followed by the formation of the $\text{CH}_3\text{-C=C-CH}_3$ entities, without a cleavage of the $\text{CdC}$ and $\text{CdN}$ bonds on an imidazole ring.

Trace A of Figure 8d illustrates the ATR FT-IR spectrum of the Ar microwave plasma reactions on the PDMS surface. The bands at 1075 and 1045 cm$^{-1}$ are attributed to the formation of the $\text{Si-CH}_2\text{-N}$ and $\text{Si-CH}_2\text{-CH}_3$ linkages, respectively. When CO$_2$ microwave plasma is employed in the same imidazole reactions, the appearance of a new band at 1061 cm$^{-1}$ is detected (trace C), and the band intensity increases when discharge times range from 10 (trace C) to 30 s (trace E). Because this band is attributed to the $\text{CH}_2\text{-N}$ stretching modes, these observations indicate that the $\text{CH}_3\text{-C=C-CH}_3$ entities of imidazole, which already reacted to the PDMS surface, are now being hydrogen abstracted to form $\text{CH}_3\text{-CdC}$ radicals. These radicals react with subsequent imidazole molecules through hydrogen abstraction of the $\text{N-H}$ bonds, which form $\text{CH}_2\text{-N}$ linkages between imidazole rings. A proposed mechanism responsible for these reactions at the PDMS surface is shown in Figure 9.

In summary, quantitative analysis of imidazole reactions in the presence of O$_2$ plasma shows the highest yields, namely, 9.73 $\times$ 10$^{-7}$ mol/L. As shown in Figure 7, the formation of two different lengths of reactive sites, $\text{Si-O-}$ and $\text{Si-O-CH}_2\text{-}$ radicals in the presence of O$_2$ microwave plasma reduces the occurrence of crowding effects with neighboring imidazole rings on the PDMS surface. Therefore, formation of two reactive sites is responsible for the highest yields of these reactions. On the other hand, the CO$_2$ microwave plasma reactions show the lowest yields of imidazole, 0.42 $\times$ 10$^{-7}$ mol/L, resulting from the formation of the $\text{CH}_2\text{-N}$ linkages with imidazole. This is illustrated in Figure 9. At discharge times above 20 s under O$_2$ and CO$_2$ microwave plasma conditions, the imidazole concentrations vary linearly with the discharge times. However, Ar microwave plasma reactions result in a decrease of the imidazole concentrations on the PDMS surface. Although there is a limited supply of the monomer above 20 s discharge times, chemically active O$_2$ and CO$_2$ are incorporated in the plasma reactions to form reactive sites for further reactions. On the other hand, in the presence of Ar microwave plasma, surface ablation is predominant at the discharge times above 20 s. Our recent
studies using atomic force microscopy confirmed this conclusion.\textsuperscript{15}

**Conclusions**

Based on ATR FT-IR spectroscopic analysis, which allowed us to do surface analysis at 1.3 \( \mu \)m from the surface, when Ar microwave plasma are utilized, imidazole molecules react to the PDMS surface to form Si\(-\text{CH}_2\)\(-\text{imidazole}\) species through hydrogen abstraction of the N\(-\text{H}\) bonds. However, when O\(_2\) or CO\(_2\) microwave plasma is employed, reactive discharge gases alter imidazole reactions. O\(_2\) microwave plasma reactions reveal that the imidazole radicals react with Si\(-\text{O}\) and Si\(-\text{O}\)-\text{CH}_2\(\text{R}\) species, which form Si\(-\text{O}\)-imidazole and Si\(-\text{O}\)-\text{CH}_2\(\text{R}\)-imidazole entities on the PDMS surface. When CO\(_2\) is utilized in the presence of microwave plasma, these species form Si\(-\text{O}\)-imidazole linkages. However, protons on the H\(-\text{C}=\text{C}=\text{H}\) entities in the presence of imidazole are substituted with the CH\(_3\) groups. These reactions are followed by the hydrogen abstraction to form Si\(-\text{O}\)-imidazole\(-\text{CH}_2\text{R}\) radicals. These radicals react with subsequent imidazole molecules through the formation of the CH\(_2\)-N linkages, which result in the formation of multi-layers of imidazole rings on the PDMS surface.

Quantitative ATR FT-IR analysis shows that the highest yields of the imidazole reactions occur when the O\(_2\) microwave plasma conditions are employed. Ar microwave plasma reactions result in a decrease of the imidazole concentrations above 20 s discharge times. It is believed that the diminished supply of imidazole into the gas phase results in lowering the imidazole content of the PDMS surface. In contrast, concentration levels of imidazole on the PDMS surface in the presence of the O\(_2\) and CO\(_2\) microwave plasma increase linearly for the discharge times above 20 s.

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