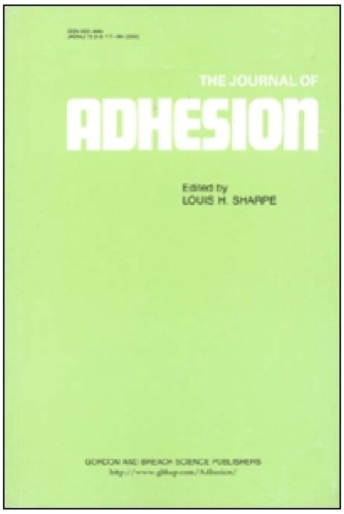

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Enhancement of Surface Wettability of Abhesive Silicone Rubber by Oxidation[†]

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A new method to detect surface oxidation of an otherwise untreated, cross-linked and filled silicone rubber is described. Our method is established on the principle that surface wettability increases during the progress of oxidation. Surface wettability is determined in terms of critical surface tension.

Abhesive polymers, of which silicone rubber is a typical example, are characterized by low surface energy, low friction coefficient and low release value. The problem associated with silicone rubber is its poor adhesion to other polymers. Its adhesional ability, however, can be improved by surface modification, e.g., oxidation, treatment with corona discharge, or ionic bombardment with inert gases.

By our method we found that the oxidation of silicone rubber is comparatively mild below 260°C, but is intensified at 287°C. Excessive oxidation at 316°C results in the formation of low molecular weight siloxanes which lower the wettability of the oxidized surface. Mechanisms of thermal oxidation are discussed.

INTRODUCTION

Abhesive polymers[1] are characterized by low surface energy, low friction coefficient, and low release value.[2] One of the well-known abhesive polymers is polysiloxane, which can be formulated into silicone rubbers by either a free radical or an ionic process. The surface of silicone rubber imparts good release properties as long as the polysiloxane remains chemically intact. However, upon exposure to oxygen at elevated temperatures, chemical reaction takes place on the surface as well as in the bulk of the rubber. While an extensive oxidation is detrimental to mechanical properties, a controlled

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oxidation may be advantageous in enhancing surface wettability and changing the abhesive polymer to adhesive.

It is of utmost importance that the extent of oxidation, especially on the surface, can be detected. For a non-crosslinked, non-filled silicone rubber, the detection may be achieved by infrared analysis, especially by the total reflectance technique. But, for the cross-linked, rubber-containing fillers, there is no sensitive method which can determine the progress of surface oxidation. In this paper, we describe a new approach which has proven to be satisfactory in detecting the oxidation on the silicone rubber surface. We hope that this method can be applied to the study of oxidation of other rubbers as well.

Our method involves the determination of critical surface tension of the rubber surface at various intervals of oxidation. Critical surface tension may not be satisfactory in obtaining absolute surface tension of a solid,[3] but it is extremely useful in following the change of wettability of a polymer.[4] For the latter, it is the relative value which counts.

EXPERIMENTAL

The silicone rubber used in our experiments was Dow Corning Silastic CF144. This rubber contained reinforcing fillers, e.g., silica, inhibitors, and a small amount of pigment. The rubber was compounded into a sheet 0.029 cm thick. This sheet was then cut into small samples (2.54 cm × 7.62 cm) and each sample was hung separately in a forced-air oven. Samples were withdrawn at various intervals and were not cleaned prior to the determination of contact angle.

The NRL contact-angle goniometer, Model A-100, manufactured by Rame-Hart, Inc., was equipped with an environmental chamber to maintain constant humidity and temperature at 20°C. The liquids used for the determination of contact angles have been shown[5] to give reproducible results. Surface tensions of these liquids were redetermined and are as follows: *n*-butanol, 24.2 dynes/cm; *n*-hexanol, 25.8 dynes/cm; *n*-octanol, 27.0 dynes/cm; polyglycol P-1200, 31.8 dynes/cm; polyglycol 15-200, 36.5 dynes/cm; polyglycol E-200, 44.8 dynes/cm; and glycerol, 65.5 dynes/cm.

Critical surface tension is determined by plotting the cosine of the contact angle ($\cos \theta$) against the surface tension of the liquid used, γ_{LV}.

RESULTS AND DISCUSSION

Oxidation at 232°C

Poly(dimethyl siloxane) has a critical surface tension, γ_c, of 24 dynes/cm. After the addition of fillers, which are generally of high surface energy, one might expect the surface energy of the rubber to be higher than 24 dynes/cm, if the fillers were exposed at the surface. But, we found that the surface tension remained unchanged (Fig. 1). This may indicate that the fillers are well protected by the polymer.

When the silicone rubber was oxidized at 232°C, we noted a slight increase in γ_c at the beginning, but no significant increase later on (Fig. 2). The contact angle versus liquid surface tension ($\cos\theta - \gamma_{LV}$) plots shift to the right only slightly, even after 72 hours of oxidation.

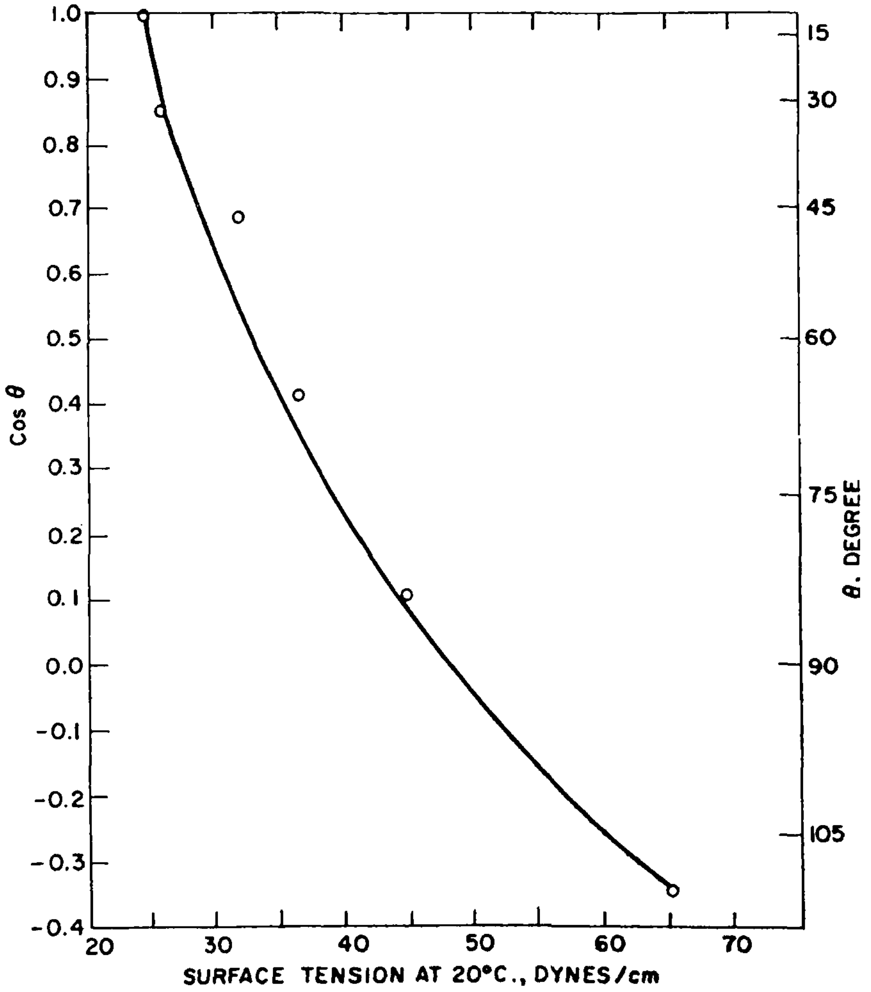


FIGURE 1 Critical surface tension of silicone rubber—silastic CF-144.

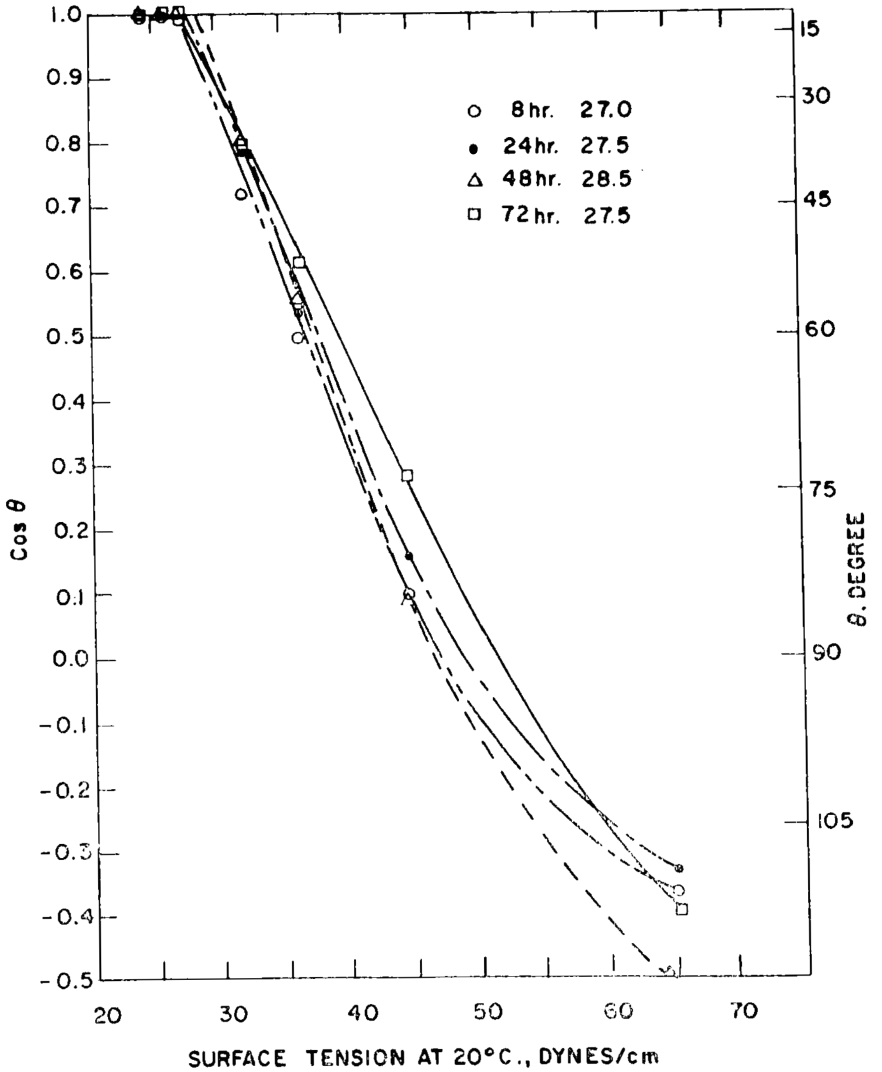


FIGURE 2 Critical surface tension of silicone rubber—silastic CF-144, oxidized at 232°C.

Oxidation at 260°C

After eight hours of oxidation at 260°C, the initial increase in γ_c was 3.5 dynes/cm, which is nearly equal to the initial increase of the γ_c for the sample oxidized at 232°C. However, the subsequent increase in γ_c was more consistent, though the increase was still small (Fig. 3). After 72 hours of

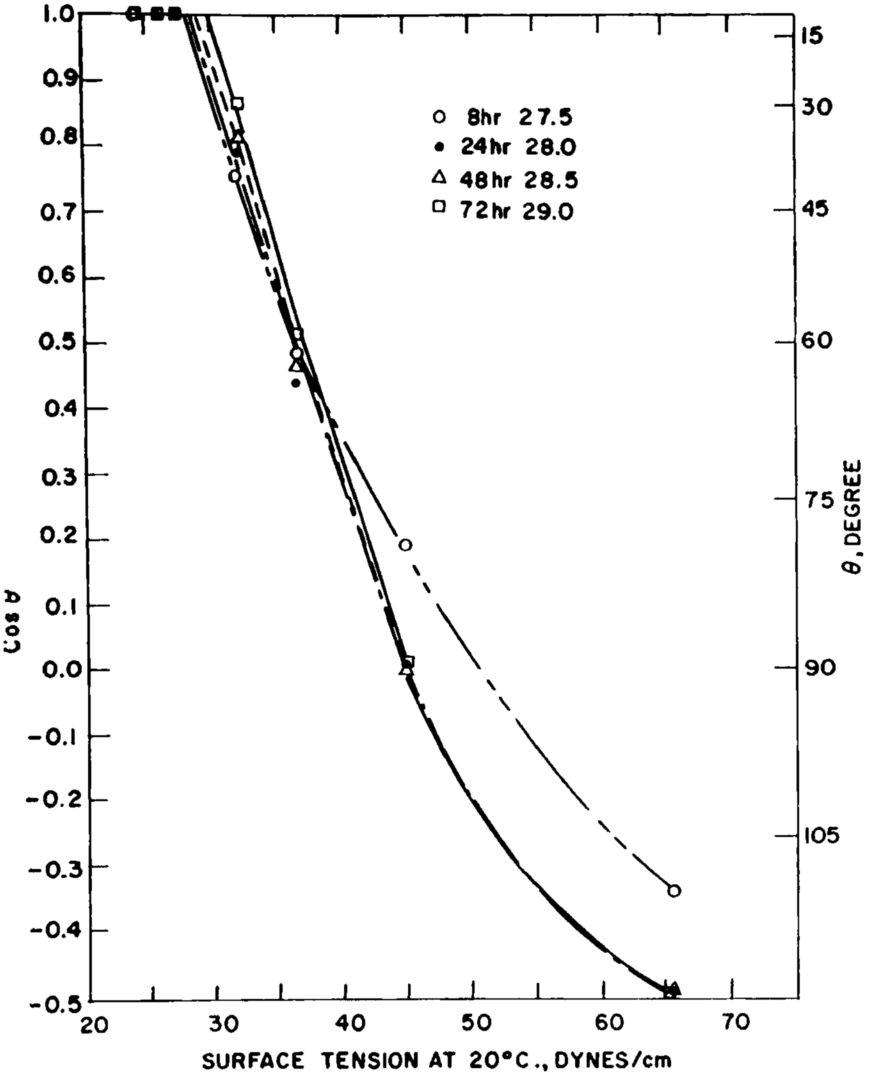


FIGURE 3 Critical surface tension of silicone rubber—silastic CF-144, oxidized at 260°C.

oxidation, a net increase of 5 dynes/cm was detected by our method. From the abhesive-property standpoint, we now have a polymer surface equivalent to that of polypropylene instead of that of poly(dimethyl siloxane). We may expect that the adhesional ability will be somewhat increased, even for the small increase in γ_c of 5 dynes/cm.

Oxidation at 287°C

At 287°C, the oxidation became more intense. In Fig. 4, we note that not only do γ_c's change significantly, but the $\cos\theta - \gamma_{LV}$ plots also shift to the right. The total increase in γ_c was 8.5 dynes/cm after 72 hours of oxidation. The oxidized surface is no longer abhesive because the wettability has been significantly changed to that of poly(propylene oxide), 33 dynes/cm. As a result of this increase in γ_c, adhesional ability should be further significantly improved.

Oxidation at 316°C

The oxidation at 316°C appeared to be rather drastic. The γ_c increased to 32.0 dynes/cm after 24 hours of oxidation (Fig. 5), and reached 32.5 dynes/cm after 48 hours, but decreased abruptly after 72 hours of exposure to air at 316°C. We also noticed that the surface of the sample withdrawn after 72 hours contained some low molecular weight material, presumably polysiloxanes.

Owing to the presence of these low molecular weight polysiloxanes, the wettability was significantly lowered; hence, the original abhesive property was temporarily recovered. However, this temporary regain of release property, caused by the severe oxidation, was made at a sacrifice of mechanical properties of silicone rubber.

In Fig. 6, we plot γ_c vs time for the oxidation at various temperatures. The rates of the increase in γ_c can be readily compared.

Mechanisms of thermal oxidation

Formation of silanol

In a recent review article,[6] several mechanisms related to the thermal oxidation of silicone rubbers have been discussed. One mechanism, proposed by Andrianov and Sokolov,[2] can best explain the formation of polar silanol groups on the surface. The pendant methyl group is first oxidized into a hydroperoxide group which then decomposes into formaldehyde, a siloxy

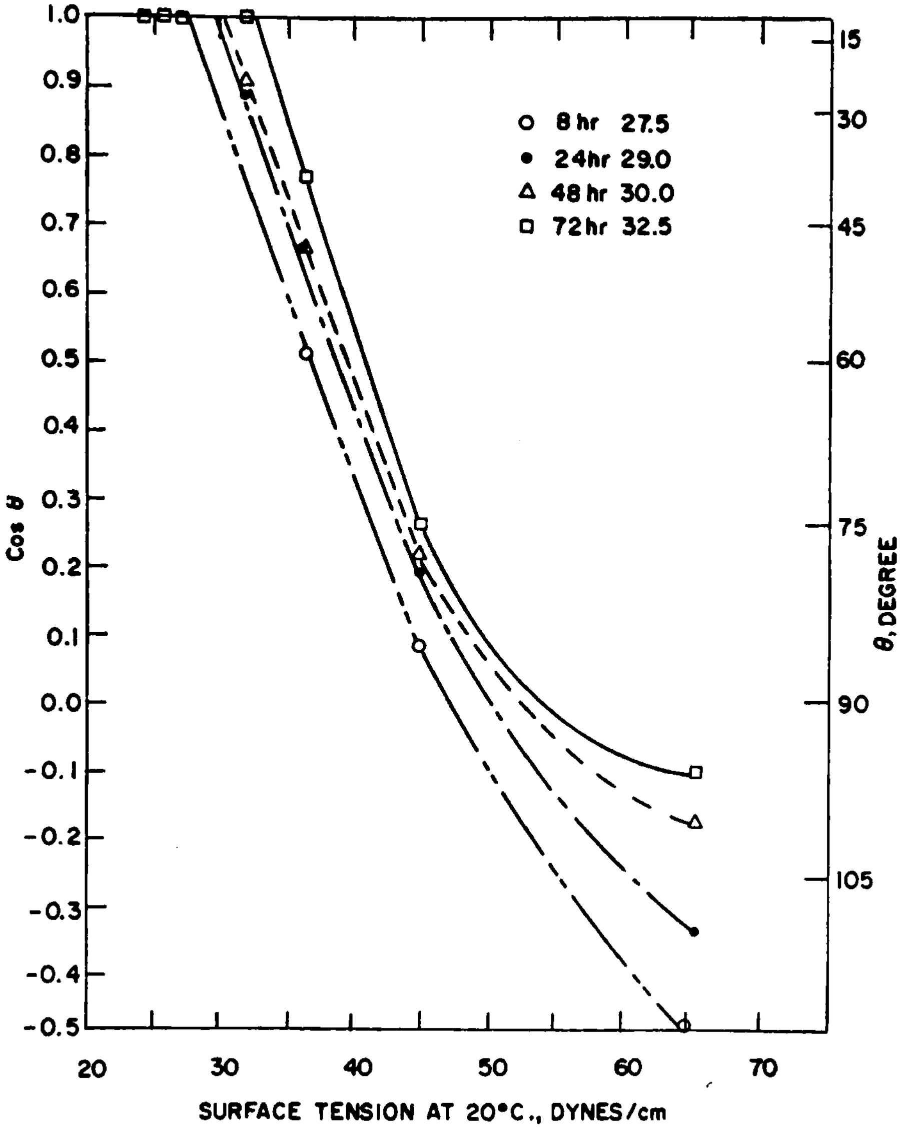


FIGURE 4 Critical surface tension of silicone rubber—silastic CF-144, oxidized at 287°C.

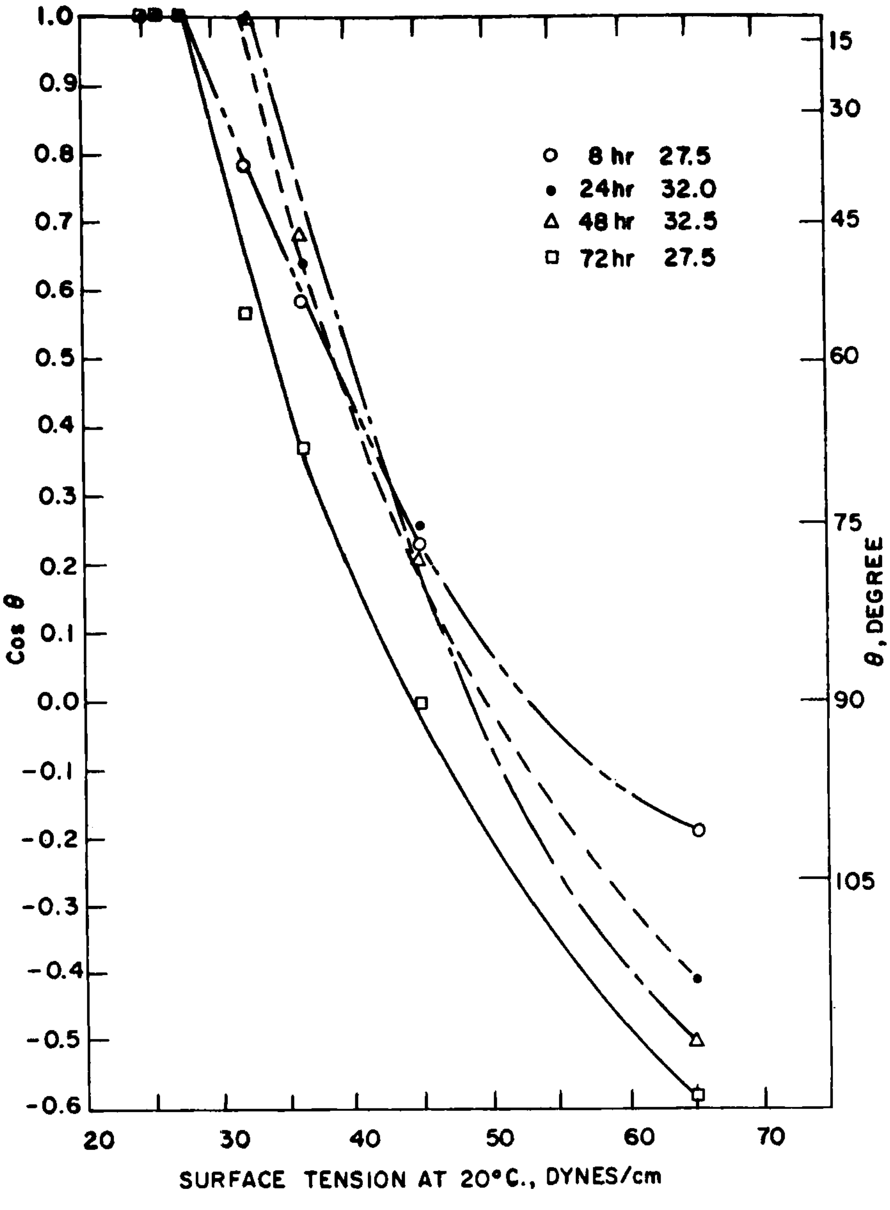


FIGURE 5 Critical surface tension of silicone rubber—silastic CF-144, oxidized at 316°C.

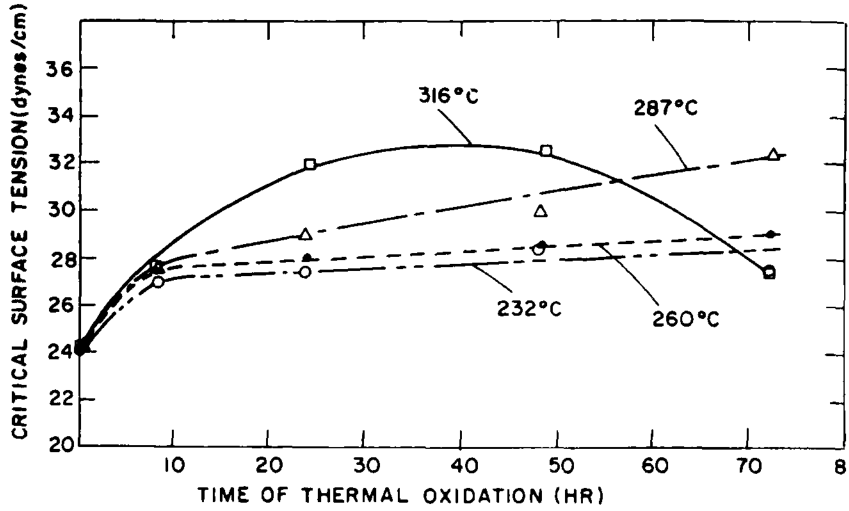
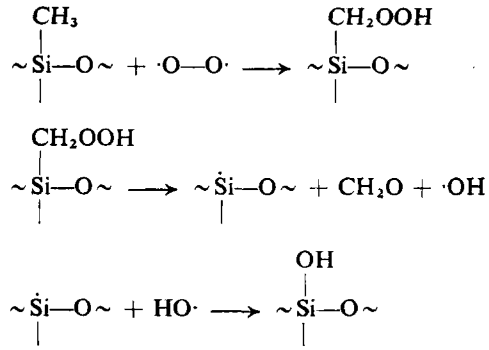


FIGURE 6 Effect of thermal oxidation on critical surface tension of silastic CF-144.

radical, and a hydroxy radical. These two radicals presumably recombine to form a silanol group:



$$\sim\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{Si}}}-O\sim + \cdot O-O\cdot \longrightarrow \sim\overset{\displaystyle CH_2OOH}{\underset{|}{\overset{|}{Si}}}-O\sim$$

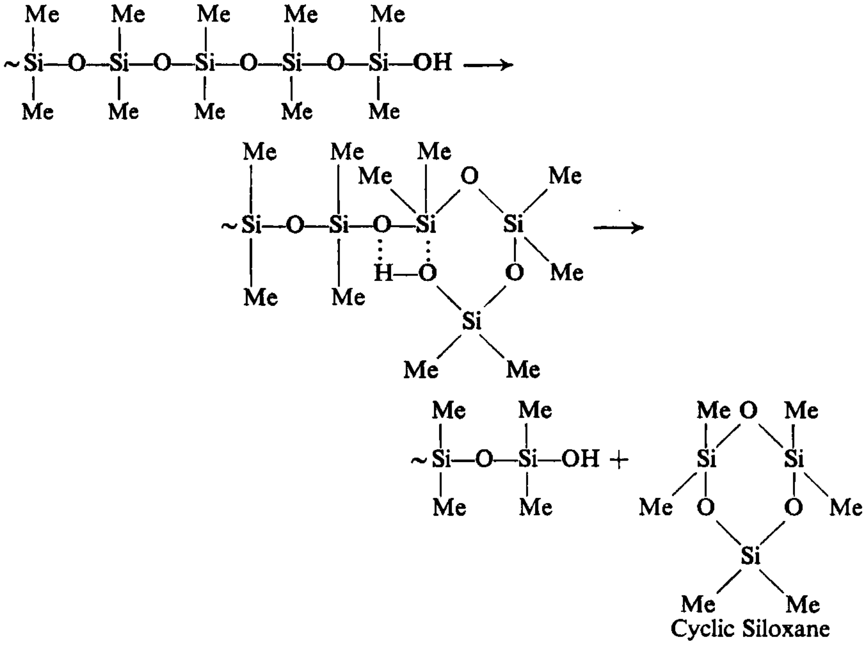
$$\sim\overset{\displaystyle CH_2OOH}{\underset{|}{\overset{|}{Si}}}-O\sim \longrightarrow \sim\underset{|}{\dot{Si}}-O\sim + CH_2O + \cdot OH$$

$$\sim\underset{|}{\dot{Si}}-O\sim + HO\cdot \longrightarrow \sim\overset{\displaystyle OH}{\underset{|}{\overset{|}{Si}}}-O\sim$$

The enhancement in wettability is partly caused by the formation of silanol groups on the surface. If the oxidation could be terminated at this point, it would be a beneficial means in improving the surface wettability.

Formation of cyclic siloxanes

However, if the oxidation were carried on further, the second major product of the thermal decomposition at elevated temperatures would be cyclic siloxanes. Several mechanisms have been proposed. Among them, the following mechanism appears to be well supported by experimental facts.[8]



If the oxidation were carried to the stage that depolymerization takes place with the formation of cyclic siloxanes, the surface wettability would decrease as observed. The cyclic siloxanes would then lubricate the surface as a thin film. This might be advantageous if lubrication were badly needed, regardless of the deterioration of silicone rubber. However, if the sole purpose is to enhance the wettability of silicone rubber, the oxidation should not be carried to the point of the autocatalytic depolymerization. Temperatures lower than 287°C and shorter times are preferred in order to confine the oxidation to the surface of the rubber.

CONCLUSIONS

A useful method has been developed for the detection of surface oxidation of cross-linked and filled silicone rubber derived from poly(dimethyl siloxane). We found that as a result of oxidation the critical surface tension of the rubber generally increased considerably. The extent of oxidation on the surface could then be detected by the change in the critical surface tension.

From these changes in γ_c, we were able to conclude that the oxidation of silicone rubber is relatively mild below 260°C within 72 hours, but becomes intensified at 287°C. This increase in wettability is at least partly caused by the formation of silanol groups on the surface.

An unusual phenomenon was observed on the sample overoxidized at 316°C. The wettability decreased instead of increasing. This decrease in wettability can be attributed to the formation of low molecular weight cyclic siloxanes as a result of depolymerization. If the sole purpose is to enhance surface wettability, the oxidation should be carried out at temperatures lower than 287°C for shorter times to prevent the formation of cyclic siloxanes and the drastic deterioration of mechanical properties. Ideally, the oxidation should be confined to the surface of the rubber.

Acknowledgement

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