Hydroxylation of Polymethylsiloxane Surfaces by Oxidizing Plasmas

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Synopsis

The reaction of a radiofrequency-excited oxygen plasma with the surfaces of cured and uncured polymethylsiloxane produces intense hydroxylation of the surface region as followed by FMIR spectroscopy. Characteristic infrared features indicative of intra- or intermolecular hydrogen bonding are evident. Plasma oxidation differs markedly from thermal oxidation processes. Reactions of polymethylsiloxane with nitrogen and air plasmas were also investigated and compared to corona reactions of oxygen, nitrogen, and air. In air corona, nitrogen moieties appear to be introduced. The behavior of polymethylsiloxane surfaces in oxidizing acids is also described.

INTRODUCTION

The stability of polymers in various oxidizing environments has been a subject of exhaustive investigation. Problems associated with weatherability, upper atmosphere stability, adhesion, printability, etc., have all generated research into oxidative behavior of polymers.[1] Most of the attention has been directed toward hydrocarbon backbone or heterocyclic polymers and volume oxidation processes studied in higher temperature ranges. Little attention by comparison has been given to oxidation of nonhydrocarbon backbone polymers, processes in which the oxidation is limited only to the surface region and which are attended by lower temperature, ca. 25°–200°C.

The present work describes the nature of plasma and corona reactions ensuing at the surface of polymethylsiloxane. Such reactions are usually limited only to the surface region and differ greatly from thermal oxidation processes. The reaction of atomic oxygen with a variety of polymers has been studied by Hansen[1] employing a radiofrequency-excited oxygen plasma. Although elastomers were investigated, silicone materials were not included in this study. Investigators have spoken of "atomic oxygen" reactions in these types of studies; however, it must be remembered that directly within the plasma glow one will have a multiplicity of species. With oxygen plasmas, for example, the following species have been identi-

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fied: O^+, O_2^+, O^-, O_2^-, $O(^3P)$, $O_2(^1\Delta_g)$, and free electrons. Depending on the choice of plasma parameters, such as electric field strength and pressure, impurity or contaminant gases (some of which are derived from reaction products), and wall effects, the concentration of ions and electrons will vary from 10^{11} to 10^{12} cm^{-3}, while the concentrations of the neutral species $O(^3P)$ and $O_2(^1\Delta_g)$ are several orders of magnitude greater, 10^{15} to 10^{16} cm^{-3}. Properly, one would like to know the relative contributions of each species to the oxidation of polymers. Such measurements entail great difficulties. Some insight into this problem can be derived from mass spectrometric ion–molecule reaction studies.

The plasma does not only contain ionic and neutral species but also contributions from photochemical processes. Depending on the plasma chemistry occurring, ultraviolet emissions of varying energies will also be taking place. The ultraviolet effects may contribute to the reaction processes as well.

Thus, the plasma medium can be quite complex if every mode of interaction is considered. It is true, however, that in an oxygen plasma, the primary reactions will be associated with $O(^3P)$ and $O_2(^1\Delta_g)$. The farther away the polymer surface is from the direct generation of the plasma, the less will be the ionic influence, since the life times of ions are shorter than those of the neutral species.

EXPERIMENTAL

Radiofrequency (RF) Equipment and Plasma Experiments

The RF equipment in this study is the same as that described previously[2] for the addition of amino groups to polymer surfaces. The reactor geometry has also been described recently.[3] The samples, either cured or uncured, were flat 0.5 × 1.5-in. films, $\sim^1/_{16}$ in. thick, and were situated approximately 7 in. from the capacitive exciter region.

Corona Experiments

The coronas of air, oxygen, and nitrogen were produced at 1 atm at the tip of a Telsa coil. Samples were rotated $^1/_4$ in. below the stationary tip of the coil. A visible glow and striations emanated from the tip and impinged on the sample surfaces.

Oxidizing Acid Treatments

Either nitric or dichromic acid immersions were employed at elevated temperatures for given times.

Materials

The silicone materials investigated are Dow Corning formulations designated S2000 and S2000U, for the cured and uncured materials, respectively. The curing agent is 2,4-dichlorobenzoyl peroxide, 1.6% of the
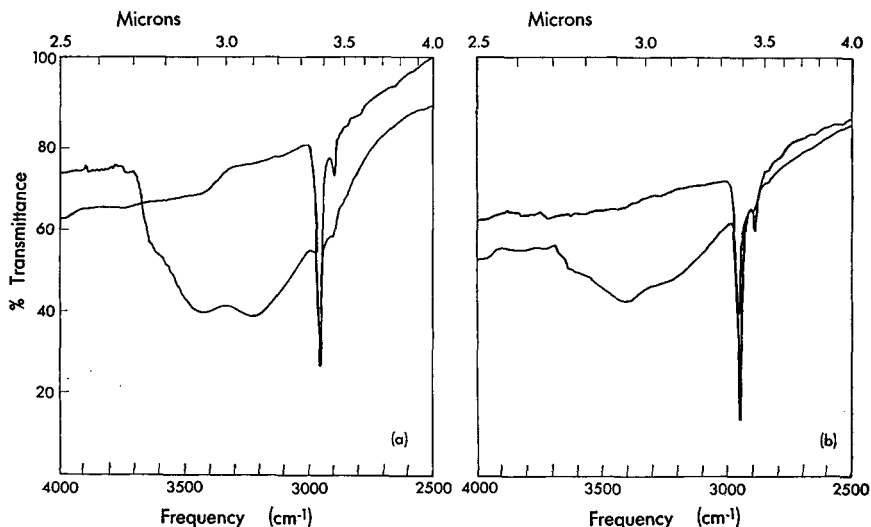
Fig. 1. Infrared spectrum of (a) cured and (b) uncured polymethylsiloxane surfaces showing hydroxylation in the 3000–3700 cm^{-1} range over the reference untreated polymer, which shows no absorption in this region.

formulation by weight. Formulation S2000 consists of 0.14 mole-% of methyl vinyl substituents on the silicon atoms. The remainder of the substituents are methyl groups.

Gases utilized and stated purities are: oxygen, 99.95% min. (Matheson); nitrogen, 99.997% min. (Matheson).

Infrared Spectroscopy

A Perkin-Elmer 237B spectrophotometer with internal reflection optics (FMIR), 25 reflections, covered the range 2.5 to 16 μ. Care was taken to insure that the FMIR crystals were cleaned and free of contaminants between runs. Initial experience indicated that these silicone materials block and readily contaminate the KRS 5 crystal surfaces after the oxygen treatments.

RESULTS

Plasma Experiments

The infrared spectra of cured and uncured polymethylsiloxane are shown in Figures 1a and 1b over the range of 2.5 to 4 μ. The spectra agree excellently with published spectra of polymethylsiloxane materials over the full range of 2.5 to 16 μ.[4] After oxygen plasma exposure, the great absorption in the range 3000 to 3700 cm^{-1} is evident. One sees two broad bands with maximum intensity at approximately 3225 and 3425 cm^{-1} for both the cured and uncured samples. The exposure times to oxygen plasma were 3 hr at 200 watts RF power and 2 hr at 100 watts RF power for the
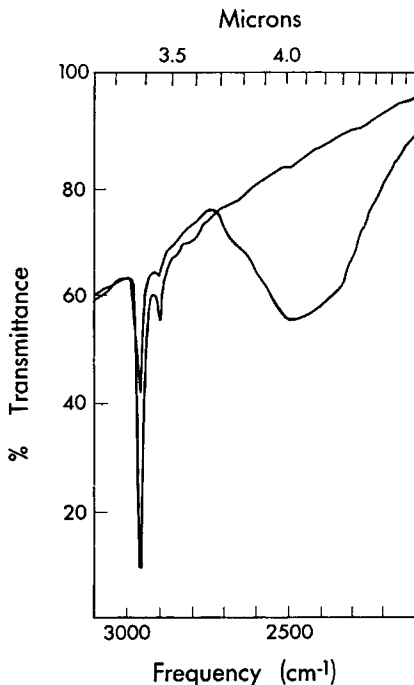
Fig. 2. Infrared spectrum showing shift of the hydroxyl-absorbing region on deuterium substitution.

cured and uncured samples, respectively. The power was lower in the case of the uncured sample because of its lower thermal stability. Both types of samples were exposed to a 1.0 torr plasma.

Samples of RF oxygen plasma-treated silicone materials were placed in D_2O. Although exchange was quite rapid, the samples were permitted to remain in D_2O for 1 hr at 50°C. Control samples not exposed to plasma experienced the same conditions in D_2O. The control sample spectrum was unchanged from that of the reference spectrum of samples not pre-treated in any manner. The hydroxylated samples showed a pronounced shift of approximately 900 cm^{-1} (see Fig. 2). This shift is common for —OD versus —OH adsorption[5] and indicates that the exchange process takes place between hydroxyl and deuteroxyl groups. Spectroscopic studies in pure silica[6] and poly(vinly alcohol)[7] indicate that hydroxyl groups readily exchange with deuterium oxide.

To insure that the changes in the spectrum are due to plasma effects alone, the samples of silicone material were exposed to boiling water for several hours and at room temperature in water for several days. After allowing the samples to dry, the FMIR spectra did not indicate permeation of water to any detectable extent into the surface region. Thus moisture adsorption during sample transfer, sample aging effects, etc., can be elimi-

nated from contributing to the infrared results in Figures 1a and 1b.   There
is some indication in oxygen plasma-treated samples of a band increase at
~ 1630 cm^{-1} above that of the reference spectrum of the untreated sample
material.   This could result from the formation of some water via surface
reactions due to the plasma or the enhancement of unsaturation in the
surface region.   However, on deuteration, that particular band did not
move.

The effects of vacuum thermal heating were also investigated.   The
samples were heated without the plasma to the temperatures they attain
in a plasma, 50°–80°C, and, during the residence times covered by this
study, in a 1.0-torr vacuum of oxygen.   No difference in the spectra was
observed due to possible decomposition of the curing agent, any other
low-level polymer additives, or the polymer itself under these vacuum
thermal conditions.

It appears that the reaction of oxygen plasma with polymethylsiloxane
develops a high density of —OH groups on the surface of the polymer.
Since the band at 2960 cm^{-1} associated with the aliphatic stretching modes
is also present without significant decrease in intensity, it is suggested
that —OH formation is predominantly of a —CH$_2$OH structure rather
than —SiOH, although some of the latter undoubtedly forms as well.

Heating a sample of hydroxylated cured polymethylsiloxane for 6 hr
at 110°C produced a decrease in the intensity of the —OH bands but not a
significant reduction of the aliphatic modes.   The reduction in this band
intensity results from the probable elimination of water via —OH group
condensation.   This can take place intermolecularly, forming ether cross-
link units between chains, or intramolecularly, in which cyclic structures
could be formed.

The Si—CH$_3$ deformation band at 1260 cm^{-1} is decreased in intensity
after oxygen plasma exposure.   However, the band intensity remaining
indicated that not all the —CH$_3$ groups have been affected by the plasma.

Reaction of polymethylsiloxane with active nitrogen at 100 watts for
for 2 hr at 1.0 torr produced no noticeable change in the infrared spectrum
over the range of 2.5 to 16 microns.   However, this does not preclude the
possibility of some crosslinking processes from occurring.[8]   The infrared
absorption for such crosslinked units is obscured by the intense and broad
absorptions in the range 1000–1100 cm^{-1} due to Si—O linkages.   A plasma
of the ambient air composition produced intense absorption in the 3000–
3700 cm^{-1} range having identical features to the pure oxygen plasma re-
sults.   Again, two bands appeared at 3225 and 3425 cm^{-1}.   Otherwise,
the remaining spectral features were unchanged, except in the case of the
cured polymer where band broadening appeared in the 1000–1250 cm^{-1}
range.   This could be indicative of greater crosslinking processes occurring,
since $\equiv$SiCH$_2$CH$_2$Si$\equiv$ units will absorb in this region at 1134 and 1058
cm^{-1}.[9]   In an air RF plasma, nitrogen oxides will form,[10] but these species
apparently do not add to the structure of the polymer in the form of nitro
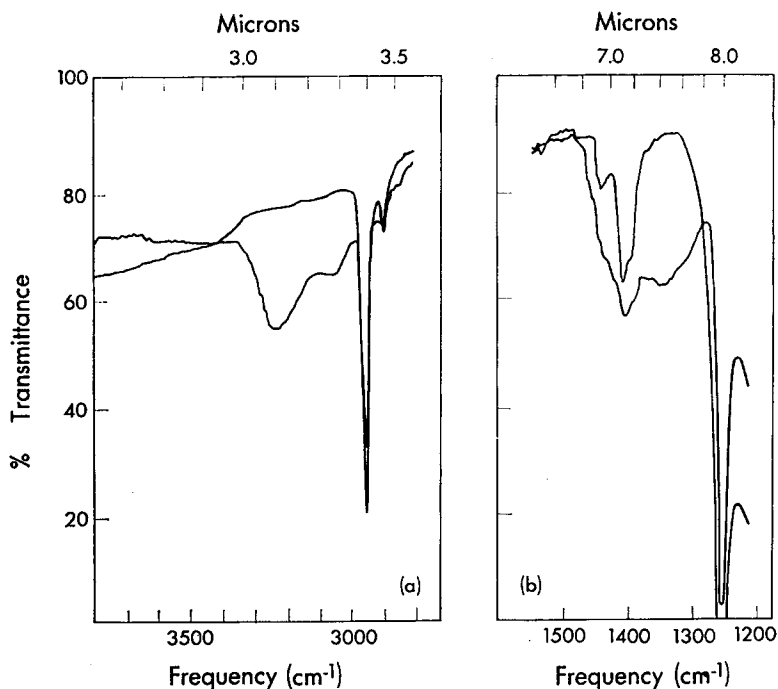groups, in contrast to the case of air corona to be discussed later.

Fig. 3. Infrared spectra showing (a) the hydroxyl absorption bands after air corona oxidation; (b) the apparent incorporation of a nitrogen-containing group absorbing at 1335 cm^{-1} into the polymer surface.

Corona Experiments

The pure oxygen corona experiment for a 2-hr exposure time produced results very similar to air or oxygen RF plasma exposure: bands appearing at 3225 and 3425 cm^{-1}; however, the 3225 cm^{-1} band was much less intense than the 3425 cm^{-1} band.

A pure nitrogen corona treatment for 2 hr did not produce any apparent change in the infrared spectrum. Nonetheless, crosslinking processes may be occurring.

Air corona produced some interesting features not seen in air RF plasma treatments. Figure 3a shows the portions of interest in the infrared spectra for samples treated 2 hr. In the 3000–3700 cm^{-1} range, hydroxyl development is quite evident; however, low-frequency bands at 3225 cm^{-1} and 3050 cm^{-1} appear, and the 3425 cm^{-1} band is missing. In the 1200–1600 cm^{-1} range (see Fig. 3b), a new band at 1335 cm^{-1} develops, due to a nitrogen oxide species introduced into the polymer surface structure. The band frequency is lower than is usually observed for —NO$_2$ groups in polymers.[11] Moreover, there is no indication of any asymmetric stretching mode at higher frequencies, ca. 1630 cm^{-1}. The 1410 cm^{-1} band is considerably broadened, which could be due to the asymmetric band appearance at much lower frequencies.

Oxidizing Acid Experiments

Both dilute nitric acid and dichromic acid produced an indication in the infrared spectrum that surface hydroxylation is taking place to some modest extent. The infrared spectrum indicated a broad but weak absorption in the range 3200–3400 cm^{-1}. Samples held 2–3 hr in these acid media at either room temperature or at 60°–65°C turned a very dark brown in the dichromic acid medium and yellow in the case of dilute nitric acid. Plasma and corona treatments produced no color changes on the surface of the silicone materials.
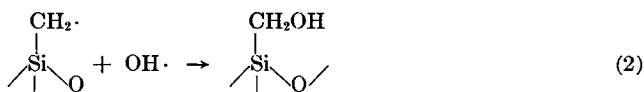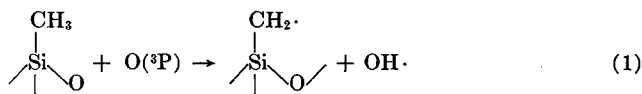
DISCUSSION

The infrared spectra for RF oxygen plasma- and corona-treated silicone materials indicate a high density of hydroxyl groups and extensive hydrogen bonding. This oxidation process is in marked contrast to thermal oxidation of methylsilicones where stripping of methyl groups and their oxidation to formaldehyde occur.[12] In the case of corona treatment, the localized temperature at the plasma surface region could be quite high compared to treatment by the nonequilibrium RF plasma. Stripping of methyl groups might be more extensive with corona treatments, producing predominantly ≡Si—OH groups. The frequency of the —OH band at 3425 cm^{-1} is consistent with the observation on poly(vinyl alcohol),[4] where the intensity and breadth of absorption at about 3400 cm^{-1} is attributed to a considerable amount of hydrogen bonding. Because of the number of different possible configurations for hydrogen bonding in the siloxane structure, a distribution of hydrogen bond strengths is expected, which will broaden the absorption bands considerably.

The development of hydroxylated surfaces appears to be quite facile and somewhat independent of the mode of oxidation by the use of plasmas or coronas. Recently, the photochemical decomposition of polymethylsiloxane was investigated.[8] In that study, ultraviolet irradiation formed ≡SiCH₂Si≡ or ≡SiCH₂CH₂Si≡ crosslink units in the polymer, depending on the radiation wavelength. When the polymer was irradiated with a germicidal mercury vapor lamp in the presence of air, an abundance of —OH groups were produced. However, the aliphatic stretching frequency at 2960 cm^{-1} decreased markedly with the appearance of the broad —OH band centering at about 3330 cm^{-1}. There appeared to be no evidence for a double band in this spectral region as in the plasma- and corona-treated samples (Figs. 1a and 1b). The authors concluded from that photochemical study that the —OH groups are predominantly bonded to the silicon atom directly, Si—OH. In the plasma and corona cases, the intensity of the aliphatic stretching modes indicates that no significant reduction of the C—H bonds has occurred. Thus it appears that —OH group development is predominantly associated with ≡SiCH₂OH structures, with little from ≡Si—OH entities. There is undoubtedly a certain

fraction of —CH_3 groups remaining which has not been attacked by the excited oxygen species.

The development of $SiCH_2OH$ structures can take place by the following sequence:

$$\begin{array}{c} CH_3 \\ | \\ /Si\diagdown_O \end{array} + O(^3P) \rightarrow \begin{array}{c} CH_2\cdot \\ | \\ /Si\diagdown_O/ \end{array} + OH\cdot \qquad (1)$$

$$\begin{array}{c} CH_2\cdot \\ | \\ /Si\diagdown_O \end{array} + OH\cdot \rightarrow \begin{array}{c} CH_2OH \\ | \\ /Si\diagdown_O/ \end{array} \qquad (2)$$

Crosslinking processes from radical recombination[12] will occur via

$$2 \equiv SiCH_2\cdot \rightarrow \equiv SiCH_2CH_2Si\equiv \qquad (3)$$

and

$$\equiv SiCH_2\cdot + \equiv Si\cdot \rightarrow \equiv SiCH_2Si\equiv \qquad (4)$$
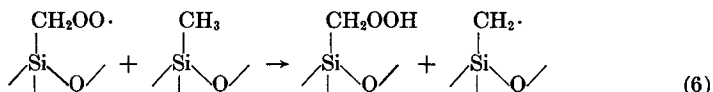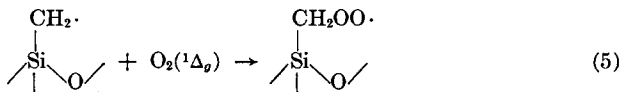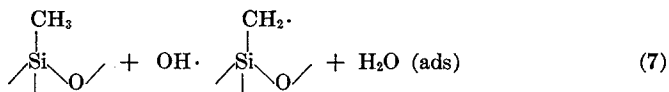
The possible stripping of methyl groups to form $\equiv Si$—$OH + CH_2O$ may be occurring to some extent. However, formaldehyde in the product gases could not be detected; this compound which may be formed was probably also subjected to secondary gas-phase reactions with the excited oxygen species.
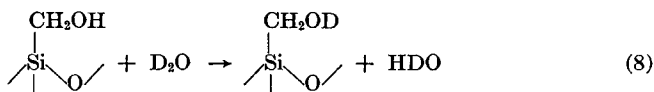
Some hydroxylation may occur via hydroperoxide formation,[13] due to reactions of —CH_3 groups with singlet oxygen:

$$\begin{array}{c} CH_2\cdot \\ | \\ /Si\diagdown_O/ \end{array} + O_2(^1\Delta_g) \rightarrow \begin{array}{c} CH_2OO\cdot \\ | \\ /Si\diagdown_O/ \end{array} \qquad (5)$$

$$\begin{array}{c} CH_2OO\cdot \\ | \\ /Si\diagdown_O/ \end{array} + \begin{array}{c} CH_3 \\ | \\ /Si\diagdown_O/ \end{array} \rightarrow \begin{array}{c} CH_2OOH \\ | \\ /Si\diagdown_O/ \end{array} + \begin{array}{c} CH_2\cdot \\ | \\ /Si\diagdown_O/ \end{array} \qquad (6)$$

Any water that may form during the plasma experiments on the polymer surface, for which there is some slight indication in the infrared 1630–1650 cm^{-1} region, could arise by the following reaction:

$$\begin{array}{c} CH_3 \\ | \\ /Si\diagdown_O/ \end{array} + OH\cdot \begin{array}{c} CH_2\cdot \\ | \\ /Si\diagdown_O/ \end{array} + H_2O \text{ (ads)} \qquad (7)$$

where hydroxyl radicals are derived primarily by reaction (1). The exchange reactions with D_2O occur rapidly,

$$\begin{array}{c} CH_2OH \\ | \\ /Si\diagdown_O/ \end{array} + D_2O \rightarrow \begin{array}{c} CH_2OD \\ | \\ /Si\diagdown_O/ \end{array} + HDO \qquad (8)$$

With deuterium substitution, there is considerable interaction between deuterium and oxygen to produce broadening similar to —OH hydrogen bond formation. Exchange reactions with other hydrogens, such as those

in methyl groups, are considerably slower, and no shift in —CH absorption frequencies occurred.

Molecular models indicate that the —CH$_2$— group offers a good many more configurational possibilities for the —SiCH$_2$OH structure to hydrogen bond than are available for the Si—OH structure. The double-band absorption feature shown in Figure 1a has been observed in many cases where both intra- and intermolecular hydrogen bonding can occur.[14]

The various structures that can represent hydrogen bonding in siloxanes are shown below:
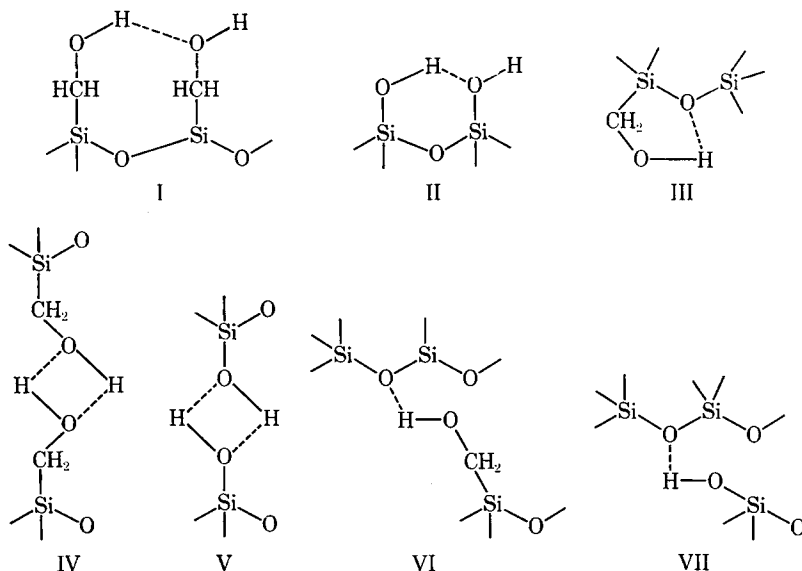
The high and low frequency bands are associated with intramolecular (structures I through III) and intermolecular (structures IV through VII) hydrogen bonding, respectively. Free hydroxyls appear at much higher frequencies (3500 cm^{-1}). The 3425 and 3225 cm^{-1} bands correlate well with intra- and intermolecular hydrogen bond absorption frequencies observed with a variety of organic compounds such as the dihydric alcohols.[14] The spectra of plasma- and corona-treated samples suggest that most of the hydroxyls are bound up in hydrogen-bonded structures and that there is relatively little free —OH concentration. The absorption between 3500 and 3700 cm^{-1} indicates the possibility of some free —OH groups. The separation $\Delta\nu$ between bands of free, intra-, and intermolecular hydroxyl adsorption is a measure of the hydrogen bond strength and has been correlated with the hydrogen bond distance. In general, $\Delta\nu$ will be larger for solids than for concentrated solutions. The separation between bands in hydroxylated surfaces of polymethylsiloxane is approximately 200 cm^{-1}, which is a value in the range found for polymeric alcohols. If a correlation is valid in this case, this separation corresponds to an average O$\cdots$H distance of 1.98 Å in the hydroxylated surface.[14]

It would be of interest to study the surface oxidation characteristics of other polysiloxane materials and compare them to the present case. It is well known that volume oxidation rate processes are dependenet on the structure of the polymer, and the same structure dependence should also be reflected in surface oxidation processes. One could, for example, investigate the effect of phenyl and vinyl groups on the development of surface structures during oxidation.

Note added in proof: Recently M. L. Kaplan and P. G. Kelleher (*Science,* **169,** 1206 (1970)) discussed hydroperoxide formation on *cis*-polybutadiene surfaces by $O_2(^1\Delta_g)$ from a microwave plasma. From this work it should be reasoned that reactions (5) and (6) above may have a more significant role, and the infrared results, Figures 1a and 1b, reflect more —OOH contribution, however in frequency ranges overlapping those due to —OH groups.

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