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Photodecomposition of Polymethylsiloxane

ALVIN D. DELMAN,* MILTON LANDY,† and
BERNARD B. SIMMS, *Naval Applied Science Laboratory,*
Brooklyn, New York 11251

Synopsis

Infrared spectroscopy studies were undertaken to determine the effects of ultraviolet light radiation on a methylsiloxane resin. The results indicate that $SiCH_2Si$ linkages were formed as a result of irradiation at wavelengths above 281 mμ from a xenon arc lamp; on the other hand, Si—OH and $SiCH_2CH_2Si$ linkages were formed instead when the resin was exposed to the lower wavelengths emitted from a mercury vapor lamp. The different effects on the resin induced by the two ultraviolet light sources are attributed to the fact that only the energies from the mercury vapor lamp radiation are sufficient to cause the excitation of oxygen molecules in the air surrounding the irradiated polymer. The excited oxygen molecules prevented the formation of $SiCH_2Si$ structures by interacting with active $\equiv Si^{\cdot}$ units that were formed as a result of Si—C bond rupture to produce Si—OH; $SiCH_2CH_2Si$ linkages were formed as the result of a secondary reaction.

INTRODUCTION

Polysiloxanes are widely employed as protective surface coatings for a variety of specialized applications. Because they have been shown to be highly water repellent and their moisture absorption is generally very low, polysiloxanes have been designed for use as deicing coatings. For example, Baker and co-workers[1] developed a low-torque semifluid polysiloxane grease which was compatible with oil-resistant rubber and resisted the anchorage of ice. Spawn[2] found that a 0.1% polysiloxane solution in the top coat of a refrigerator gave a 30–40% improvement in runoff of water. Andrianov et al.[3] reported that the adhesion of ice to rubber, plastics, and aluminum surfaces coated with varnish was reduced by the application of a film of methyl, ethyl, or isoamyl polysiloxane. More recently, it has been shown that the durability of the ice-phobic effectiveness of polysiloxanes is limited to only short time periods because of the degradation of the coating by solar radiation.[4] To obtain a better understanding of this phenomenon, a study was undertaken to determine the effects of accelerated weathering on the molecular structure of a polysiloxane resin. Preliminary findings of this study were presented previously;[4] results are reported in more detail in this article.

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* The Wool Bureau, Inc., Woodbury, New York 11797.

† Institute for Fibres and Forest Products Research, P.O. Box 8011, Jerusalem, Israel.

EXPERIMENTAL

Material

The methylsiloxane resin employed in this investigation was prepared by evaporating the solvent from a xylene solution containing a mixture of methyltrimethoxysilane and cyclic dimethylsiloxane polymers, $[(CH_3)_2SiO]_{4-10}$, having an average molecular weight of approximately 370. Methyltrimethoxysilane hydrolyzed in moist air to form a methylsiloxane network that entrapped the cyclic polymer in the resin matrix.

Accelerated Weathering

Films of the resin on potassium bromide optical crystals were mounted vertically in an Atlas Electric Products Company Weather-Ometer that was modified by replacing the usual twin-carbon arcs with a 6000-W xenon lamp. The samples were exposed for preselected time intervals up to about 1500 hr. To obtain information about the effects of shorter ultraviolet wavelengths on the methylsiloxane polymer, similar resin films on sodium chloride infrared optics were exposed for time periods up to 355 hr to the radiation emitted from a General Electric Company, type G4S11, 4-W germicidal lamp placed 1 in. above the specimens.

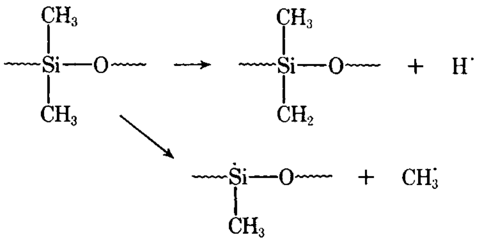
Infrared Spectroscopy

The samples coated on potassium bromide optics were measured over the 2.5–25.0 μ range with a Perkin-Elmer, Model 337, grating spectrophotometer. Infrared absorption spectra of the films cast on sodium chloride crystals were obtained over the 2.5–15.0 μ region with a Perkin-Elmer, Model 137 prism spectrophotometer.

RESULTS

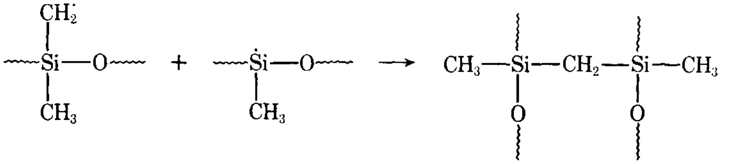
Xenon Arc Lamp Radiation

The infrared spectra of the resin before and after 1524 hr of exposure to the xenon lamp are presented in Figure 1. These data show that, except for the new absorption band appearing at 7.3 μ in the spectrum from the irradiated resin, the spectra are alike. The absorbance at 7.3 μ indicates the presence of $SiCH_2Si$ linkages in the irradiated sample,[5] which may have formed as a result of C—H and Si—C bond cleavage.



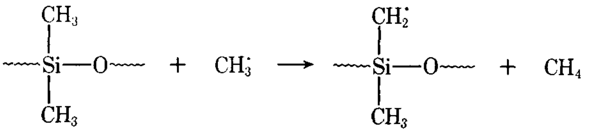
$$\sim\underset{CH_3}{\overset{CH_3}{Si}}-O\sim \;\longrightarrow\; \sim\underset{CH_2}{\overset{CH_3}{Si}}-O\sim \;+\; H^{\cdot} \qquad (1a)$$

$$\searrow\; \sim\underset{CH_3}{\dot{Si}}-O\sim \;+\; CH_3^{\cdot} \qquad (1b)$$



$$\sim\overset{\overset{\textstyle CH_2^{\cdot}}{|}}{\underset{\underset{\textstyle CH_3}{|}}{Si}}-O\sim \;+\; \sim\overset{\cdot}{\underset{\underset{\textstyle CH_3}{|}}{Si}}-O\sim \;\longrightarrow\; CH_3-\overset{\wr}{\underset{\underset{\underset{\textstyle \wr}{\textstyle O}}{|}}{Si}}-CH_2-\overset{\wr}{\underset{\underset{\underset{\textstyle \wr}{\textstyle O}}{|}}{Si}}-CH_3 \qquad (1c)$$

It is also possible that the $\equiv SiCH_2^{\cdot}$ radical formed because $CH_3^{\cdot}$ abstracted a hydrogen atom from a methyl group on the same or a neighboring molecule. Bovey[6] indicates that this is the main reaction when methylsiloxane polymers are initially exposed to high-energy radiation. It is suspected from the ultraviolet radiation studies of Zhuzhgov and co-workers[7] that reactions (1) and (2) probably occur concurrently.



$$\sim\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{Si}}-O\sim \;+\; CH_3^{\cdot} \;\longrightarrow\; \sim\overset{\overset{\textstyle CH_2^{\cdot}}{|}}{\underset{\underset{\textstyle CH_3}{|}}{Si}}-O\sim \;+\; CH_4 \qquad (2)$$

Of course, it is conceivable that the reactive decomposition products could have combined to produce Si—H, Si—CH_2CH_3, Si—CH_2CH_2-Si, and Si—Si structures. The absence of new absorption bands for the first three structures at 4.4–4.8,[8] 13.5–13.6,[9] and 8.85 μ,[10] respectively, indicates that such molecular configurations were not formed when the polymer was exposed to radiation from the xenon arc lamp. Since the vibration modes of Si—Si bonds do not occur in the 2.5–25.0 μ region of the infrared spectrum, it cannot be ascertained from these data whether such linkages were produced during the irradiation process. It might be inferred from the studies by Miller,[5] however, who did not observe the formation of Si–Si crosslinks after exposing methylsiloxanes in the solid state to high-energy radiation, that such linkages were also not produced by the xenon arc lamp.

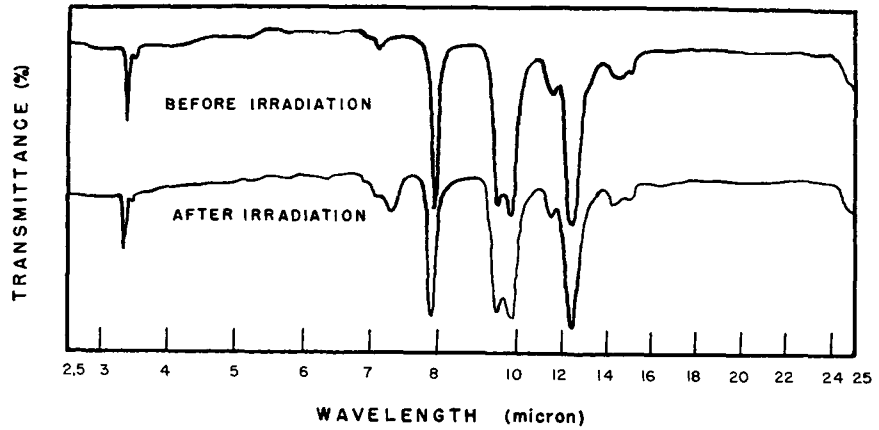


Fig. 1. Infrared spectra of untreated and xenon arc lamp-irradiated resin.

Figure 2 shows the change in intensity of the 7.3 μ absorption band as a function of time. It is evident from these data that the growth of $SiCH_2Si$ bonding is directly proportional to the amount of irradiation. Zhuzhgov and co-workers,[7] employing electron spin resonance (EPR) techniques, found that $CH_3\cdot$ and $\equiv SiCH_2\cdot$ radicals are produced in a linear relation to the radiation dose when polymethylphenylsiloxane is initially exposed to an ultraviolet light source. Although they were unable to detect the presence of $\equiv Si\cdot$ radicals in the EPR spectra of the polymer, they suggest that its absence is probably due to the occurrence of a reaction involving the recombination of radicals. It seems reasonable to assume from this study that the recombination occurred as shown in reaction (1c), wherein a $\equiv Si\cdot$ fragment interacted with a $\equiv SiCH_2\cdot$ radical that was produced as a result of ultraviolet radiation induced C—H bond rupture or through the abstraction of hydrogen from $\equiv SiCH_3$ by a $CH_3\cdot$ radical.

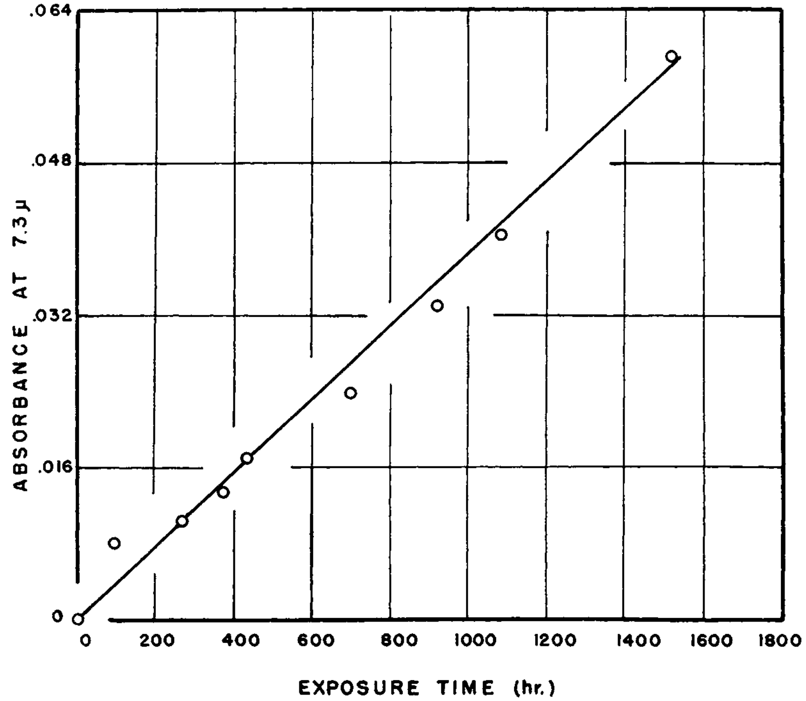


Fig. 2. Effect of irradiation on absorbance at 7.3 μ.

Mercury Vapor Lamp Radiation

The infrared spectra of the methylsiloxane resin, before and after 355 hr exposure to the ultraviolet wavelengths emitted from the mercury arc lamp, are presented in Figure 3. It is evident from a comparison of these data with the infrared spectra shown in Figure 1 that the resin underwent more structural changes due to exposure to the lower frequencies of ultraviolet radiation from the mercury vapor lamp than because of the higher wavelengths emitted by the xenon arc lamp.

The spectrum of the irradiated resin exhibits a new absorption mode at 3.0 μ that is associated with Si—OH bonding. The characteristic Si—CH_3 band at 7.94 μ appears to be less intense than in the spectrum from the original polymer. The strong Si—O frequencies in the 9–10 μ region are less sharp, particularly at 9.18 μ, and broader in the irradiated resin spectrum than in that from the untreated product. The Si—CH_3 band at 11.55 μ in the spectrum of the original polymer has been replaced by two absorption modes at about 11.15 and 11.75 μ that are attributed to the Si—OH structure.[8,11] The broad Si—CH_3 absorption band at 12.5 μ in the spectrum from the original polymer is much less intense and appears as a doublet at 12.5 and 12.78 μ in the spectrum of the irradiated resin. The band at 12.78 μ is probably associated with the Si—OH linkage.[12] The spectrum exhibited no evidence of the production of Si—H, $SiCH_2CH_3$, and $SiCH_2Si$ structures as a result of radiation from the mercury vapor lamp.

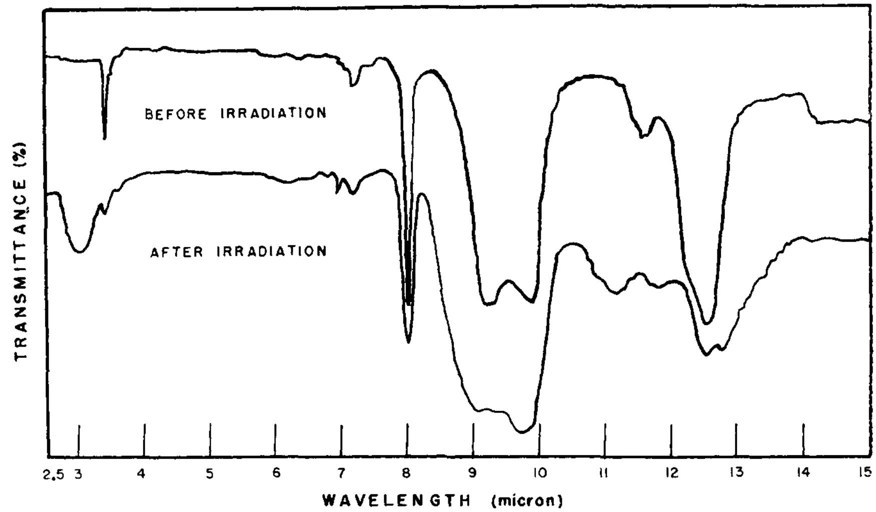


Fig. 3. Infrared spectra of untreated and mercury vapor lamp-irradiated resin.

Figure 4 shows the increase in the intensity of the 3.0 μ band as a function of irradiation time. It is evident from the results that the rate of production of Si—OH bonds was quite rapid at first and then leveled off in almost a linear manner. It is interesting to note that, as in the case of the 355-hr treated sample, the infrared spectrum of the resin after 50 hr exposure contained Si—OH vibration modes at 11.15 and 11.75 μ instead of the Si—CH_3 band at 11.55 μ in the original polymer spectrum.

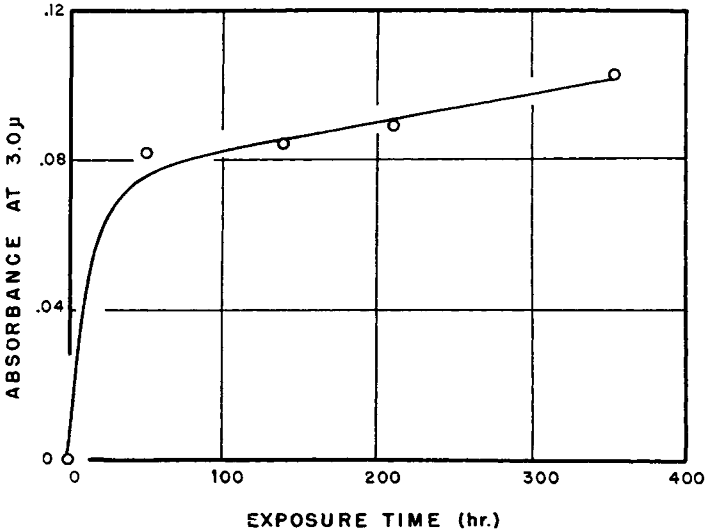
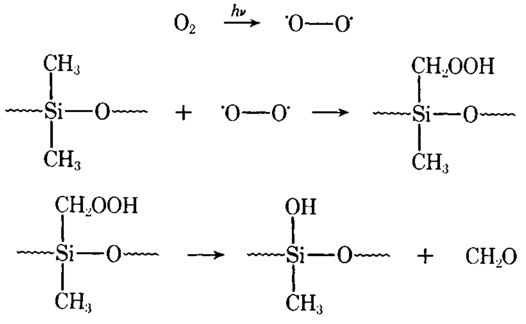


Fig. 4. Effect of irradiation time on absorbance at 3.0 μ.

The silanol structure might have formed because of the ultraviolet radiation-induced oxidation and cleavage of methyl groups [eqs. (3)].



$$O_2 \xrightarrow{h\nu} {}^{\cdot}O—O^{\cdot} \qquad (3a)$$

$$\sim\underset{CH_3}{\overset{CH_3}{Si}}—O\sim + {}^{\cdot}O—O^{\cdot} \longrightarrow \sim\underset{CH_3}{\overset{CH_2OOH}{Si}}—O\sim \qquad (3b)$$

$$\sim\underset{CH_3}{\overset{CH_2OOH}{Si}}—O\sim \longrightarrow \sim\underset{CH_3}{\overset{OH}{Si}}—O\sim + CH_2O \qquad (3c)$$

This series of decomposition reactions explains, at least partially, why the Si—CH$_3$ absorption band at 7.94 μ was less intense after irradiation of the resin. Figure 5 shows the change of intensity at 7.94 μ in relation to radiation time. The shape of the curve is the converse of that shown in Figure 4 for the intensity of the 3.0 μ absorbance of the Si—OH structure; the intensity of the Si—CH$_3$ band decreased rapidly during the initial 50 hr of radiation and then the rate fell off during the remainder of the exposure period.

Kuzminskii and Goldovskii[13] indicate that Si—O bonds of the main chain rupture as a result of the accumulation of reactive groups from the oxidation of methyl pendant groups. Thus, it is possible that hydrogen ions, produced probably according to eq. (1a) could have combined with ≡SiO· ions formed when main chains ruptured to give Si—OH. Bovey[6] indicates, however, that there is little, if any, rupture of Si—O bonds when high mo-

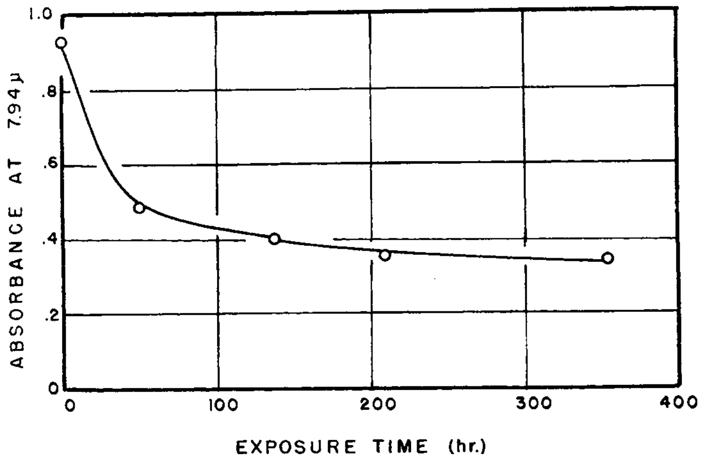
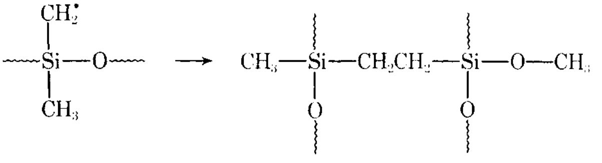


Fig. 5. Effect of irradiation time on absorbance at 7.94 μ.

lecular weight polysiloxanes are treated with high-energy radiation. It seems more reasonable, therefore, that Si—OH linkages were produced as shown in eqs. (3a)–(3c).

The decrease in sharpness and increase in width of the Si—O absorption frequency at 9.18 μ is probably due to an overlap of this band by new vibration modes that formed as a result of the decomposition of the methylsiloxane resin by radiation from the mercury vapor lamp. In this connection, Curry[10] notes that $SiCH_2CH_2Si$ groups give infrared absorptions at 8.85 and 9.5 μ that can be obscured if the structure is present in a symmetrical molecule or contains strong vibration modes from S—O bonds in the 9–10 μ region. The development of an 8.85 μ mode could account for the increase of half-width of the 9.18 μ frequency, while the 9.5 μ band might explain the decrease of sharpness.

Miller[5] as well as Dewhurst and St. Pierre[14] found that $SiCH_2CH_2Si$ crosslinks formed when polymethylsiloxanes were treated with high-energy radiation. Although several investigators[15–17] were unable to detect such crosslinks under similar conditions and they were not observed after the resin was exposed to radiation from the xenon arc lamp, infrared data suggest that they were produced as a result of the mercury vapor lamp treatment, probably as shown in eq. (4).



$$-\overset{\overset{\displaystyle CH_2^{\bullet}}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O- \longrightarrow CH_3-\overset{|}{\underset{\underset{\displaystyle |}{O}}{Si}}-CH_2CH_2-\overset{|}{\underset{\underset{\displaystyle |}{O}}{Si}}-O-CH_3 \tag{4}$$

Figure 6 shows the increase in the half-width of the 9.18 μ band with the time of radiation. Similar measurements made of the spectra from the resin sample irradiated by the xenon arc lamp showed no changes in the

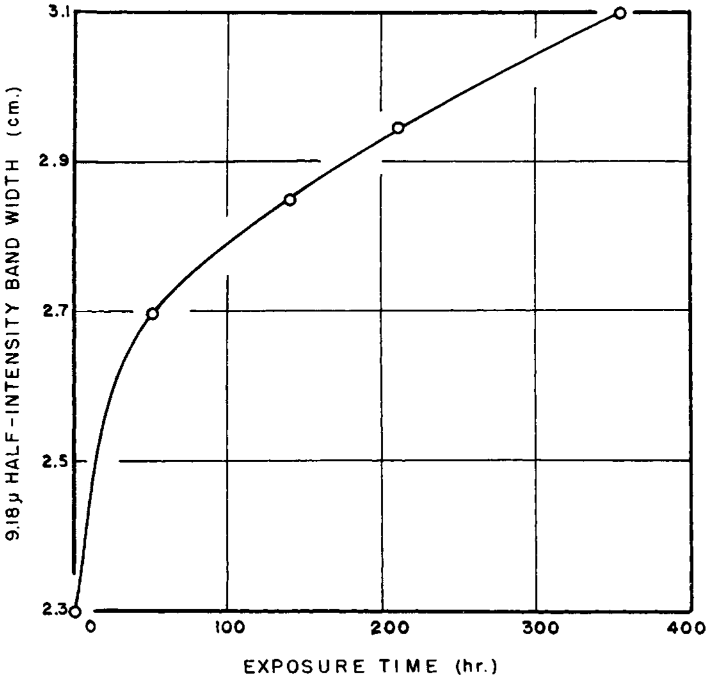
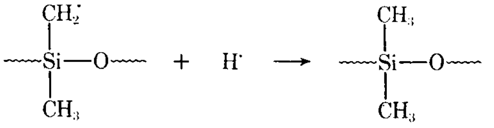


Fig. 6. Effect of irradiation time on 9.18 μ half-intensity band width.

half-width of this absorption mode. If the differences in the 9.18 μ band from the mercury vapor lamp treatment was due to the production of $SiCH_2CH_2Si$ crosslinks, then it is obvious from the results that the rate of formation of these structures decreased as the time of radiation increased. This is probably explained by the fact that the rate of $\equiv SiCH_2\cdot$ radicals that formed during ultraviolet light radiation decreased because of a reverse process [eq. (5)] that occurred concurrently.[7]



$$\text{---}\overset{\displaystyle CH_2^{\cdot}}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}\text{---O---} + H^{\cdot} \longrightarrow \text{---}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}\text{---O---} \qquad (5)$$

DISCUSSION

It is well known that electronically excited states are created when ultraviolet light energy is absorbed by molecules. Burkhard and Winslow[18] have reported that methylsiloxanes exhibit absorption maxima at about 240–270 mμ.

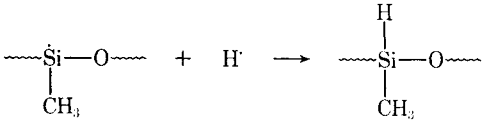
If the energy of excitation is equal to or higher than the bond dissociation energy of the weakest link in the molecule then cleavage reactions might occur. Because the absorbed energy might be transferred, however, the site at which the ultraviolet light is absorbed is not necessarily the same one where bond rupture might take place. The relation between the wavelength λ and absorbed energy is expressed by the Bohr equation:

$$E = 28.635 \times 10^3/\lambda \qquad (6)$$

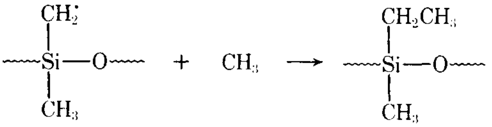
Table I lists the bond dissociation energies of linkages present in the methylsiloxane resin and the ultraviolet wavelengths, calculated from eq. (6), that are required for their rupture. Since this irradiation study was conducted in the presence of air, the list also includes oxygen.

The results of this study show that the polymethylsiloxane resin behaves differently when exposed to ultraviolet radiation emitted from a xenon arc or a mercury vapor lamp; the former light source produced $SiCH_2Si$ linkages while the latter formed $SiCH_2CH_2Si$ and Si—OH structures. This is probably due to the fact that the xenon arc lamp employed in this study emitted light over a broad, continuous spectrum at wavelengths above 281 mμ that would furnish energies up to only about 102 kcal/mole. On the other hand, the mercury vapor lamp supplied ultraviolet radiation over the region of approximately 185–436 mμ with a very strong peak at 253.7 mμ, giving energies of about 66–155 kcal/mole from these wavelengths.

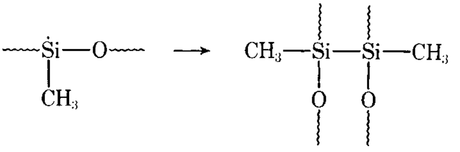
The energy of ultraviolet light from the xenon arc lamp is sufficient to rupture C—H and Si—C bonds as shown in eqs. (1a) and (1b). The reactive structures thus formed might conceivably undergo a number of different competitive reactions. For example, the $\equiv Si^{\cdot}$ and $\equiv SiCH_2^{\cdot}$ active structures may combine as shown in eq. (1c). The $CH_3^{\cdot}$ radical may abstract a hydrogen atom to form additional $\equiv SiCH_2^{\cdot}$ radicals and CH_4 as indicated in eq. (2). The $\equiv SiCH_2^{\cdot}$ radicals might interact to produce $\equiv SiCH_2CH_2Si\equiv$ linkages as shown in eq. (4). The hydrogen ions resulting from C—H rupture could undergo reaction with $\equiv SiCH_2^{\cdot}$ radicals as shown in eq. 5. Other reaction processes [eqs. (7)–(9)] should also be considered.



$$\sim\overset{\cdot}{\underset{CH_3}{Si}}-O\sim \; + \; H^{\cdot} \longrightarrow \; \sim\overset{H}{\underset{CH_3}{Si}}-O\sim \qquad (7)$$



$$\sim\overset{CH_2^{\cdot}}{\underset{CH_3}{Si}}-O\sim \; + \; CH_3^{\cdot} \longrightarrow \; \sim\overset{CH_2CH_3}{\underset{CH_3}{Si}}-O\sim \qquad (8)$$



$$\sim\overset{\cdot}{\underset{CH_3}{Si}}-O\sim \; \longrightarrow \; CH_3-\overset{|}{\underset{\underset{|}{O}}{Si}}-\overset{|}{\underset{\underset{|}{O}}{Si}}-CH_3 \qquad (9)$$

The infrared spectrum of the resin after irradiation by the xenon arc lamp only gave evidence of the production of $\equiv SiCH_2Si\equiv$ linkages. Although $\equiv SiSi\equiv$ bonds also might have formed, this is considered rather unlikely

TABLE I
Bond Dissociation Energies and Associated Ultraviolet Wavelengths

Bond	Dissociation energy E, kcal/mole	Wavelength λ, mμ
C—H (from CH_3)[18]	88	325
Si—C (from $SiCH_3$)[19]	73	392
Si—O[18]	185	155
O—O (from O_2)	118.9	243

because the methylsiloxane was exposed in the solid-state to the xenon arc lamp.[5]

To produce $\equiv SiCH_2Si \equiv$ structures it would be necessary to have both $\equiv Si^{\cdot}$ and $\equiv SiCH_2^{\cdot}$ active groups available to interact. If the radiation from the xenon arc lamp induced C—H bond rupture, and the $CH_3^{\cdot}$ radicals produced as a result of reaction (1b) abstracted hydrogen atoms from methyl groups as shown in eq. (2), then an excess of $\equiv SiCH_2^{\cdot}$ radicals would have been formed. Thus, the production of some $\equiv SiCH_2CH_2Si \equiv$ bonding should have been evident in the infrared spectrum of the irradiated resin. Of course, it is possible that any excess $\equiv SiCH_2^{\cdot}$ might have been consumed by the reversal reaction shown in equation 5. This is considered unlikely, since reactions (1a) or (2) and (5) would have to occur at the same rate to give the linear curve shown in Figure 2 for the increase of $SiCH_2Si$ units in relation to irradiation time. It seems more reasonable to postulate that the initial reaction induced by the radiation from the xenon arc lamp was Si—C bond rupture to form active $\equiv Si^{\cdot}$ and $CH_3^{\cdot}$ groups. Evidently, to accomplish this the resin investigated herein possessed absorbancies at higher frequencies than those reported by Burkhard and Winslow[18] for liquid methylsiloxanes. The $CH_3^{\cdot}$ radicals then abstracted hydrogen atoms from other methyl groups to produce active $\equiv SiCH_2^{\cdot}$ groups which in turn interacted with $\equiv Si^{\cdot}$ units to form $SiCH_2Si$ linkages.

Since the energies of the ultraviolet wavelengths supplied by the mercury vapor lamp were also adequate to produce the scission of Si—C and C—H bonds, other conditions must have existed during the radiation process which blocked the formation of $SiCH_2Si$ structures.

In this connection, it is interesting to note from Table I that the energies furnished by the mercury vapor lamp are in the range required to excite oxygen molecules in the air surrounding the irradiated resin. On the other hand, the energies released by the xenon arc lamp were insufficient for the excitation of oxygen molecules. This explains the formation of Si—OH bonds, probably by the reaction sequence shown in eqs. (3a)–(3c), during the mercury lamp radiation, and the lack of such structures resulting from the xenon arc lamp treatment.

Another possible result of the excitation of oxygen molecules by the energies from the mercury vapor lamp must also be considered. From the electronegativities of the elements involved,[20] it would be expected that the strongly electropositive silicon atom would react more readily with a strongly electronegative oxygen atom rather than with a less negative carbon atom. Hence, if the initial reaction induced by the radiation from the mercury vapor lamp was Si—C bond cleavage, as in the case of the xenon arc lamp, then the active $\equiv Si^{\cdot}$ groups thus formed would preferably seek to combine with excite odxygen molecules rather than with $\equiv SiCH_2^{\cdot}$ radicals. Thus, the active $\equiv Si^{\cdot}$ groups would be consumed, leaving the $\equiv SiCH_2^{\cdot}$ radicals to combine and form $SiCH_2CH_2Si$ linkages as in reaction (4).

$$\equiv Si + O^{\cdot}—O^{\cdot} \rightarrow \equiv Si—O—Si\equiv \qquad (10)$$

Since no precautions were taken to eliminate moisture from the air surrounding the resin sample irradiated by the mercury vapor lamp, another possible explanation for the lack of formation of $SiCH_2Si$ structures might be that the active $\equiv Si^{\cdot}$ groups entered into a reaction with water vapor. Hydrogen ions thus produced might have combined to form hydrogen gas or interacted with $CH_3^{\cdot}$ or $\equiv SiCH_2^{\cdot}$ radicals to yield CH_4 and $\equiv SiCH_3$, respectively. The latter reaction may have contributed to the decrease in the rate of formation of $SiCH_2CH_2Si$ linkages as shown in Figure 6. It is interesting to note, however, that the ratio of the intensity of the Si–OH absorption mode to the half-width of the 9.18 μ band, connected with the formation of $SiCH_2CH_2Si$ linkages, in the spectra from the irradiated samples remained constant. This indicates that the number of Si–OH bonds formed during radiation was proportional to that of the $SiCH_2CH_2Si$ structure produced. It is unlikely that these reactions would have occurred in this manner if Si–OH bonds were produced as a result of the oxidation sequence shown in eqs. (3a)–(3c) as well as by the interaction of active $\equiv Si^{\cdot}$ units with water vapor. Furthermore, the reaction of $\equiv Si^{\cdot}$ structures and moisture, although possible, did not occur when the resin was irradiated by the xenon arc lamp. Thus, it is believed that reaction (11) probably contributed little, if at all, to preventing the production of $SiCH_2$-Si linkages during the irradiation of the methylsiloxane resin by the mercury vapor lamp.

$$\equiv Si + H_2O \rightarrow \equiv Si—OH + H^{\cdot} \qquad (11)$$

The opinions and assertions contained in this paper are the private ones of the authors and are not to be construed as official or reflecting the views of the Naval Service at large.

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