

Slow Decomposition of Silicone Rubber

P. VONDRÁČEK* and A. N. GENT, *Institute of Polymer Science,
The University of Akron, Akron, Ohio 44325*

Synopsis

The sol content of previously extracted samples of lightly crosslinked silicone rubber has been found to increase during prolonged storage under relatively mild conditions. Simultaneously, the tensile stress slowly decreases in samples held stretched, and the equilibrium degree of swelling increases somewhat. Thus, the polymer network appears to undergo slow decomposition. This process is accelerated by moisture, by ammonia vapor, and by raising the temperature of storage. It is slowed down by prior treatment of the polymer with a silazane reagent which reduces the number of residual OH groups. It is therefore attributed to hydrolytic decomposition of the poly(dimethylsiloxane) molecules initiated by OH groups.

INTRODUCTION

Silicone rubber is generally considered to be stable under mild conditions.¹⁻³ It is regarded as one of the most weather-resistant elastomers, even though some lowering of the mechanical properties has been reported after storage in the open air for several years¹ or after long-term implantation in the human body.⁴ Recently, however, we have observed the spontaneous adhesion of crosslinked silicone rubber to various substrates.⁵ This bonding process appeared to be associated with OH groups generated by hydrolytic decomposition of silicone rubber under relatively mild conditions. A detailed study has therefore been carried out of the chemical stability of poly(dimethylsiloxane) polymers and crosslinked materials made from them. Measurements were made of the sol fraction of the crosslinked materials and of stress relaxation during long periods of storage. The results are reported here.

EXPERIMENTAL

Materials and Sample Preparation

The materials employed have been described elsewhere.⁵ One was poly(dimethylsiloxane), denoted PDMS (SE-30, General Electric Company); and the other was basically similar except for the incorporation of a small amount of methylvinylsiloxane units (SE-33, General Electric Company). Both were crosslinked with dicumyl peroxide (Di-Cup R, Hercules Chemical Company).

Determination of Equilibrium Swelling in Toluene and Sol Content

Weighed samples of the crosslinked materials, about 1 mm thick and weighing about 0.2 g, were immersed in toluene at room temperature for 48 h. The toluene

* On leave from the Department of Polymers, Institute of Chemical Technology, 16628 Prague 6, Czechoslovakia.

was replaced after 24 h. The swollen samples were weighed in order to determine the amount of toluene absorbed and then dried at 80°C or at room temperature *in vacuo* for 16 h to determine the dry weight of the sample.

Stress Relaxation

A strip of crosslinked material about 90 mm long, 10 mm wide, and 2 mm thick was secured with its lower end held in a fixed clamp and its upper end held in a clamp connected by a long thin wire to a force transducer. The sample was surrounded by a heated glass tube so that its temperature could be maintained at any desired level in the range 25–200°C. By adjusting the position of the force transducer, the sample could be stretched to various extents and then held at constant elongation over long periods of time. Most of the experiments were carried out at an extension of 20%. Provision was made for a preheated stream of air or ammonia vapor to circulate around the sample.

RESULTS AND DISCUSSION

Sol Formation and Degree of Crosslinking

Measurements of the sol fraction of lightly crosslinked silicone rubber gave continuously increasing values as the extraction process continued (Fig. 1). This feature has been noted previously by Bueche.⁶ It suggests that the molecular network decomposes slowly with the passage of time to form additional un-crosslinked material.

As shown in Figure 2, when an extracted sample is stored under relatively mild conditions, a considerable amount of new soluble material is generated. This process is accelerated somewhat at higher temperatures and strongly by the presence of ammonia vapor. As it does not appear to take place under dry conditions, it is attributed to a hydrolytic decomposition catalyzed by ammonia.

Similar, but much smaller, effects were observed with the vinyl-containing PMVS polymer, crosslinked to different degrees. The measured amounts of soluble material after storage under various conditions are given in Table I.

It was noted that removal of the newly formed soluble material by extraction

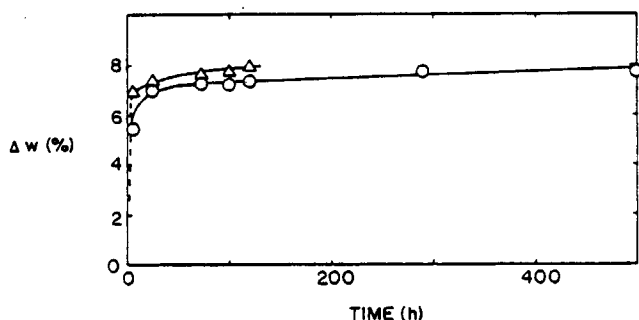


Fig. 1. Weight loss Δw of a lightly crosslinked PDMS material after extraction with toluene for various periods: (O) cold extraction; (Δ) hot (Soxhlet) extraction.

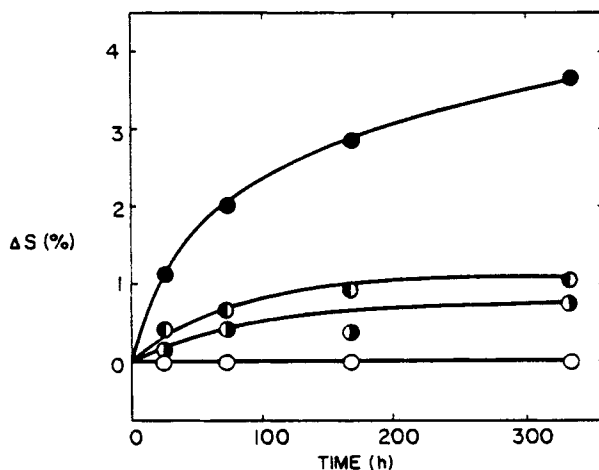


Fig. 2. Soluble fraction ΔS generated in a previously extracted sample of a lightly crosslinked PDMS material by exposure for various periods to different environments: (●) NH_3 , 25°C; (◐) air, 110°C; (●) air, 25°C; (○) dry air, 25°C.

caused an increased rate of formation of sol, (Fig. 3). Apparently, an equilibrium is established between the sol and gel fractions; and when the soluble portion is removed, decomposition proceeds further to replace it.

Simultaneously with the formation of new soluble material, the equilibrium degree of swelling of the materials increases slightly (Table II), suggesting again that this polymer is chemically unstable under relatively mild storage conditions. Although decomposition of silicone rubber has been noted previously at relatively high temperatures⁷⁻⁹ and attributed to hydrolysis, it has not previously been reported to take place under relatively mild conditions, at least as far as the present authors are aware.

Stress Relaxation and Permanent Set

Continued relaxation of the tensile stress in crosslinked materials held in the stretched state reflects changes in the network structure. Some relaxation is

TABLE I
Weight Fraction of Soluble Material (%) Formed in Previously Extracted Samples of PMVS Silicone Rubber when Stored under Various Conditions

| Storage conditions | Storage time, h | Samples | |
|-------------------------------|-----------------|-----------------------------|---------------------------|
| | | Crosslinked with 0.025% DCP | Crosslinked with 0.5% DCP |
| Air, 25°C | 48 | 0.06 | 0.09 |
| | 240 | 0.01 | 0.00 |
| | 410 | 0.00 | — |
| Air, 135°C | 48 | 0.1 | 0.12 |
| | 240 | 0.22 | 0.00 |
| | 410 | 0.29 | — |
| NH_4OH , 25°C | 48 | 0.20 | 0.21 |
| | 240 | 0.33 | 0.15 |
| | 410 | 0.68 | 0.33 |

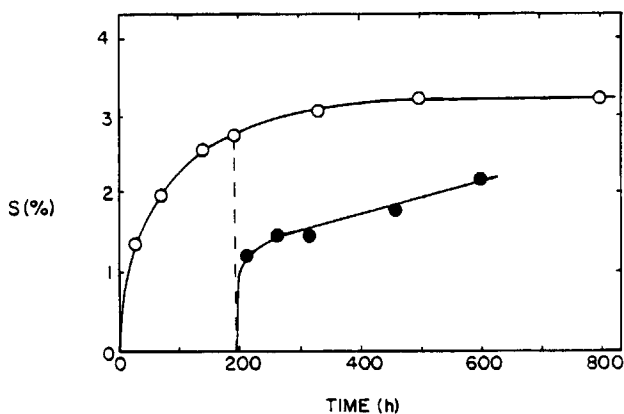


Fig. 3. Soluble fraction S generated in a previously extracted sample of a lightly crosslinked PDMS material by exposure to ammonia vapor at room temperature (O); sample extracted after 200 h of exposure and then re-exposed (●).

associated solely with physical processes such as the slow rearrangement of entangled molecules. When a stretched strip of lightly crosslinked PDMS was exposed to ammonia vapor, the tensile stress decreased by about 10% in a period of an hour or two (Fig. 4). This change is attributed solely to a physical process, i.e., the uptake of ammonia by the elastomer. When the surrounding ammonia gas stream was removed and the absorbed ammonia slowly diffused out of the stretched strip, the tensile stress returned to its original level (Fig. 4).

Nevertheless, continued relaxation of stress due to network decomposition was evident at long times, at elevated temperatures, and especially in the presence of ammonia vapor (Fig. 5). In this case, when the ammonia was removed after prolonged exposure, the stress no longer returned to the level expected from air exposure (Fig. 5). Moreover, the continued relaxation in air and accelerated relaxation in ammonia suggest that virtually all of the network chains would be broken after about 1000 h in air and 100 h in ammonia. Thus, the decomposition process at 110°C is relatively rapid and extensive.

However, the materials after a substantial degree of stress relaxation had occurred, i.e., when only 35–40% of the initial stress remained, were found to swell in toluene to about the same extent as originally. Thus, the total density of network chains was not significantly altered by prolonged storage. This indicates that the decomposition process leading to stress relaxation must be primarily a process of bond *interchange* rather than bond scission, probably catalyzed by

TABLE II
Equilibrium Volume Swelling Ratios in Toluene after Storage for Three Weeks under Various Conditions.

| Storage conditions | Samples | | |
|--------------------------|----------------------|--------------------|------------------|
| | PMVS (0.025% DCP) | PMVS (0.5% DCP) | PDMS (2% DCP) |
| (Initial values) | (7.85) | (4.55) | (9.5) |
| Air, 25°C | — | 4.65 | — |
| Air, 135°C | 9.1 | — | — |
| NH ₄ OH, 25°C | 9.0 | 4.65 | 11.25 |

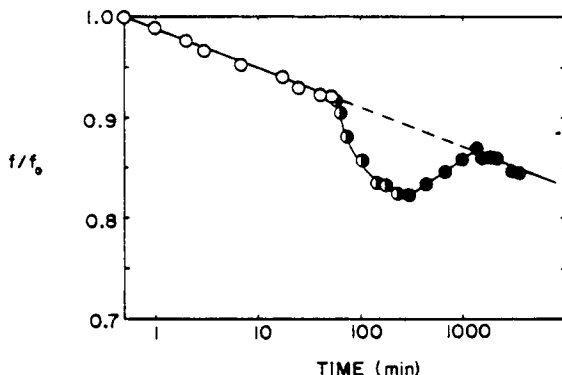


Fig. 4. Relaxation of tensile stress f , relative to the initial value f_0 , for a lightly crosslinked sample of PDMS at 70°C: (O) air atmosphere; (●) NH_3 admitted after 1 h; (●) NH_3 atmosphere removed after 3 h.

moisture and by residues of the catalysts introduced for polymerization. This conclusion is supported by the rather large amount of permanent set, about 50%, shown by the same samples when the tensile stress was removed.

Silanol groups in poly(dimethylsiloxane) polymers may be partly responsible for the relatively facile bond rearrangement and decomposition that have been observed. These groups are relatively reactive. Together with ionic impurities or catalyst residues, they could well reduce the stability of unfilled silicone polymers.^{7,9-12} It should be noted that the materials used for relaxation experiments were unextracted and so contained impurities arising from both the polymerization and crosslinking reactions. It appears that this sensitivity toward impurities is greatly reduced in the presence of fillers, as is usually the case in commercial formulations.¹³

Evidence for the presence of silanol groups in the original polymer was obtained by reacting PDMS with tetraethoxysilane, yielding a substantial amount, 76%, of gelled polymer. Thus, there must have been at least one silanol group

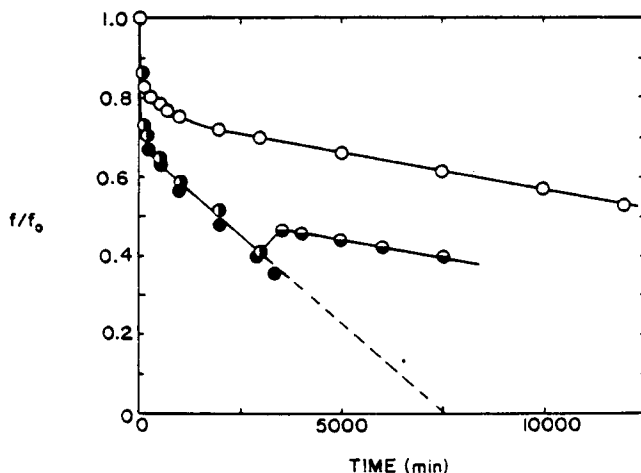


Fig. 5. Relaxation of tensile stress f , relative to the initial value f_0 , for a lightly crosslinked sample of PDMS at 110°C: (O) in air; (O, ●) in ammonia; (●) after ammonia was removed.

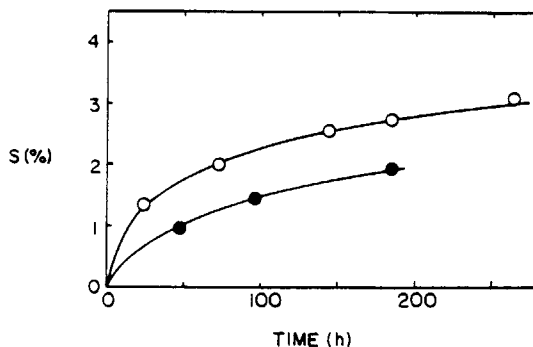


Fig. 6. Soluble fraction S generated in lightly crosslinked samples of treated (●) and untreated (○) PDMS on exposure to ammonia vapor at room temperature.

on each polymer molecule in order to be able to achieve this high degree of gelation.

An attempt was also made to block these OH groups by reacting PDMS with hexamethyldisilazane to yield trimethylsiloxy groups in their place.⁵ Crosslinked samples made from this modified polymer were found to generate soluble material to a considerably smaller degree on prolonged storage (Fig. 6), indicating an increased stability. However, the relaxation of stress at 110°C and in the presence of ammonia vapor was found to take place to the same degree and at much the same speed as for the corresponding unmodified material.

Thus, it appears that while OH groups present in the original polymer play an important role in the processes leading to the formation of soluble material, they do not appear to affect significantly the process, probably bond interchange, that is responsible for the observed relaxation of stress.

CONCLUSIONS

Evidence has been put forward for slow hydrolytic decomposition of poly(dimethylsiloxane) under relatively mild conditions. The amount of soluble material in lightly crosslinked materials increases continuously, and the stress in stretched strips relaxes continuously. These processes are catalyzed by the presence of moisture and of ammonia, and by raising the temperature. Moreover, when the number of silanol groups in the polymer was reduced, the stability was found to be increased. This suggests that silanol groups in poly(dimethylsiloxane) polymers play an important role in initiating the hydrolytic reactions that are inferred to be responsible for stress relaxation, sol formation, and chemical bonding to silica fillers¹⁴ or to OH-containing substrates.⁵

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