Quantitative analysis of the Si-H groups formed on poly(dimethylsiloxane) surfaces: an ATR *FT*i.r. approach

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Attenuated total reflectance Fourier transform infra-red (ATR *FT*i.r.) spectroscopy was utilized to quantify the concentration of Si-H groups formed on poly(dimethylsiloxane) (PDMS) elastomer surfaces as a result of Ar or N_2 plasma modifications. Kramers–Kronig transformation of the ATR spectra of standard solutions containing Si-H species allows construction of calibration plots which are independent of the angle of incidence, crystal coverage and sample refractive index. The Si-H concentrations of the plasma-treated PDMS are calculated from the calibration plots, and indicate that gas/plasma treatments of PDMS substrates result in Si-H functionality gradients with higher concentrations near the elastomer surface.

(Keywords: attenuated total reflectance *FT*i.r. spectroscopy; PDMS; analysis)

Introduction

Polymer surface modifications that utilize various plasma methods have received considerable attention[1–3]. The primary benefit of using such approaches is the ability to favourably alter a polymer surface without changing the structure and properties of the bulk polymer. Because of this, as well as other advantages, plasma surface modifications including both film forming and non-film forming methods have become of interest for the improvement of polymer biocompatibility[2,4,5]. The non-film forming methods are useful primarily because they may generate surface reactive groups with functionalities that enable further reactions with other species[2,5,6].

Due to inertness and suitable mechanical characteristics, crosslinked siloxane elastomers are one of the most widely used synthetic biopolymers and have been studied extensively[7–10]. In a recent study[11], we utilized attenuated total reflectance Fourier transform infra-red (ATR *FT*i.r.) spectroscopy to illustrate that the presence of residual chloro-functional molecules in poly(dimethylsiloxane) (PDMS) inhibits surface functionalization when ammonia/plasma is used. Most recently, we[12] have used Ar and N_2 gases in microwave plasma environments to modify PDMS surfaces. ATR *FT*i.r. analysis of such treated PDMS surfaces revealed the formation of Si-H functional groups. Although the Si-H groups can be used for further surface reactions, it is important to be able to quantify the amount of surface Si-H groups not only for optimization of plasma treatment but also, as in this study, to provide an experimental and theoretical basis for quantifying surface Si-H functionalities using ATR *FT*i.r. spectroscopy and to propose a possible mechanism for Si-H formation.

Experimental

Substrate preparation. PDMS films were prepared from a linear dimethyl-vinylmethylsiloxane copolymer ($M_w = 28\,000$, Huls America Inc.). The reaction between vinyl groups was initiated by addition of 0.5 w/w% t-butyl perbenzoate (Aldrich Chemical Co.) to the linear PDMS. Films containing 0, 20 and 40 w/w% Aerosil 200 SiO_2 filler (Degussa Corp.) were prepared. To ensure complete dissolution of the initiator, the linear PDMS resin and initiator were initially premixed for 24 h followed by addition of SiO_2. The mixture was then mixed for an additional 24 h in a rolling ball mill. The crosslinking reaction was accomplished by pressure moulding the resin mixture for 15 min at 149°C and post-curing for 4 h at 210°C. In an effort to remove surface contaminants and residual low molecular weight sole species before plasma treatment, the post-cured PDMS films were placed for 3 min in a bath containing diethyl ether. The residues of diethyl ether were removed from the crosslinked PDMS elastomer by vacuum desiccating the sample for 24 h.

Calibration standards were prepared using a linear PDMS polymer ($M_w = 17\,250$). The PDMS was combined with various amounts of bis(trimethylsiloxy)-methylsilane (BTMS) (Huls America Inc.) to obtain standard solutions containing known Si-H concentrations varying from 0.1 to 0.32 M. Prior to use, the mixture was stirred for 15 min.

Methylhydro-dimethylsiloxane copolymer containing 0.5–1.0% methylhydro units was obtained from Huls America Inc.

Gas/plasma surface treatments. The plasma chamber and plasma treatment procedures have been described elsewhere[12].

Spectroscopic measurements. ATR *FT*i.r. spectra were collected on a Digilab FTS-14B equipped with a liquid

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N_2 cooled MCT detector. A resolution of 4 cm^{-1} and a mirror speed of 0.3 $cm\,s^{-1}$ were used. An ATR cell (Spectra Tech Inc.) was aligned at various angles of incidence, varying from 45 to 60°, using a 45° end parallelogram KRS-5 crystal. For calibration measurements of standard solutions, the cell was modified such that liquid sample spectra could be recorded. All spectra were collected with a perpendicular polarization using an aluminium wire grid polarizer with 0.4 μm grid spacing (Specac Ltd). The instrument and the ATR cell compartment were continuously purged with purified air (Balston Filter Products). Each spectrum represents 400 coadded scans ratioed against a reference spectrum obtained by coaddition of 400 scans of an ATR crystal. All spectral manipulations were performed using Spectra Calc software (Galactic Industries).

In order to quantify the amount of Si-H functional groups, a Kramers-Kronig (KK) transformation together with Fresnel's equations were utilized, allowing the construction of calibration curves independent of the sample refractive index, crystal coverage and the angle of incidence.

Results and discussion

Recently, we have shown that by using microwave gas/plasma treatments of PDMS surfaces in an Ar or N_2 atmosphere it is possible to generate surface Si-H groups[12]. This was demonstrated by the presence of Si-H stretching and bending bands at 2158 and 912 cm^{-1} in the ATR *FT*i.r. spectra shown in *Figure 1*. As a result of the treatment, other bands associated with various methyl vibrational modes decrease in intensity upon treatment. *Figure 2* illustrates methyl C-H stretching (2965 and 2907 cm^{-1}) and methyl C-H bending bands (1447 and 1414 cm^{-1}) which indeed decrease upon plasma treatment. The same trends are observed for the bands due to methyl rocking and Si-C stretching modes, and are attributed to ablation of the PDMS network resulting from the gas/plasma treatment.

It is well known that direct measurement of the band intensities in ATR spectra is limited for quantitative analysis because the band intensities and their vibrational energies depend upon the refractive index of the sample.

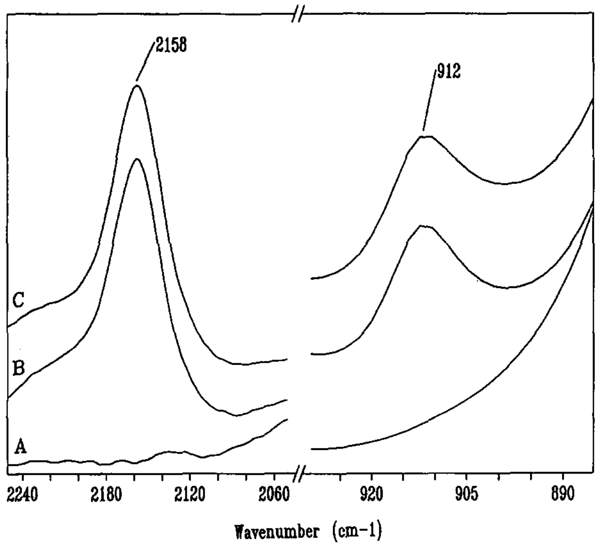


Figure 1 ATR *FT*i.r. spectra of PDMS in the Si-H stretching and bending regions for: (A) untreated; (B) N_2/plasma treated; (C) Ar/plasma treated

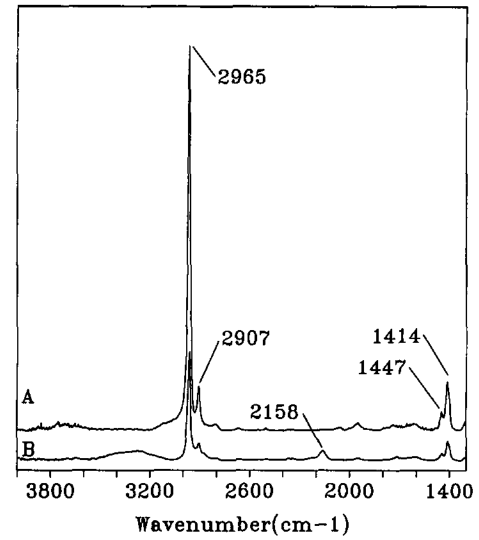


Figure 2 ATR *FT*i.r. spectra of PDMS in the 4000–1300 cm^{-1} region for: (A) untreated; (b) Ar/plasma treated

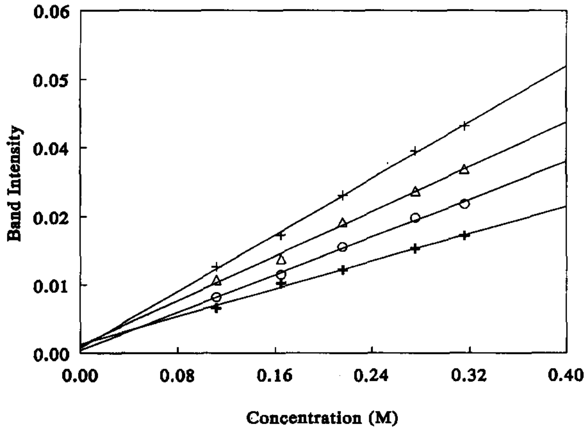


Figure 3 Concentration as a function of Si-H band intensity for BTMS standard solutions recorded at various angles of incidence: (+) 45°; (△) 50°; (○) 55°; (+) 60°

The latter varies with wavenumber as well as optical effects at the sample–ATR crystal interface[13]. This issue is particularly important for strong bands which may have a different ATR response to the corresponding transmission measurements. For these reasons we have utilized Dignam's approach to account for these effects and to correct the original ATR spectra[14]. Such spectra were used for quantitative analysis.

An inherent drawback of vibrational spectroscopic measurements is a lack of internal calibration methodology. Because quantitative analysis of i.r. spectra requires an internal calibration curve, the first step is to construct such a curve. In our case, this was achieved by measuring the ATR spectra of homogeneous liquid standards containing 0.1–0.32 M BTMS and plotting the Si-H intensity as a function of concentration. Liquid PDMS resin was used as the solvent since it has no absorption in the Si-H stretching or bending regions.

In an effort to establish the difference between the raw and transformed spectra, the raw band intensities of the Si-H bands obtained from the polarized ATR spectra of the BTMS solutions before KK transformations were employed and are plotted as a function of concentration in *Figure 3*. It should be noted that in ATR experiments the crystal coverage and refractive index of the standards were constant, giving a linear dependence between BTMS concentrations and band intensity for a fixed angle of incidence, such as illustrated in *Figure 3*. However, since the plasma-treated samples may have non-uniform crystal coverage or different refractive indices, the calibration curves shown in *Figure 3* are not directly usable to determine the Si-H concentration. Although the crystal coverage and refractive index changes of the plasma-treated samples mean that *Figure 3* cannot be used as a calibration curve, these factors are accounted for when the spectra are subjected to KK transformation. *Figure 3* also shows that for the standards with a common refractive index and crystal coverage, the band intensities increase with a decreasing angle of incidence. This is expected since the spectra obtained at greater angles of incidence contain information from a thinner surface layer and fewer reflections. This is reflected in a smaller effective sample thickness being analysed at larger angles and therefore, the observed angle of incidence dependence. However, 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. *Figure 4* illustrates the effect of the KK transformation on the data presented in *Figure 3* and, as predicted, the plots are linear and superimposed. A slight deviation of the 60° plot is most likely attributed to random polarization effect. This effect increases as the angle of incidence deviates away from the angle that allows light to pass perpendicularly into the crystal end face. In our experiments this angle was 45° and although the slopes may slightly deviate from the ideal 45°, each line has a linear correlation coefficient of >0.996 and is therefore suitable for determining the Si-H concentration of the gas/plasma-treated PDMS elastomers using ATR spectra recorded at the corresponding angles of incidence.

Although the plots presented in *Figure 4* appear to be suitable as a calibration curve, it should be kept in mind that they were obtained for chemically and conformationally similar liquids. Because our goal is to quantify Si-H functionality on the PDMS elastomer surface, it is important to test and estimate the accuracy of the calibration curves shown in *Figure 4*. In an effort to do so, ATR *FT*i.r. spectra of methylhydro-dimethylsiloxane copolymer were collected. First, the calculated concentrations were obtained using KK transformed spectra to obtain the linear absorptivity (β) values for the Si-H peak. The calculated concentration can be directly obtained from the calibration curves in *Figure 4*. *Table 1* shows the calculated results and compares them to the actual Si-H concentrations of the copolymer. These results show good precision with a deviation of 0.01 M between the four calculated values. Furthermore, the accuracy of the calculated values is high with the deviations varying between 0.01 M and 0.02 M from the actual concentration.

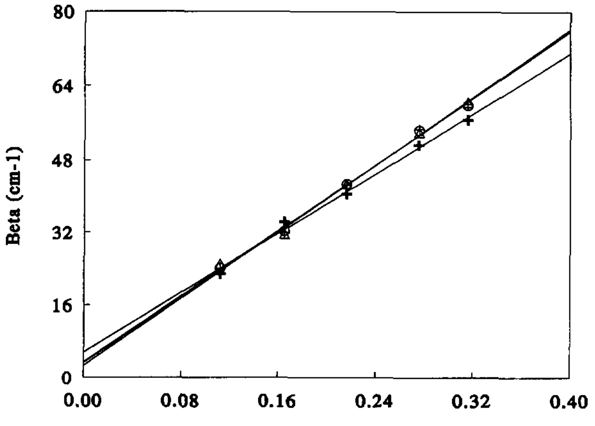


Figure 4 Plot of BTMS concentrations as a function of Si-H band intensity after KK transformation recorded at various angles of incidence. For symbols see *Figure 3*

Table 1 PDMS samples with known Si-H concentration

Effective angle (deg)	β	Actual Si-H concentration (M)	Calc. Si-H concentration (M)
45.00	21.18	0.10	0.08
47.10	22.18	0.10	0.08
49.28	22.96	0.10	0.09
51.24	24.78	0.10	0.09

Table 2 PDMS samples with different crystal coverage

Effective angle (deg)	β	Actual Si-H concentration (M)	Calc. Si-H concentration (M)
45.00	45.28	0.21	0.20
47.10	45.09	0.21	0.20
49.28	46.40	0.21	0.21
51.24	46.41	0.21	0.21

As indicated earlier, the calibration curve should theoretically be independent of the ATR crystal coverage. To test this relationship, ATR *FT*i.r. spectra were obtained for a standard with the crystal coverage reduced by ~35%. Again, the calculated concentration was obtained by the same method as described for methylhydro-dimethylsiloxane. The results are illustrated in *Table 2* and indicate that there is good agreement between actual and calculated concentrations of the Si-H species. Therefore, the calibration curve is indeed independent of the crystal coverage with a degree of accuracy having a maximum deviation of 0.01 M. The same precision is obtained for all calculated concentrations.

At this point, let us go back to the main theme and use the calibration curve constructed in *Figure 4* to determine the Si-H concentration of the gas-/plasma-treated PDMS elastomers containing 20% silica. After gas/plasma treatment, ATR *FT*i.r. spectra were collected at the angles of incidence corresponding to the calibration curve angles, KK transformed to obtain β values, and the Si-H concentrations were calculated. These data, along with the depth of penetration for each angle of incidence, are shown in *Table 3*. It appears that when going from 0.6 to 0.8 μm into the PDMS surface, the concentration of Si-H species changes by ~25%, indicating that at the greater depths there are most likely Si-H functionalities that may potentially be accessible for bonding. It should be kept in mind that the concentrations shown in *Table 3* are not local concentrations at a given specific depth, but average concentrations of the entire depth of penetration

Table 3 Si-H concentration on plasma-treated PDMS at various depths of penetration

Effective angle (deg)	β	Depth of penetration (μm)	Calc. Si-H concentration (M)
45.00	31.04	0.807	0.15
47.10	31.76	0.719	0.16
49.18	35.24	0.657	0.18
51.24	37.36	0.611	0.19

Table 4 Si-H concentration on plasma-treated PDMS with varying amounts of silica filler

Effective angle (deg)	β	Silica content (wt%)	Calc. Si-H concentration (M)
49.18	5.80	40	0.01
49.18	35.90	20	0.18
49.18	81.72	0	0.43

Table 5 Energies of methyl silicone bonds

Species	Energy (eV)
Si-C	3.3
Si-O	4.7
Si-H	4.3
C-H	3.3

thickness. According to the data presented in *Table 3*, the gas/plasma treatment of PDMS is more effective at the top surface, as demonstrated by the increase of Si-H concentration at shallower depths. This observation is known for other plasma treatment methods and reinforces the consistency of the ATR *FT*i.r. methodology employed in this study.

Since the presence of silica is necessary to impart mechanical properties of PDMS, it is useful to understand how the silica filler might affect Si-H formation during plasma treatment. PDMS samples containing 0, 20 and 40 w/w% silica filler were plasma treated using the experimental parameters outlined earlier and ATR *FT*i.r. spectra were collected. *Figure 5* shows the Si-H stretching region and indicates that increasing the amount of silica filler in the PDMS corresponds to a decrease in the Si-H surface functionalization. The Si-H concentration for these samples was quantified as described previously, and the results are shown in *Table 4*.

Although, at this point the mechanism for the Si-H formation is not fully understood, it is possible to discuss possible reaction paths for the Si-H formation based on the above observations, the bond energies of methyl silicones shown in *Table 5*[15], and spectroscopic analysis. Based on the bond energies given in *Table 5*, it is believed that the lower Si-C and C–H bond energies will cause these bonds to be preferentially cleaved by the excited gas/plasma particles. This would result in a decrease of the band intensities due to Si–C and C–H species, such as illustrated in *Figure 2*. This process would yield reactive silicon sites on the surface polymer backbone as well as highly reactive carbon and hydrogen fragments in the gas phase. If indeed such a scenario is possible, the

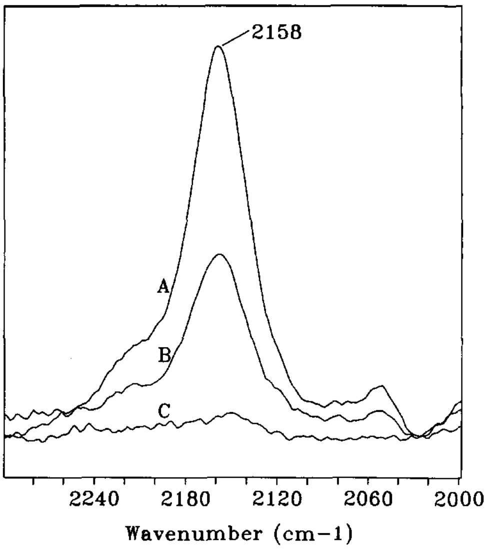
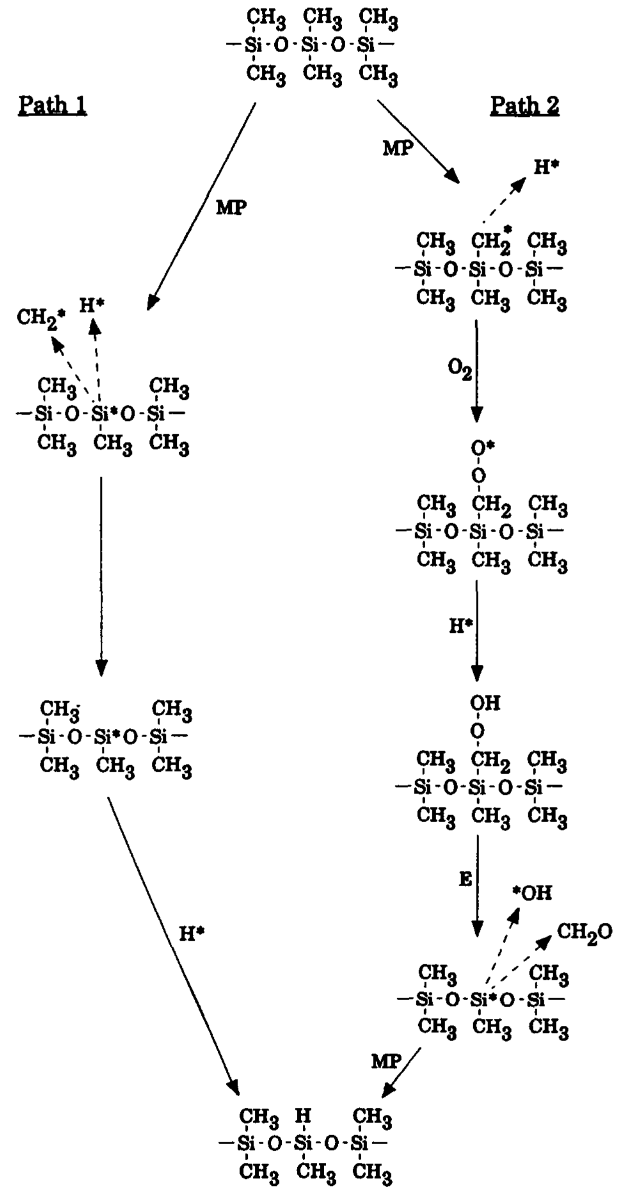


Figure 5 ATR *FT*i.r. spectra in the Si-H bending region for PDMS with: (A) 0% silica; (B) 20% silica; (C) 40% silica



MP designates microwave plasma energy
*** designates a reactive species**

Figure 6 Proposed reaction paths for Si-H formation on PDMS elastomers during plasma treatment reactive silicon sites may recombine with the reactive hydrogen species. This is supported by the appearance of Si-H bands in the ATR *FT*i.r. spectra of the plasma-treated PDMS shown in *Figure 1*. Similar Si-H formation can be found in the studies of plasma polymerization of organosilicon monomers[16–18]. For example, the use of ATR *FT*i.r. spectroscopy in recent studies[19,20] of hexamethyldisiloxane (HMDS) plasma polymerization has shown marked similarities to the results discussed in this study. They include the appearance of Si-H groups and a significant reduction of various methyl stretching and bending modes.

A schematic representation of a tentative reaction path for Si-H formation which seems to be consistent with our current results is shown in *Figure 6* by path 1. This path illustrates that the fragments cleaved from the polymer are primarily CH_3 groups that may further dissociate in the gas phase to various hydrocarbon and hydrogen fragments. In addition, the number of hydrogen species in the gas phase may be further increased by cleavage of hydrogen from carbon atoms which remain attached to the polymer chain. This excess of hydrogen species compared to carbon species would lead to a statistically higher probability for hydrogen to react with silicon. Although there is no direct evidence that molecular oxygen is involved in the reaction, reaction path 2 in *Figure 6* should be considered. It is known that crosslinked silicone elastomers are gas permeable and capable of trapping gases such as oxygen. If residual oxygen diffuses out of the network during plasma treatment, its presence in the plasma may lead to an oxidative degradation type reaction, as shown in path 2. This type of oxidative degradation is known for methyl silicone fluids[21]. Although we realize that additional studies are required to further justify or disprove the proposed reaction paths, at this point our main focus is on quantitative analysis of the Si-H groups produced as a result of the gas/plasma reactions.

Conclusions

In this study we have shown that using the strong band approach for the treatment of ATR *FT*i.r. bands due to Si-H, a calibration curve can be constructed for quantitative analysis of the surface species. The calibration plots are linear for all angles of incidence and, as predicted by the theory, superimposable. Most importantly, the calibration curves are accurate when tested against materials with known Si-H concentration. This allows the determination of the surface Si-H concentration produced as a result of gas/plasma treatments of PDMS elastomers. Recently the above analysis has been extended to both weak and strong bands[22,23].

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