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Long-Term Aging of Elastomers: Chemorheology of Viton B Fluorocarbon Elastomer

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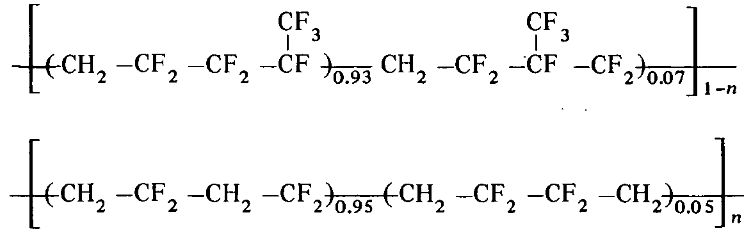
Elastomers have extensive aerospace applications. They are used as bladder materials for liquid propellant expulsion systems, propellant binders, and fuel tank sealants for high-speed aircraft. Predicting the long-term behavior of these materials is of primary importance. This article is the continuation of a study to ascertain the nature, extent, and the rate of chemical changes that take place in certain selected elastomers. Under discussion is Viton B, regarded as a temperature and fuel resistant fluorocarbon rubber. The kinetic analysis of the chemical stress relaxation, and infrared and gel permeation chromatography analysis results are discussed.

Introduction

Previously, as part of studies on high-temperature and fuel-resistant elastomers, results of chemical stress relaxation and other measurements for the peroxide vulcanizate of LS 420, a fluorosilicone gum, were reported (Reference 1). Presently, investigations carried out with Viton B are discussed. The fluorocarbon elastomers known under the trade name Viton are copolymers of vinylidene fluoride and perfluoropropylene. Viton B is reported to contain also a third component, tetrafluoroethylene (Reference 2, p. 280). The detailed structure assigned to the polymer as a result of nuclear magnetic resonance studies was as follows (Reference 2, p. 282):



$$\left[(CH_2-CF_2-CF_2-\overset{\overset{\displaystyle CF_3}{|}}{CF})_{0.93}\; CH_2-CF_2-\overset{\overset{\displaystyle CF_3}{|}}{CF}-CF_2)_{0.07} \right]_{1-n}$$

$$\left[(CH_2-CF_2-CH_2-CF_2)_{0.95} (CH_2-CF_2-CF_2-CH_2)_{0.05} \right]_{n}$$

Vulcanization with diamines is the commercial method. In the present study, *N,N*-dicinnamylidene-1,6-hexanediamine (Diak No. 3) was used with magnesium oxide as the acid acceptor. Chemical stress relaxation was the method most extensively used to determine the network changes taking place in the heat-aged Viton fluoroelastomer. Swelling, gel permeation chromatography (GPC), infrared (IR) spectroscopy, and thermogravimetric analyses were also used to obtain supporting information.

IR Studies

Figure 1 shows the IR spectrum of uncured Viton B gum, before and after a thin film of the polymer was heated in air at 300°C. A new peak at 1580 cm^{-1} appeared, which was assigned to conjugated double bonds. Conjugation is likely to be caused by the elimination of HF from the polyvinylidene fluoride block of the Viton B chain, in particular from the head-to-tail portion of the structure. Peaks existing originally at 1710 and 3220 cm^{-1} disappeared. The bond at 1710 cm^{-1} is assigned to carbonyl from the carboxyl group, and the one at 3220 cm^{-1} is assigned to the OH group. It is possible that the carboxyl and hydroxyl groups originally present as end groups in the polymer (Reference 2, p. 282) are eliminated at the elevated temperatures by dehydration and decarboxylation. The peak at 1750 cm^{-1} is assigned to terminal $-CH=CF_2$ groups.

The peaks at 1580 and 1750 cm^{-1} increased in area during the first hour of heating at 300°C, but no changes took place thereafter. Kinetic data could not be obtained from the IR studies.

Gel Permeation Chromatography Studies

Gel permeation chromatography studies of unheated and uncured Viton B gumstock showed a monomodal distribution having an average molecular

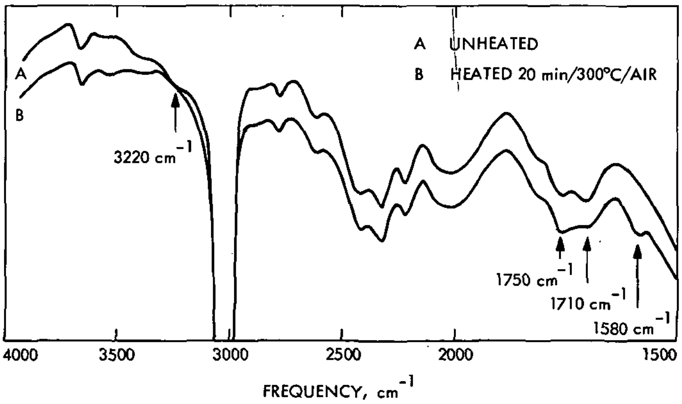


Figure 1. Infrared spectra of Viton B gum

weight, corresponding to the distribution maximum, of 250,000. The gum heated at 325–375°C for three hours gave a molecular weight of 96,000, indicating chain scission. Part of the sample (about 7–10%) could not be dissolved in tetrahydrofuran, showing that crosslinking was taking place, as well.

Swelling Measurements

Three batches of Viton B, molded at 149°C (300°F) for 1 hour with 1, 3, and 4.5% Diak No. 3, were swollen in acetone before and after postcuring 24 hours at 260°C to determine the crosslink density ν_e. Values obtained by using the Flory-Rehner equation along with the interaction constant $\chi_1 = 0.232$ (Reference 3) are shown in Table 1.

The values in the table show that postcuring reduces the number of network chains (crosslink density), and that the ratio of ν_e's of the postcured batches is close to the ratio of Diak No. 3 used, namely, 1:3:4.5%. A more stable network results after postcuring as discussed below.

Stress Relaxation Studies

Stress relaxation measurements on batches 1, 2, and 3 were carried out at temperatures ranging from 150 to 300°C. Experiments were performed in air, nitrogen, and JP-4 aircraft fuel. Samples were about 0.038 cm thick.

The continuous stress relaxation curves obtained in air for batch 3 are shown in Figure 2, where f_t and f_0 are tensile forces at time t and t_0, respectively. Similar curves were obtained for batches 1 and 2 in air and nitrogen.

The data from the chemical stress relaxation experiments were used to calculate energy of activation values (Figure 3) from plots of $-\log t$ (t = time to 30% relaxation) versus $1/T$ (T = temperature in kelvins). Inasmuch as this method for calculating activation energies is strictly applicable for first-order reaction kinetics, the reported activation energies are approximate only. It can be noticed that the activation energies are about the same for runs in air and nitrogen, although chemical relaxation is more rapid in air. This may mean that the mechanism of degradation is the same in air and

Table 1. Crosslink densities from swelling measurements

	ν_e, after molding 1 h at 149°C and aging 1 mo at room temperature		ν_e, after postcuring 24 h at 260°C	
Batch	Moles/g	Moles/m^3	Moles/g	Moles/m^3
1	—	—	4.1×10^{-5}	76.3
2	15.4×10^{-5}	286.4	11.5×10^{-5}	213.9
3	26.2×10^{-5}	487.3	17.4×10^{-5}	323.6

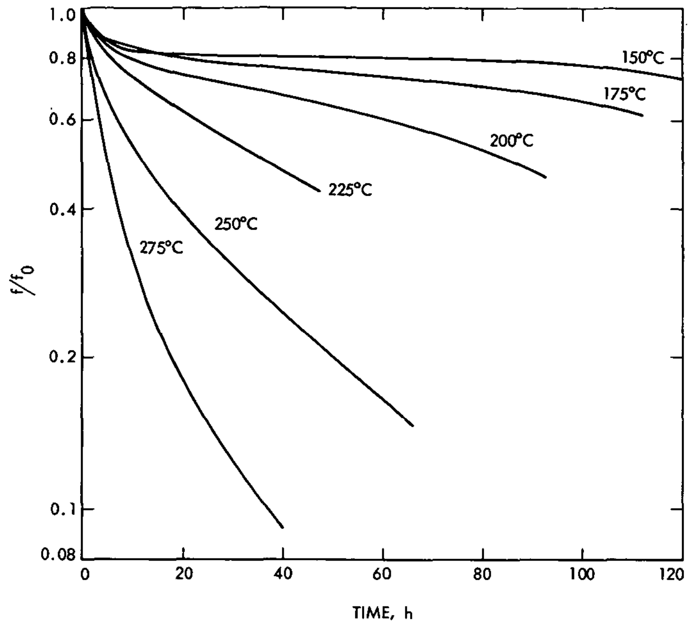


Figure 2. Stress relaxation of Viton B batch 3 in air

nitrogen, and one may suspect that O_2 was not totally excluded from the experiments carried out in nitrogen, although analysis of the effluent nitrogen from the relaxometer gave repeatedly 99.98% N_2 and 0.02% argon by mass spectroscopy. One cannot exclude the possibility of some oxygen combined to the cured polymer, particularly to the amine moiety, which could initiate scission by an oxidative mechanism.

Intermittent relaxation measurements were also performed in air and nitrogen. The continuous and intermittent relaxation curves would be identical if only scission were occurring. If, on the other hand, the stress at a given time in the intermittent experiment is larger than in the continuous experiment, the difference represents the contribution of the crosslinking reaction (Reference 4).

Examination of the curves shown in Figure 4a indicates that Viton B undergoes crosslinking as well as scission during thermal aging in air. Intermittent and continuous stress relaxation experiments conducted in nitrogen at 200°C also show simultaneous crosslinking and scission taking place in an inert atmosphere (Figure 4a). The results from stress relaxation measurements were supported by the thermal aging of uncured Viton B in air, nitrogen, and vacuum (10^{-5} torr). In all three cases the samples darkened, indicating conjugation in the chain, and the aged samples did not dissolve in tetrahydrofuran, as did the original gum.

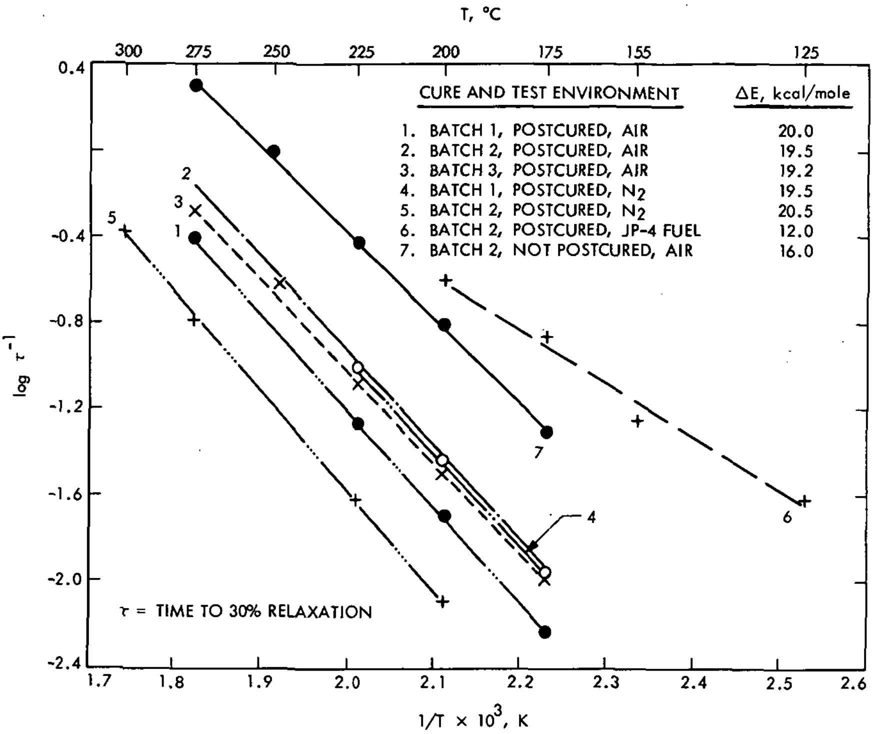


Figure 3. Temperature dependence of (fractional life) obtained from stress relaxation measurements

Plots of ν_e versus time showed that crosslinking of postcured Viton B batches increases initially, and then levels off, in both air and nitrogen. Exceptions were postcured batch 2 tested in air and nitrogen, which showed an initial decrease in the number of crosslinks.

Stress relaxation curves obtained for runs carried out in pure nitrogen lie above those carried out in air (Figure 4a), showing that relaxation due to chemical changes is caused more by atmospheric oxygen than by thermal effects at the experimental conditions used.

When the rate of relaxation is independent of crosslink density, scission at the crosslink is indicated, rather than random scission in the polymer chain (Reference 4). Figure 5 suggests that scission is taking place at the crosslinks in the Diak No. 3 cured Viton B network, at least during the initial period of aging at 275°C. Similar results were obtained at other temperatures.

Although postcuring at 260°C reduces the number of network chains (see Table 1), the rate and extent of stress relaxation of the postcured batches is still less than those cured at lower temperatures. Figure 4b shows that 80%

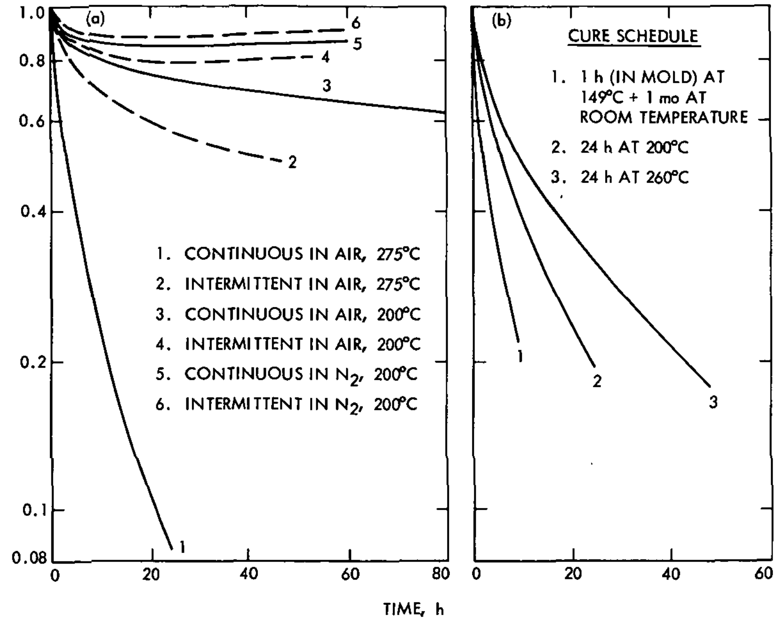


Figure 4. Stress relaxation of Viton B batch 2: (a) intermittent and continuous in air, and N$_2$; (b) in air at 250°C after various cure schedules

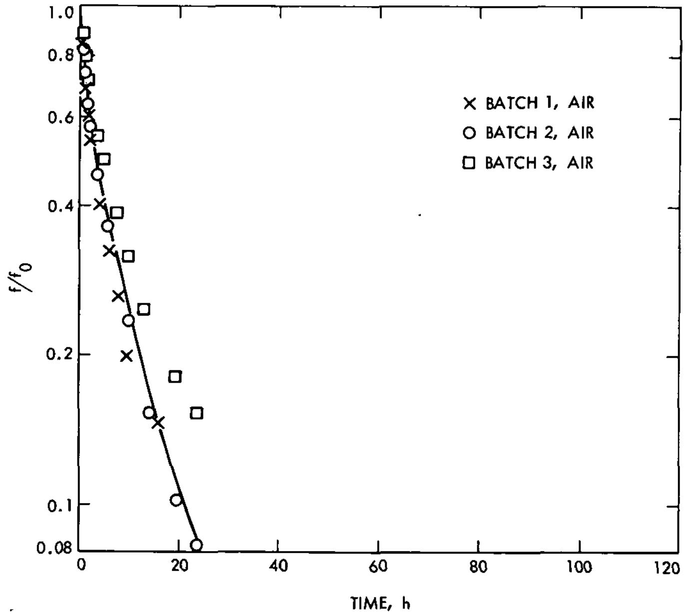
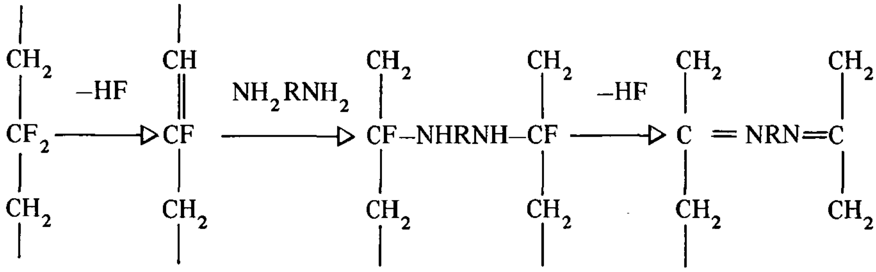


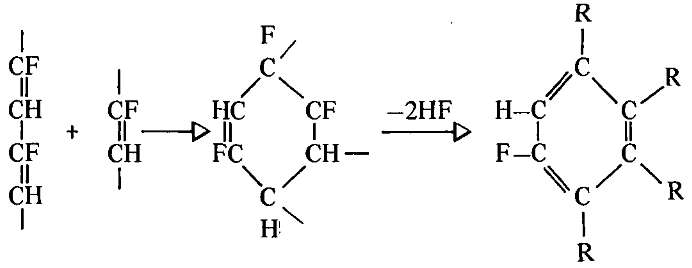
Figure 5. Stress relaxation of Viton B of various crosslink densities in air at 275°C

of the network chains of the unpostcured batches are broken in 24 hours or less. New network chains (crosslinks) are formed on postcuring which are more stable thermally than the original crosslinks. The somewhat higher activation energy found for the postcured batch 2 samples suggests the same *contention (Figure 3, compare No. 2 with No. 7).*

It has been shown (Reference 5) that diamine cures of Viton occur as follows:



Postcuring probably enhances another type of crosslinking (Reference 6). A conjugated center formed by dehydrofluorination may react with a double bond in an adjacent chain by a Diels-Alder type addition, and subsequently a benzenoid ring forms, which explains the stability of the new network (crosslinks):



Viton B samples were found to relax faster in JP-4 fuel and gave lower activation energy of degradation than those relaxing in air (Figure 3, No. 6)

Conclusions

The results of these experiments permit the following conclusions:

(1) The fluorocarbon rubber, uncured Viton B gum, loses HF when heated in air, inert atmosphere (N_2), and vacuum to give both conjugated double bonds and random unsaturation.

(2) Scission in the polymer chain predominates when the uncured gum is heated above 325–350°C.

(3) The uncured gum undergoes crosslinking reaction on heating, and the crosslinks are stable below 275–300°C.

(4) The original amine (Diak No. 3) vulcanizate network breaks down almost completely in a day or so at 250°C, but a new more thermally stable network is formed.

(5) Scission in the new network takes place preferably at the crosslinks.

(6) Network breakdown is faster in air, suggesting an oxidative mechanism.

(7) The lower activation energy for the Viton B amine-cured elastomer, as compared to the peroxide-cured LS 420 fluorosilicone (Reference 1), shows a lower stability for this Viton system in air at room conditions. The weak links in the latter are at the crosslink sites. Some other crosslink system, such as that brought about by γ irradiation or peroxides should lead to improved thermal stability in presence of oxygen.

(8) The amine-cured Viton B network is less stable in JP-4 fuel than in air at comparable temperatures.

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