Long-Term Aging of Elastomers: Chemical Stress Relaxation of Fluorosilicone Rubber and Other Studies
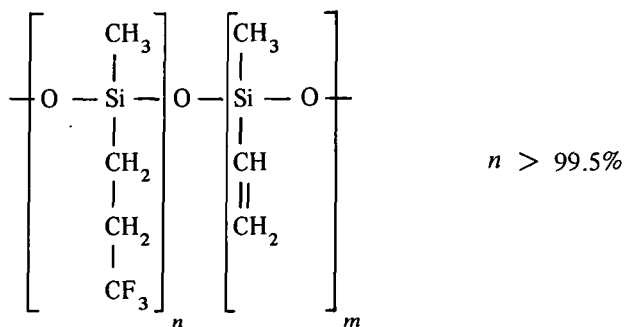
S. H. Kalfayan, A. A. Mazzeo, and R. H. Silver

Propulsion Division

Elastomers have varied aerospace applications, including: propellant binders, bladder materials for liquid propellant expulsion systems, and fuel tank sealants, particularly for high-speed aircraft. Predicting the long-term behavior of these materials is of paramount importance. A comprehensive molecular theory for mechanical properties has been developed at JPL. It has only been tested experimentally in cases where chemical degradation processes are excluded. Hence, a study is underway to ascertain the nature, extent, and rate of chemical changes that take place in some elastomers of interest. The results can then be incorporated in the theoretical framework. This article reports progress on the investigations of chemical changes that may take place in the fluorosilicone elastomer, LS 420, which is regarded as a fuel and high-temperature-resistant rubber. The kinetic analysis of the chemical stress relaxation and gel permeation chromatography studies comprise the major portion of this article.

Introduction

The nature and extent of chemical changes that take place in a number of selected elastomers at long times is under study. Previously, investigation of the chemical degradation of styrene-butadiene rubber (SBR) was reported (References 1, 2, and 3). Presently, the fluorosilicone gum rubber LS 420 and its peroxide vulcanizate is under examination. The structure of this elastomer is represented as follows:

$$\left[\begin{array}{c} CH_3 \\ | \\ -O-Si- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CF_3 \end{array}\right]_n \left[\begin{array}{c} CH_3 \\ | \\ O-Si-O- \\ | \\ CH \\ || \\ CH_2 \end{array}\right]_m \qquad n > 99.5\%$$

Silicones are noted for their resistance to extremes of temperature, but they lack resistance to hydrocarbon-based fuels and lubricating oils used in aircraft. The introduction of fluorine atoms imparts resistance to non-polar fluids. The vinyl groups in the fluorosilicone chain provide sites for crosslinking (curing). Their concentration is less than 0.2% by weight. LS 420 was selected because it represented a suitable test material to support the theoretical developments for viscoelastic behavior generated at JPL (Reference 4), and also because it related this study to the advanced sealants, particularly the fuel tank sealants program at the Marshall Space Flight Center.

Four different methods were applied to determine the network changes that take place when the fluorosilicone elastomer is heat-aged. These were: (1) infrared spectroscopy, (2) gel permeation chromatography (GPC), (3) thermogravimetric analysis or weight-loss measurements, and (4) stress-relaxation measurements. This article discusses the results of these measurements.

Results and Discussion

IR Studies

The residues of the samples of LS 420 gum heated in air from 180 to 315°C showed no changes in the IR spectra, although degradation, particularly at the higher temperatures, was severe as evidenced by the high weight losses and the change in the physical condition of the samples. This indicates that possible alterations in the structure of the repeating unit of the elastomer must be less than 4–5%, i.e., the sensitivity limit for IR. Elemental analyses of the degraded and undegraded polymer showed no significant change in composition, indicating the absence of new functional groups, such as $-OH$, $-OOH$ or $>C=O$. These results are unlike those obtained for the hydrocarbon rubber, SBR, which on oxidation showed the presence of $-OH$ and $>C=O$ groups in the polymer network (Reference 3).

LS 420 was also subjected to oxygen plasma at 20 N/m² (0.15 mm of Hg).[1] Changes in the IR spectra were not observable, although the samples showed some crazing and hardening.

Gel Permeation Chromatography

The GPC chromatogram of the unheated LS 420 gum showed two peaks, the larger representing a compound of molecular weight 450,000 (polystyrene calibration) and the smaller representing a compound of molecular weight 630 (polypropylene glycol calibration). Peak area measurements indicated 93–95% high molecular weight species and 5–7% low molecular weight compound. A molecular weight of 624 corresponds to a tetramer of $\gamma, \gamma', \gamma''$-trifluoropropyl methyl siloxane, the principal repeating unit of LS 420. The tetramer most probably is cyclic, because that represents the most stable configuration (actually the polymer is made from the cyclic tetramer), and because no end-groups such as —OH, —OR were detected by IR or wet chemical analysis. As heat aging of the fluorosilicone progressed, GPC analysis showed a gradual increase in the concentration (increase in the peak area) of the 630 molecular weight compound, and a gradual decrease in the concentration of the high molecular weight compound, indicating the possibility of using GPC for degradation rate studies. But this intent was complicated by the finding that THF, the solvent used in analysis, degrades the polymer even at room temperature. This was proved by viscosity and molecular weight measurements of THF solutions of the polymer. Reduction in both viscosity and molecular weight was observed. Moreover, the degradation was enhanced when the THF solution was filtered through an asbestos filter prior to GPC analysis. No acceleration was noticed when the solution was filtered through fritted glass. The pH of the asbestos is the suspected cause of this phenomenon.

Other solvents that attacked LS 420 chemically were acetone and MIBK, both of which, like THF, are mildly nucleophilic and could attack the slightly positive silicone atom in the fluoropropyl siloxane chain.

The GPC chromatograms also indicated that degradation or scission of the siloxane chain is most probably random as opposed to the ordered unzipping of the repeating unit, because molecular weight decrease was very rapid.

Weight-Loss Studies

The weight loss versus time studies were made in air at temperatures from 240 to 315°C. The data obtained fitted a first-order rate equation. The Arrhenius plot yielded an activation energy, ΔE, of 1.037×10^5 J/mole (24.7 kcal/mole) (Figure 1).

---

[1] Values in customary units are included in parentheses after values in SI (International System) units if the customary units were used in the measurements or calculations.
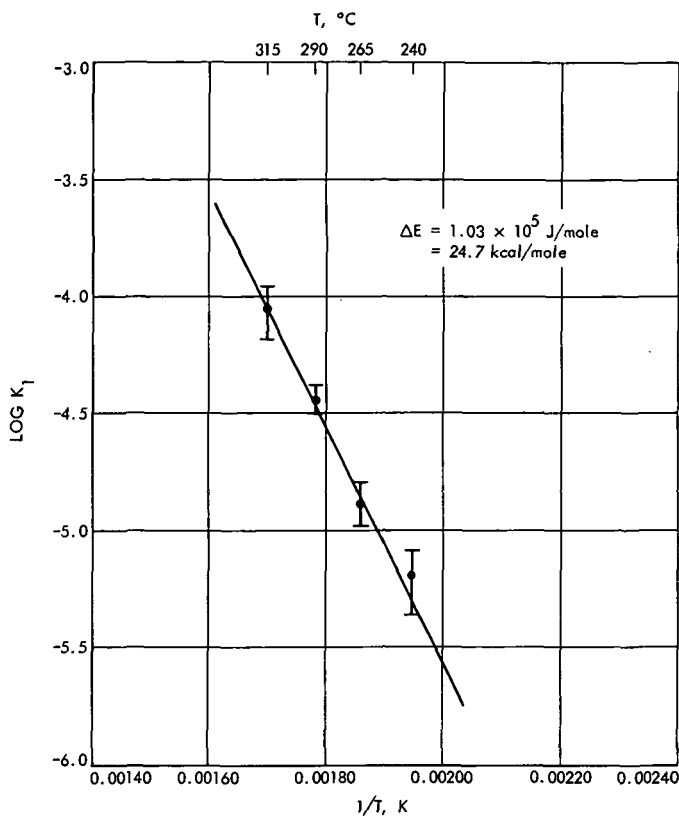
Figure 1. Temperature dependence of rate constants obtained from weight-loss measurements for LS 420 fluorosilicone rubber

Stress-Relaxation Measurements

Stress relaxation is a valuable technique to obtain data of fundamental significance concerning the aging or the chemical degradation of elastomers. It was developed by Tobolsky and others in the early 1940's (Reference 5). The stress-relaxation experiments were carried out with dicumyl peroxide (Di-cup)-vulcanized LS 420 in air, in nitrogen, and in JP-4 fuel. A specially constructed relaxometer capable of measurements at high temperatures, i.e., up to 260°C, and in fuel, was used. Some of the results shown in Figure 2 are plots of the logarithms of relative stress-relaxation f_t/f_0 versus time, where f_t and f_0 are the tensile force at time t and t_0, respectively.

Energy of activation values were obtained from Arrhenius plots (Figure 3) by using two sets of data obtained from the stress-relaxation experiments carried out in air: (1) half-times, and (2) shift factors, log K_t along the time
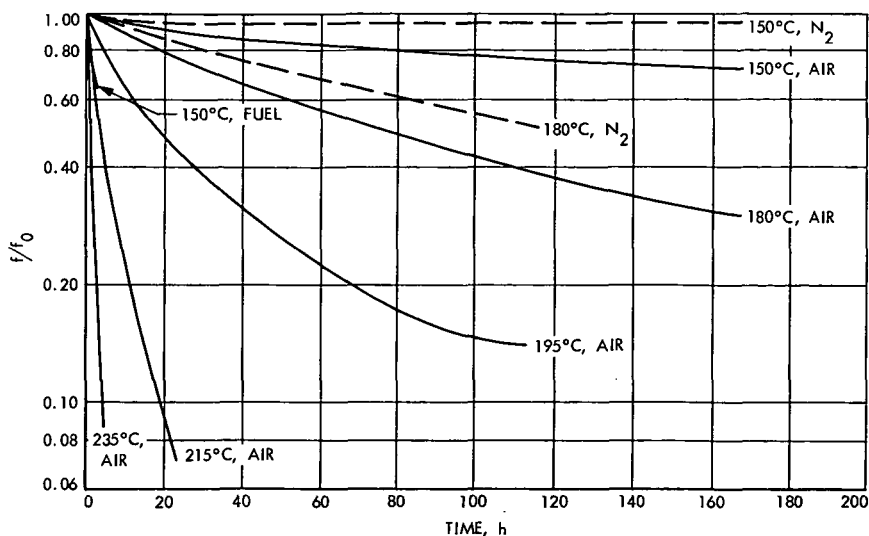
41

Figure 2. Effect of temperature on stress relaxation of peroxide-cured LS 420 fluorosilicone rubber

axis. The shift factors were obtained by superposition of f_t/f_0 versus log t curves at various temperatures over the curve obtained at 215°C, the reference temperature. Half-times refer to the time it takes for the initial stress to decay 50%. Activation energies, ΔE, were as follows:

(1) 1.52×10^5 J/mole (36.3 kcal/mole) from half-time data.

(2) 1.58×10^5 J/mole (37.7 kcal/mole) from shift factors.

These values are in good agreement. However, ΔE obtained from weight-loss measurements is much lower. The two processes, chemical stress relaxation and thermal degradation, are most probably due to different reaction mechanisms.

Continuous and intermittent stress-relaxation measurements enable the determination of the number of network chains, ν_e, formed during aging. Intermittent relaxation measures the net result of both scission and crosslinking during network breakdown. Continuous relaxation measurements cannot distinguish between new network chains formed by crosslinking from the original chains. If at anytime during the intermittent relaxation experiment the stress is larger than during the continuous relaxation experiment, the difference represents the contribution of the crosslinking

42

reaction (Reference 6). The number of new network chains, or the number of crosslinks formed, ν_e, can be calculated from the following equation:

$$\nu_e = \frac{1}{RT\left(\lambda - \dfrac{1}{\lambda^2}\right)}\left[\frac{\left(\dfrac{f_t}{f_0}\right)^i (f_0)^i}{A^i} - \frac{\left(\dfrac{f_t}{f_0}\right)^c (f_0)^c}{A^c}\right]$$

where

λ = the extension ratio

A = the cross-sectional area of specimen
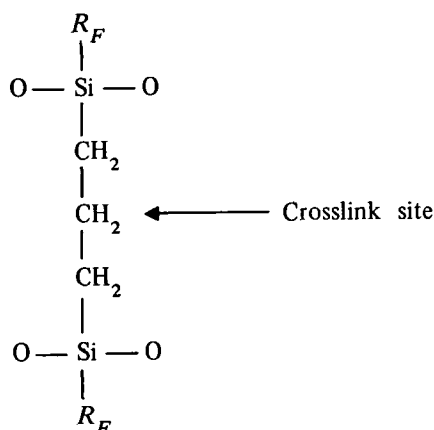
f_t, f_0 = stresses at time t and t_0

R and T have their usual meanings. The superscripts i and c denote intermittent and continuous stress relaxation.

Examination of the intermittent and continuous stress-relaxation curves (Figure 4) shows that vulcanized LS 420 undergoes crosslinking during thermal aging in air at 195 and 215°C, the two temperatures at which intermittent runs have been made so far. Plots of ν_e versus time (Figure 5) show that crosslinking first increases with time and then decreases for experiments carried out in air. The experiment performed in nitrogen at 180°C (Figure 5) was discontinued after 50 h because of specimen failure. It is probable that this curve would also slope downwards after reaching a maximum, as in the case of the two other curves in the same figure.

Stress-relaxation curves obtained for runs carried out in pure nitrogen at 150 and 180°C lie above those carried out in air at the same temperatures (Figure 2), indicating that relaxation due to chemical changes is caused more by atmospheric oxygen than by thermal effects at the temperatures used. Values of stress decay in air and nitrogen are given in Table 1.

It is of interest to know whether scission takes place randomly along the polymer chain, or at the crosslink sites. The crosslink site in LS 420 is

probably as follows (Reference 7), formed from the vinyl-free radical of one chain and the $-CH_3$ of another chain:

$$
\begin{array}{c}
R_F \\
| \\
O-Si-O \\
| \\
CH_2 \\
| \\
CH_2 \quad \longleftarrow \quad \text{Crosslink site} \\
| \\
CH_2 \\
| \\
O-Si-O \\
| \\
R_F
\end{array}
$$

where R_F represents $-CH_2-CH_2-CF_3$.

It has been stated that random scission along the polymer chain is indicated when the rate of relaxation is found to be inversely proportional to the crosslink density, and scission at the crosslink is indicated when the rate of relaxation is independent of crosslink density (Reference 6). The stress-relaxation rate of an LS 420 specimen cured with 0.05% Di-cup, yielding a rubber of lower crosslink density than those used in this study, was much higher, indicating that random scission along the polymer chain predominates.

Table 1. Values of stress decay in air and nitrogen

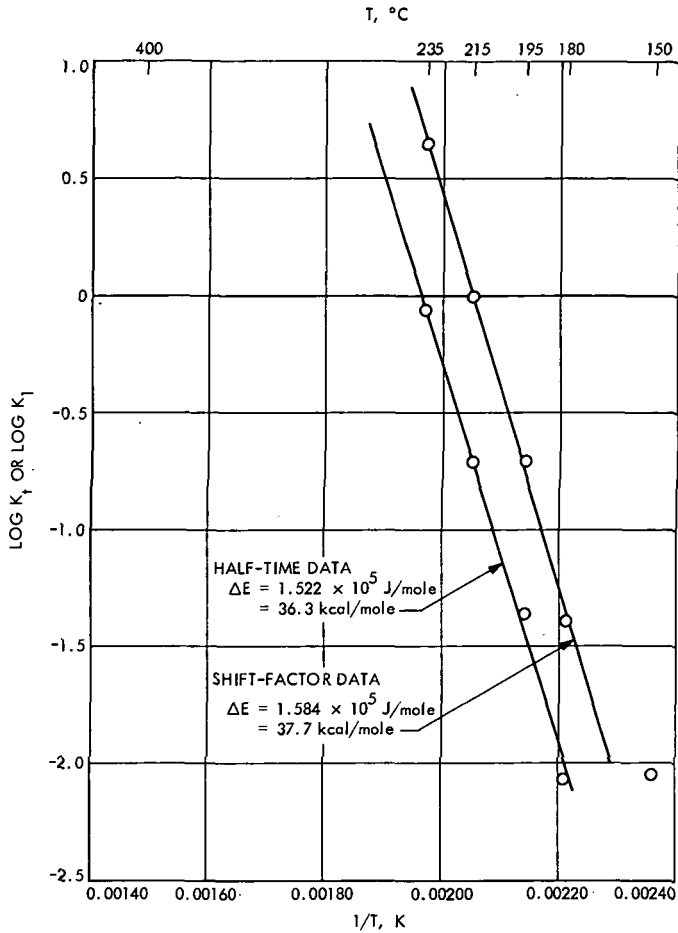| Test condition	Decay of tensile force, %	
	150°C	180°C
Air		
After 14 h	14	22
After 168 h	30	70
Nitrogen		
After 14 h	4	12
After 168 h	5	40

Figure 3. Temperature dependence of shift factors and half-time
data obtained from stress-relaxation measurements

Conclusions

Results of these experiments indicate that:

(1) Some crosslinking takes place when the fluorosilicone rubber, LS 420, is heated in air, but scission predominates.

(2) Scission takes place randomly along the chain, rather than by an orderly unzipping of monomer units from the polymer molecule.

(3) Chain scission rather than scission at the crosslink sites predominate. [The former involve the breaking of siloxane bonds, i.e., —Si—O—Si— (bond energy 88.2 kcal/mole). Scission at crosslinks involves the breaking of Si—C or C—C bonds (bond energies 69.3 and 83.1 kcal/mole, respectively). Although the siloxane bond is the strongest, its
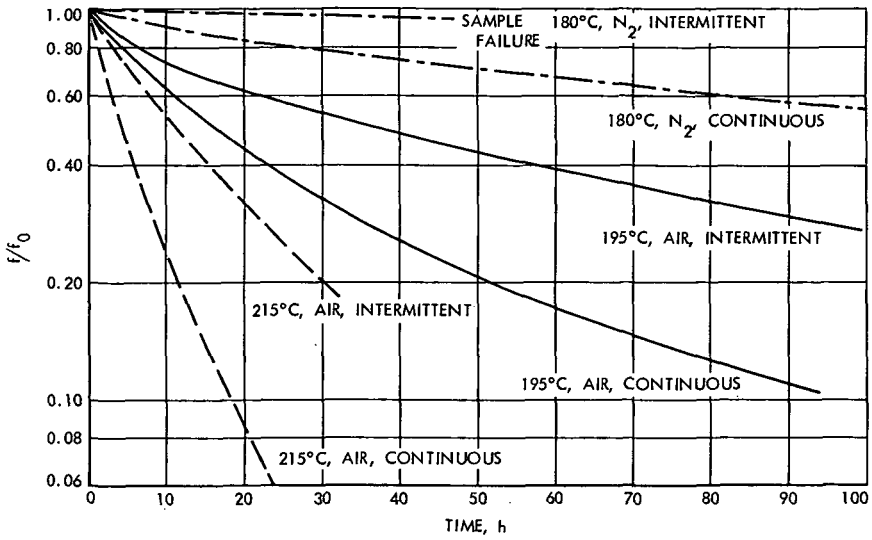
45

Figure 4. Continuous and intermittent stress relaxation in LS 420 at various temperatures in air and nitrogen
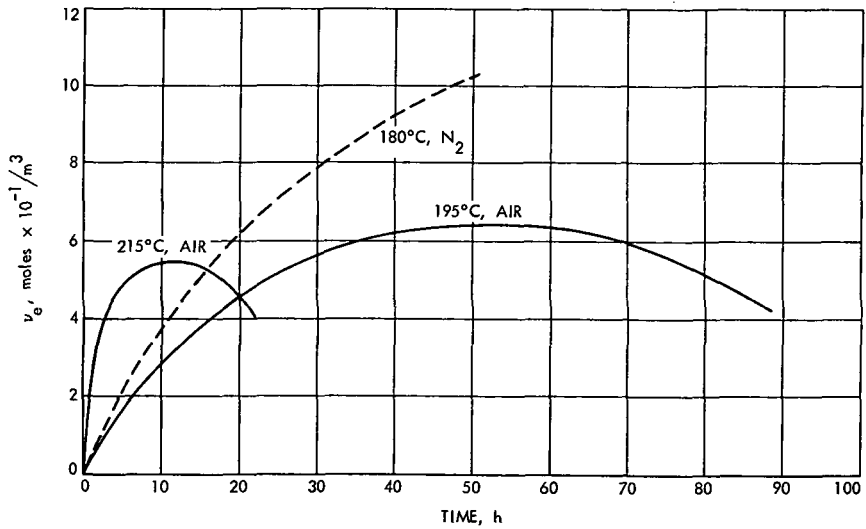

Figure 5. Additional network chains formed in LS 420

51% ionic character makes it susceptible to nucleophilic and electrophilic attack. Thus, basic and acidic impurities found in the rubber (such as polymerization catalysts) will enhance the scission of the relatively strong Si—O bond at elevated temperatures.]

(4) Analysis of the kinetic data obtained indicate that at room temperatures (20 to 25°C) the fluorosilicone rubber will show negligible chemical degradation for very, very long times, i.e., several decades.

References

1. Kalfayan, S. H., Rakutis, R., and Silver, R. H., "Long-Term Aging of Elastomers: Chemical Stress Relaxation Studies of Peroxide-Cured Styrene–Butadiene Rubber," in *Supporting Research and Advanced Development*, Space Programs Summary 37-59, Vol. III, pp. 194–198. Jet Propulsion Laboratory, Pasadena, Calif., Oct. 31, 1969.

2. Rakutis, R., and Kalfayan, S. H., "Long-Term Aging of Elastomers: Stress Relaxation of SBR With Thiophenol," in *Supporting Research and Advanced Development*, Space Programs Summary 37-62, Vol. III, pp. 242–244. Jet Propulsion Laboratory, Pasadena, Calif., Apr. 30, 1970.

3. Rakutis, R., Silver, R. H., and Kalfayan, S. H., "Long-Term Aging of Elastomers: Kinetics of Oxidation of SBR by Infrared Spectroscopy," in *Supporting Research and Advanced Development*, Space Programs Summary 37-64, Vol. III, pp. 125–130. Jet Propulsion Laboratory, Pasadena, Calif., Aug. 31, 1970.

4. Moacanin, J., and Aklonis, J. J., "Viscoelastic Behavior of Elastomers Undergoing Crosslinking Reactions," in *Supporting Research and Advanced Development*, Space Programs Summary 37-66, Vol. III, pp. 187–189. Jet Propulsion Laboratory, Pasadena, Calif., Dec. 31, 1970.

5. Tobolsky, A. V., Prettyman, I. B., and Dillon, J. H., *J. Appl. Phys.*, Vol. 15, p. 309, 1944.

6. Tobolsky, A. V., *Properties and Structure of Polymers*, p. 223. John Wiley & Sons, Inc., New York, 1960.

7. Thomas, D. K., *Heat Stability in Fluorosilicones*, Technical Report 68234. Royal Aircraft Establishment, Farnborough, England, Sept. 1968.