ATR FT-IR ANALYSIS OF SI-H FORMED ON SILICON ELASTOMER SURFACES BY MICROWAVE PLASMAS

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INTRODUCTION

Plasma surface modifications have been widely studied and used as a method of treating polymer surfaces—because of the ability of plasmas to favorably alter polymer surfaces without altering bulk polymer properties. In recent studies, a combination of dynamic mechanical analysis (DMA) and ATR FT-IR spectroscopy was utilized to correlate surface chemical changes to mechanical property changes due to surface rms roughness changes. To this context, we have also used ATR FT-IR spectroscopy to study the effects that residual chromophore-functional small molecules in polysiloxane/SiO2 (PDMS) elastomers have upon ammonia plasma surface treatments. These studies deal with a novel microwave plasma approach to modify the surface of PDMS. Nonfilm forming plasma gases, argon and nitrogen, will be used to generate Si-H groups on the surface of PDMS, and ATR FT-IR spectroscopy will be used to analyze the chemical changes. A modified Kramers-Kronig transformation can be used to ATR FT-IR spectra to provide a quantitative measure of the surface reactions.

EXPERIMENTAL

The PDMS substrate preparation, plasma equipment, and plasma treatment process were described elsewhere. For hydrofluorination experiments, methylsilane and hydrofluorocarbon (Alclair Chemicals) were dosed to 50% of the plasma treatment dose. AATR FT-IR spectra were collected on a Digilab FTS-14B equipped with a liquid nitrogen cooled MCT detector. A resolution of 4 cm⁻¹ and a mirror speed of 0.3 cm/sec was used. ATR cells (Specac Tech Inc.) were aligned at various angles of incidence, varying from 45° to 60°, using a 45° and parallal/parallelogram KRS-5 crystal. For calibration measurements of standard solutions, the cell was modified such that liquid sample spectra could be recorded. For the quantitative analysis, all spectra were collected on a power-polarity polarization using an aluminum wire grid spacer with a 0.4-μm grid spacing (Specac Ltd.). In order to quantify the amount of Si-H functional groups, a Kramer-Kronig (IK) transformation coupled with Kramers-Kronig equations with Precursa's equations has been applied, allowing the construction of calibration curves independent of the sample refractive index, crystal coverage and the angle of incidence.

RESULTS AND DISCUSSION

The crystal structures in the 2300–1500 cm⁻¹ region of untreated, nitrogen plasma and argon plasma treated PDMS samples are shown in Figure 1. The spectrum of nitrogen treated PDMS, Trace B, indicates that the predominant changes observed are the increased intensity of the 1726 cm⁻¹ band and the formation of a new band at 2158 cm⁻¹. While the band at 1726 cm⁻¹ is indicative of carbonyl species formed from surface oxidation, the 2158 cm⁻¹ band cannot be assigned to simple oxidation products. The literature suggests that the 2158 cm⁻¹ band may be attributed to the stretching mode of C≡N formed by reaction of the nitrogen plasma with the PDMS substrate. However, in order to confirm the nature of the surface functionality, PDMS films were plasma treated using argon gas. The precursor of such an approach was that with nitrogen present during argon plasma treatments, the possibility of nitrogen containing functionality can be eliminated. If C≡N was the surface species forming upon the nitrogen plasma treated PDMS, the 2158 cm⁻¹ band should be absent in the spectrum of argon treated PDMS. However, the spectrum of PDMS treated with argon plasma is almost identical to that of PDMS plasma treated under nitrogen as seen in Figure 1, Trace C. The presence of the strong 2158 cm⁻¹ band in the spectrum of the argon plasma treated PDMS indicates that this species is not due to C≡N functionality. Considering the strong present in the system and the spectral region of the new band, a second possible assignment for the band at 2158 cm⁻¹ could be Si-H stretching. The 2158 cm⁻¹ band should be accompanied by an absorbent band due to the Si-H bending mode, indeed, the appearance of the Si-H bending mode observed at 912 cm⁻¹ confirms the formation of Si-H.

The ability of Si-H functionality offers the possibility of grafting additional moieties to the PDMS surface. It has been shown that the hydroxylolation reaction is effective for grafting styrene to Si-H groups on linear poly(dimethylsiloxane). Thus, in an attempt to grafted Si-H groups formed as a result of the plasma treatments, hydroxilation utilizing styrene was chosen. Both plasma treated PDMS with the Si-H groups, and untreated PDMS used as a control, were exposed to hydroxilation conditions. ATR FT-IR spectra of the samples were collected, and the results are illustrated in Figure 2. The plasma treated sample before hydroxilation, Trace A, clearly shows the Si-H functionality in the presence of the 2158 cm⁻¹ band. After hydroxilation of the plasma treated sample, the spectrum shows that the 2158 cm⁻¹ band is diminished, Trace B, indicating that all of the Si-H groups have reacted. However, while the hydroxilated sample shows a loss of Si-H, the absence of aromatic C-H stretching modes in the 3000–300 cm⁻¹ region indicates that styrene is not grafted to the surface, but an increase in the broad absorption centered at approximately 3500 cm⁻¹ is detected instead. The 3500 cm⁻¹ band is attributed to the O-H stretching mode of silanized groups. While some silanized groups form as a result of the plasma treatment step (Figure 2, Trace A), apparently, the hydroxilation reaction is converting the Si-H groups to silanized groups as well. Even though silanized formation is not the desired reaction product, these results demonstrate that the Si-H groups formed during plasma treatment of PDMS are accessible for post-plasma reactions. As a control, unexposed PDMS was also exposed to the same hydroxilation conditions, and the resulting surface spectrum (Figure 2, Trace C) shows no silanized formation. We have shown that using microwave plasma gas treatment of PDMS surfaces in an argon or nitrogen atmosphere, it is possible to generate surface Si-H groups. At this point, quantitative analysis is desirable, but it is well known that direct measurement of the band intensity in ATR FT-IR spectra is limited for quantitative analysis because the band intensities and their vibrational energies depend upon the sample-crystal reflective indices. The latter varies with the wavenumber and as a function of optical effects at the sample-ATR crystal interface. Because quantitative analysis of infrared spectra requires a calibration curve, the first step is to construct such a curve. In our case, this was achieved by measuring the ATR spectra of homogenous liquid standards containing 0.1 M to 0.2 M heptamethyldisilazane (HMDS) and plotting the Si-H intensity as a function of concentration. In an attempt to establish the difference between the raw and transformed spectra, the raw intensities of the Si-H bands obtained from the polarized ATR spectra of the HMDS solutions were employed and plotted as a function of concentration. It should be noted that in ATR experiments the crystal curvature and reflective index of the standards were constant, giving a linear dependence between ATMS concentrations and band intensity for a fixed angle of incidence. However, since the plasma treated samples may have low-reflective indices, the reflective indices of the standard liquids are not directly usable to determine the Si-H concentration. However, these factors are accounted for when the spectra are subjected to KK transformation. For the standards with a common reflective index and crystal curvature, the band intensity increases with a decreasing angle of incidence. This is expected since the spectra obtained at greater angles of incidence contain informations from a thinner surface layer and fewer reflections. The use of KK transformation also compensates for the angle of incidence and effective number of reflection changes and, hence, the plots at all angles of incidence after KK transformation should theoretically be linear and superimposed and indeed are. As shown in Figure 3, though the slopes may slightly deviate from the ideal 45°, each line has a linear correlation coefficient exceeding 0.997, and is therefore suitable for determining the Si-H concentration of the gas plasma treated PDMS elastomers using ATR spectra recorded at the various angles of incidence.

In an effort to test and estimate the accuracy of the calibration curves, ATR FT-IR spectra of methylhydro-disilazane copolymer were collected. This material contains Si-H groups that are only slightly different from the standard liquids used to construct the calibration curves. The calculated concentration can be directly obtained from the calibration curve. The results show good precision with a deviation 0.1 M between all four calculated values. Furthermore, the accuracy of the calculated values is high with the deviations varying from 0.03 M to 0.02 M from the actual concentration.
At this point, let us go back to the main theme and use the calibration curve constructed to determine the Si-H concentration of the gas plasma treated PDMs elastomers containing 20% silica. After gas plasma treatment, ATR-FTIR spectra were collected at the angles of incidence corresponding to the calibration curve angles, R, to obtain β values, and the Si-H concentrations were calculated. This data, along with the depth of penetration for each angle of incidence is shown in Table 1. It appears that when going from 0.6 to 0.8 μm into the PDMs surface, the concentration of the Si-H species changes by about 23%. It should be kept in mind that the concentrations shown in Table 1 are not local concentrations at a given specific depth, but average concentrations of the entire depth of penetration (sample). According to the data presented in Table 1, the Si-H groups are more concentrated at the top surface of the PDMs, as demonstrated by the increase in the Si-H concentration at shallower depths. This observation is known for other plasma treatment methods and reinforces the consistency of the ATR FTIR methodology employed in this study.

<table>
<thead>
<tr>
<th>Effective Angle (°)</th>
<th>Effective Depth of Penetration (nm)</th>
<th>Calc. Si-H Conc. (X10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.00</td>
<td>21.04</td>
<td>0.17</td>
</tr>
<tr>
<td>47.10</td>
<td>32.76</td>
<td>0.16</td>
</tr>
<tr>
<td>49.18</td>
<td>25.24</td>
<td>0.18</td>
</tr>
<tr>
<td>51.24</td>
<td>27.96</td>
<td>0.20</td>
</tr>
</tbody>
</table>

While the formation of Si-H groups is apparent, the source of hydrogen for the formation of these groups is not. There are several possible sources of hydrogen in this system that must be investigated in order to better understand how the Si-H forms. The available hydrogen sources include methyl hydrogen, hydrogen from the silanol groups which serve the surface of the silanized film, and residual water in the polymer network picked up from the atmosphere. It was shown quantitatively that there is a trend of increasing Si-H formation with a higher ratio to film ratio which indicates that the residual methyl groups are the source of hydrogen. The Si-H concentration for these samples was quantified as described previously, and the results are shown in Table 2.

<table>
<thead>
<tr>
<th>Effective Angle (°)</th>
<th>Silica Content (% by weight)</th>
<th>Calc. Si-H Conc. (X10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.18</td>
<td>20.72</td>
<td>0.42</td>
</tr>
<tr>
<td>49.18</td>
<td>33.99</td>
<td>0.18</td>
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<tr>
<td>49.18</td>
<td>5.08</td>
<td>0.03</td>
</tr>
</tbody>
</table>

CONCLUSIONS

These initial microwave plasma studies show that PDMs elastomer surfaces can be modified using microwave generated argon or nitrogen plasmas, leading to desirable Si-H surface functional groups. ATR-FTIR spectroscopy can be used to follow new structures that develop upon gas plasma surface modification. Furthermore, transformation of surface Si-H groups to Si-OH indicates that the Si-H groups are accessible for post-plasma reactions, and quantitative analysis of the surface reactions is possible. New reactions involving Si-H groups are also under investigation.

REFERENCES