Microwave Plasma Reactions of Imidazole on Poly(vinyl chloride) Surfaces: A Spectroscopic Study

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ABSTRACT: Although there are various forms of energy available for conducting surface and interfacial reactions, microwave plasma energy is an attractive means for surface modifications because it is fast and it usually does not alter bulk properties. In this study, a closed-system microwave plasma reactor was used to react imidazole molecules to poly(vinyl chloride) (PVC) surfaces. Newly created surfaces were analyzed using attenuated total reflectance (ATR) Fourier-transformed infrared (FTIR) spectroscopy. These studies show that surface reactions on PVC are heavily dependent upon a prior thermal history of the PVC substrate. It appears that the plasma reactions on hot-pressed PVC not only result in the development of CH_2 linkages, but a significant increase of crystallinity in the hot-pressed PVC inhibits the reactivity of imidazole to the PVC surface. On the other hand, for a solvent-cast PVC with a significantly lower surface crystalline phase content, imidazole reacts to the PVC surface through C=C bond opening. The amount of imidazole reacted to the PVC surface changes with the depth from the surface. Using quantitative ATR FTIR spectroscopy, imidazole content can be quantified, and its concentrations are in the 10^{-6} mol/cm^2 range at about 0.8–1.2 μm for the PVC surface. A mechanism of the PVC–imidazole reactions is also proposed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1–6, 1999

Key words: microwave plasma; surface reactions on PVC; ATR FTIR spectroscopy

INTRODUCTION

Recently, we[1-4] developed a new method for reacting gaseous monomers to various substrates. This process involves the use of microwave plasma energy. Its attractiveness comes from the fact that microwave plasma reactions are fast, clean, and usually do not alter bulk polymer properties. Although one could argue, and perhaps rightfully so, that one of the drawbacks of the reactions conducted in the plasma gas phase is a complexity of the reaction mechanisms, the microwave plasma environment advantages are obvious. Recently, we[3-4] utilized microwave en-

ergy to generate plasmas that allowed us to react imidazole molecules to polydimethylsiloxane (PDMS) and polyurethane (PU) surfaces. Furthermore, during the course of these studies, we developed 2 experimental approaches that may significantly alter the nature of the produced surface species.[4] For example, using closed reactor conditions, imidazole rings are chemically bonded to the PDMS surface through a hydrogen abstraction of the N—H bonds. On the other hand, when the open reactor conditions are employed, imidazole rings open up, resulting in formation of the C–N species on the PDMS surfaces.

In this study, our efforts will concentrate on imidazole reactions to poly(vinyl chloride) (PVC) surfaces. The primary interest in conducting the studies on the PVC surfaces comes from its usefulness as an implant for numerous biomedical

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applications. In this case, we will employ closed microwave plasma reactions and focus on the surface reactivity and morphology of PVC, as well as formation of the reactive surface sites, reaction mechanisms, and quantitative analysis of the surface species at various depths. Similar to the previous studies, attenuated total reflectance ATR Fourier transform infrared (FTIR) spectroscopy will be used for surface analysis of imidazole reactions.

EXPERIMENTAL

Substrate Preparation

Poly(vinyl chloride) (PVC) films were prepared from PVC powder (Aldrich Chemical Co.) using 2 methods. In the first method, approximately 3 g of PVC powder was placed in a hot pressure plate at 17.9 kPa for 3 min at 185°C and allowed to cool to room temperature. In the second method, 2 g of PVC powder was dissolved in 10 mL of tetrahydrofuran (THF), and such a prepared solution was cast onto a poly(tetrafluoroethylene) (PTFE) plate and allowed to dry for 24 h.

Surface Reactions

Plasma reactions were conducted using closed reactor conditions, as described elsewhere.[4] In Ar plasma surface reactions, a PVC substrate, with approximate dimensions of $20 \times 20 \times 0.5$ mm, was placed into a microwave plasma closed reactor. The reactor was evacuated to 1.33 Pa, followed by purging it with Ar and O_2 gases to an atmospheric pressure, and re-evacuated to a desired experimental pressure, typically about 26.6 Pa. At this point, microwave radiation to induce plasma was turned on. The same procedures were utilized for reacting imidazole (Aldrich Chemical Co.) monomer. In this case, prior to purging and evacuating the reaction chamber, a solid monomer and PVC substrate were placed into a reactor.

Spectroscopic Measurements

ATR FTIR 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 a 45° angle of incidence using a 45° angle parallelogram KRS-5 crystal. Each spectrum represents 200 coded scans ratioed against a reference spectrum obtained from 200 coded scans of an empty ATR cell. All spectra were corrected for spectral distortions using Q-ATR software.[5]

RESULTS AND DISCUSSION

Although our earlier studies[1–4,6–10] indicated that microwave plasma can be successfully used for reactions of monomers to elastomeric surfaces, surface reactions on thermoplastic polymers may be influenced by the surface morphology of a polymer. For example, if the amounts of crystalline and amorphous components vary near the surface, these variations will influence surface reactions. For that reason, we prepared 2 specimens of PVC, which crystallized from melt and was cast from a solvent. While the former is anticipated to have a higher crystalline content, the latter will contain more amorphous network due to a plasticizing effect of a solvent. In an effort to react imidazole to PVC surfaces, several attempts utilizing various Ar plasma pressure conditions were made. In all cases, regardless of the experimental conditions, spectral analysis showed that no imidazole reactions occurred. For reference purposes, Table I provides a list of the IR bands observed in hot-pressed and solvent-cast PVC ATR FTIR spectra and their tentative assignments.

However, when oxygen gas was used in the presence of microwave energy, the situation changed. Figure 1 illustrates ATR FTIR spectra of imidazole-reacted surfaces of the hot-pressed PVC exposed to oxygen microwave plasma radiation discharged for 10 s. As a reference point, trace (A) illustrates the spectrum of unreacted PVC, with the bands listed in Table I. It appears that in hot-pressed PVC, the intensities of the C—C skeletal normal vibrations at 1073 cm^{-1}, the CH_2 deformation modes at 1430 cm^{-1}, and the CH_2 rocking modes at 960 cm^{-1} increase with the decreasing initial discharge pressures in the plasma chamber. However, no imidazole reactions are detected on the PVC surface. These observations indicate that, as the result of the microwave plasma exposure, the PVC surface contains CH_2 linkages [traces (B)–(C)] in Figure 1. Similar to previous studies,[2] lower gas plasma pressures result in the enhancement of the CH_2 deformation bands. Although there is no direct evidence for the C—Cl bond cleavage in the hot-pressed PVC specimens, plasma reactions lead to formation of C—H radicals abstracted from imi-

Table I   Tentative Band Assignments of Hot-Pressed and Solvent-Cast PVC

Band (cm^{-1})	PVC	
	Solvent-Cast	Hot-Pressed
1722	—C=O stretching	—
1573	—C=N— stretching	—
1430	—CH$_2$— deformation	—CH$_2$— deformation
1339	—CH— deformation	—CH— deformation
1255	—CH$_2$— wagging	—CH$_2$— wagging
1071	—C—C— skeletal vibration	—C—C— sketelal vibration
960	—CH$_2$— rocking vibration	—CH$_2$— rocking vibration
695	—CH— rocking vibration	—CH— rocking vibration
620	—CCl stretching	—CCl stretching

dazole monomers to increase the content of the —CH$_2$— linkages.

Figure 2 illustrates ATR FTIR spectra in the C—H stretching region for imidazole reacted to the solvent-cast PVC surface under various discharge pressures. For reference purposes, traces (A) and (B) of Figure 2 illustrate the spectra of unreacted and oxygen microwave plasma reacted to the PVC surface. The spectrum of oxygen plasma reacted to PVC surfaces exhibits the appearance of the OH stretching modes at 3410 cm^{-1} due to the formation of carboxylic acid species. It appears that when imidazole is reacted to the PVC surface, the C—H stretching bands at 2926 and 2854 cm^{-1} are detected, which is attrib-

Figure 1   ATR FTIR spectra in the 1900–500 cm^{-1} region of imidazole reacted to hot-pressed PVC in the presence of oxygen microwave plasma under various pressure conditions using a closed reactor: (A) unreacted hot-pressed PVC; (B) oxygen microwave plasma at 106.4 Pa/10 s; (C) imidazole reacted to PVC at 106.4 Pa/10 s; (D) imidazole reacted to PVC at 26.6 Pa/10; (E) imidazole reacted to PVC at 13.3 Pa/10 s.

Figure 2   ATR FTIR spectra in the 3700–2800 cm^{-1} region of imidazole reacted to solvent-cast PVC in the presence of oxygen microwave plasma under various pressure conditions using a closed reactor: (A) unreacted solvent-cast PVC; (B) oxygen microwave plasma at 106.4 Pa/5 s; (C) imidazole reacted to PVC at 106.4 Pa/5 s; (D) imidazole reacted to PVC at 53.2 Pa/5 s; (E) imidazole reacted to PVC at 26.6 Pa/5 s; (F) imidazole reacted to PVC at 13.3 Pa/5 s.

Figure 3 ATR FTIR spectra in the 1850–1000 cm^{-1} region of imidazole reacted to solvent-cast PVC in the presence of oxygen microwave plasma under various pressure conditions using a closed reactor: (A) unreacted solvent-cast PVC; (B) oxygen microwave plasma at 106.4 Pa/5 s; (C) imidazole reacted to PVC at 106.4 Pa/5 s; (D) imidazole reacted to PVC at 53.2 Pa/5 s; (E) imidazole reacted to PVC at 26.6 Pa/5 s; (F) imidazole reacted to PVC at 13.3 Pa/5 s.

uted to the C—H stretching bands of the —CH_2— linkages formed from the C=C bond opening of imidazole molecules. Similar to our previous studies,[2] these bands become stronger when initial discharge pressures decrease from 106.7 Pa [trace (C)] to 13.3 Pa [trace (F)].

With this in mind, let us analyze the C=C and the C=N stretching regions, which are illustrated in Figure 3. It appears that the appearance of 2 new bands at 1658 and 1587 cm^{-1} attributed to the imidazole I band of the ring and the C=N stretching of imidazole are detected. On the other hand, although initial discharge pressures decrease from 106.7 Pa [trace (C)] to 13.3 Pa [trace (F)], the C=C bond stretching and the —CH=C—H deformation bands of imidazole molecules are not detected. These observations indicate that imidazole reacts to PVC surfaces through a C=C bond cleavage, but the imidazole ring remains. When oxygen gas is present in the plasma environment, the C=O stretching band at 1724 cm^{-1} is detected [trace (B)], which is attributed to the formation of carboxylic acid species on

the surface of PVC. When imidazole is reacted to the PVC surface in the presence of oxygen plasma at the initial discharge pressure of 106.4 Pa [trace (C)], the intensity of the C=O stretching band at 1775 cm^{-1} also increases, indicating the formation of ester linkages between the PVC surface and imidazole molecules. In addition, the increase of the 1040 cm^{-1} band intensity, relative to the C—C skeletal vibrations at 1071 cm^{-1} [trace (F)], is attributed to the presence of ester linkages.

Let us now examine how imidazole content may change as a function of the depth from the PVC surface. These observations indicate that imidazole reacts at the PVC surface, most likely by the C=C cleavage in the presence of oxygen plasma. A possible mechanism of imidazole reaction at the PVC surface is shown in Figure 4. Although this can be accomplished by changing the angle of incidence in an ATR setup,[12] band distortions resulting from optical effects in an ATR experiment should be also taken into account. For that reason, we[5] developed an algorithm that we utilize in analysis of all ATR spectra. In this algorithm, the absorption index spectrum is refined by an iterative process that minimizes the difference between true and calculated reflectivity resulting from optical effects, while maintaining the Kramers–Kronig relation between absorption (k) and refractive index (n) components of a spectrum. This iterative process can be used in conjunction with double Kramers–Kronig transformation (KKT) method to obtain ATR spectra free of distortions, suitable for quantitative analysis using the Beer–Lambert law. Figure 5 illustrates ATR FTIR spectra of imidazole reacted to PVC surfaces recorded at various incidence angles. The reactions were conducted under 26.6 Pa and 5 s discharge times in the presence of oxygen microwave plasma. As the angle of incidence of IR light into the KRS-5 crystal changes from 40° [trace (B)] to 60° [trace (D)], the intensities of the imidazole I band of ring structure 1662 cm^{-1} and the C=N stretching band at 1585 cm^{-1} increase. These results indicate that the amount of imidazole reacted to PVC surfaces decreases with the increasing penetration depth.

While the objective of many surface studies is a determination of the chemical makeup of surface species, modern science also requires quantitative knowledge. However, one of the drawbacks of IR analysis is the necessity of obtaining a calibration curve. Typically, such a curve represents the band intensity plotted as a function of concentration, and the slope is equal to an extinction coef-

Figure 4   Proposed mechanism of imidazole reactions to solvent-cast PVC surfaces in the presence of oxygen plasma.

ficient. In our case, the imidazole ring stretching band at 1662 cm^{-1} band will be used as a measure of surface reactions on PVC. Figure 6 shows the

Figure 5   ATR FTIR spectra in the $1850-1000 \text{ cm}^{-1}$ region of imidazole reacted to solvent-cast PVC in the presence of oxygen plasma under 26.6 Pa/5 s using various incidence angles of IR light: (A) unreacted PVC at a 60° angle of KRS-5; (B) imidazole reacted PVC at a 40° angle of KRS-5 crystal; (C) imidazole reacted at a 50° angle of KRS-5 crystal; (D) imidazole reacted at a 60° angle of KRS-5.

plot of absorbance of the imidazole ring stretching band, plotted as a function of imidazole concentration in KBr powder. Using these data, the extinction coefficient of the imidazole ring stretching band is determined to be 67.81 1 mol/cm. This calibration curve, along with the double KKT analysis,[5] allows us to determine the imidazole concentration on the PVC surface at various depths. The results are shown in Figure 7. As the depth of penetration increases from 0.86 μm to 0.93 μm, the surface concentration of imidazole reacted to the PVC surface exhibits a decrease from 0.37×10^{-6} to 0.17×10^{-6} mol/cm^2. At surface depths exceeding 0.93 μm, the imidazole

Figure 6   Plot of absorbance of the imidazole ring stretching band as a function of imidazole concentrations in KBr powder.

Figure 7   Plots of surface concentration for imidazole reacted to PVC surfaces as a function of depth of penetration.

concentration decreases considerably. Thus, imidazole–PVC reactions occur largely at the top 0.8-μm surface layers.

CONCLUSIONS

In this study, a closed microwave plasma reactor was used to react imidazole molecules to PVC surfaces. Using ATR FTIR spectroscopy, quantitative analysis of newly created surface species was performed. In a hot-pressed PVC, no imidazole reactions were detected on the surfaces under argon and oxygen microwave plasma conditions. However, under oxygen microwave plasma conditions, PVC surfaces exhibit newly formed CH_2 linkages, resulting from C—Cl bond cleavages, to form CH_2 linkages on PVC surfaces. In a solvent-cast PVC, imidazole molecules react to the PVC surface through the C=C cleavage of imidazole and the formation of the ester linkages between PVC and imidazole molecules. Imidazole reactions are inhibited on the hot-pressed PVC

surfaces due to a high crystallinity content. On the other hand, imidazole reacts with the solvent-cast PVC surfaces through a C=C cleavage. Although there is no direct evidence that would account for reactivity of the solvent-cast PVC, it is believed that the presence of amorphous network due to a plasticizing effect of a solvent is responsible for imidazole reacting with the PVC surface. Quantitative analysis of imidazole reactions to the solvent-cast PVC surfaces at various depths indicates that imidazole reactions occur largely at the top 0.8-μm surface layers. As the depth increases from 0.8 to 1.2 μm, surface concentration of imidazole reacted to the PVC surfaces decreases from 0.37×10^{-6} to 0.17×10^{-6} mol/cm^2.

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