Thermal Stability of Elastomeric Networks at High Temperatures

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Synopsis

Stress relaxation experiments were carried out in a dry nitrogen atmosphere on poly-dimethylsiloxane and an ethylene–propylene terpolymer. Relaxation times much longer than expected were observed, and plots of $\ln f(t)/f(0)$ versus time were linear in all cases.

Introduction

The effect of minute amounts of oxygen and water vapor on chemical reactions is well known.[1,2] Polymeric networks seem especially sensitive to such factors, since a chemical reaction involving one bond in a thousand may have profound effects on its physical properties. One such property is the continued ability of an elastomeric network to support a stress.[3]

In the present study, a standard stress relaxometer[3a] has been housed in a nitrogen chamber. The nitrogen, of 99.996% purity, was dried over calcium chloride crystals before being passed into the inner chamber (the relaxometer housing) of the apparatus. The use of a double chamber arrangement is thought to have maintained the extra purity of the atmosphere employed.

Two types of materials were examined in the present study: an organic elastomer, ethylene–propylene terpolymer, and an inorganic elastomer, polydimethylsiloxane. It was shown that the use of a very inert atmosphere demonstrates the stability of these materials at high temperatures.

Sample Preparation

A pure gum polydimethylsiloxane elastomer was kindly supplied by Dr. A. C. Martellock of the General Electric Company, Waterford, New York. This material, which contained 0.2 mole-% vinyl groups, was end-blocked with dimethylvinyl groups. The polymer was press-cured with 0.6% di-*tert*-butyl peroxide at 100 lb. steam pressure, followed by a 16-hr. post-cure at 300°F.

Ethylene–propylene terpolymer (Enjay 3509, ethylene 55 wt.-%, propylene 42 wt.-%, unsaturation 2.6 wt.-%) was cold-milled with 3 wt.-%

of dicumyl peroxide.   The polymer was cured in a Pasadena hydraulic press at 40,000 psi and 150°C.

In both cases the crosslinked samples were extracted with benzene for 24 hr. and dried for 48 hr. *in vacuo*.   All samples were kept under nitrogen for several days and then at reaction temperature for at least 3 hr. before stress relaxation studies were initiated.

Polydimethylsiloxane

Several previous papers have been concerned with the stress relaxation properties of this elastomer in inert atmospheres.   In 1954, Osthoff et al.[4] published their classical paper.   Using a sample crosslinked with high energy electrons and employing an atmosphere of anhydrous argon, these workers arrived at an activation energy of 22.8 kcal./mole for the Si—O bond interchange reaction.   In 1962, Turner and Lewis[5] described the properties of a filled silicone elastomer in a dry nitrogen atmosphere.   The rate of stress relaxation found was slightly slower than found by Osthoff,[4] but unfortunately, no activation energy was reported.   Both of these papers, however, exhibited curved lines in their plots of $\ln f(t)/f(0)$ versus time,[2] where $f(0)$ is the force needed to maintain extension at zero time, and $f(t)$ that needed at time t.   Very recently, Thomas[6] published a paper describing the relaxation properties of polydimethylsiloxane in a high vacuum.   The duration of his experiments were short.   However, he reported[7] that his rates of relaxation were comparable to those mentioned above.

All three papers stress the need for eliminating oxygen and water vapor from the systems and point out that the polymer must be free from catalyst residues, ionic groups, etc.   Indeed, one of us[8] has also investigated the effect of acid, finding such conditions highly detrimental.

Stress relaxations were carried out at 250, 277, and 301°C.   A plot of $\ln f(t)/f(0)$ versus time for the three temperatures is shown in Figure 1. In addition, pertinent data from the literature[4,5] are included for comparison.

It is observed that the current data have yielded straight lines, while those of Osthoff et al.[4] and Turner and Lewis[5] yielded curves.   It is useful to estimate the chemical relaxation times, τ_{ch}, defined as the time necessary for $f(t)/f(0)$ to drop to $1/e = 0.368$.[3b]   These value are shown in Table I.

TABLE I
Chemical Relaxation Times

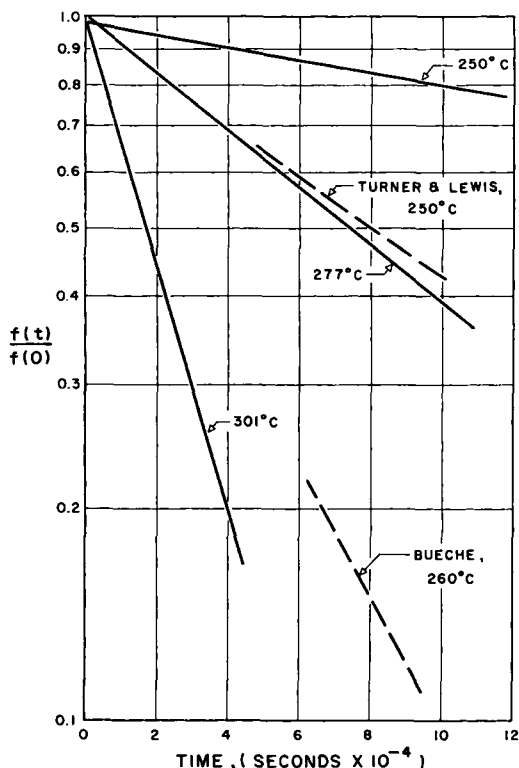| Reference	Temperature, °C.	$\tau_{ch} \times 10^{-4}$, sec.
Osthoff et al.[4]	250	8.6
Turner and Lewis[5]	250	16
Present work	250	48
Present work	277	10.5
Present work	301	2.45

Fig. 1. Stress relaxation of silicone rubber.   Note straight lines.

It is concluded that the rate of stress relaxation is markedly slower in the present work than in the other reported studies.[4,5]

A plot of ln τ_{ch} versus $1/T$ yields E_a/R for the slope.   An apparent energy of activation of 35 kcal./mole was estimated from such a plot.

Ethylene–Propylene Terpolymer (EPT)

Until recently,[9] the stress relaxation in an inert atmosphere and at high temperatures of purely hydrocarbon polymers with carbon–carbon cross-links has received very little attention.   This dearth of data is probably due to experimental difficulties.   Primarily, it is difficult to remove traces of oxygen from the system, whether it be in the apparatus, absorbed in the sample, or bound chemically to the sample.   Hydroperoxides are readily formed during the processing of the polymer and in the subsequent curing. Their decomposition can lead to degradation of the sample during the experiment.   This latter effect can be reduced to a certain extent by prior heat treatment.

These residual oxidative effects have led to a certain amount of confusion in the literature on thermal degradation, especially with oxidatively reactive
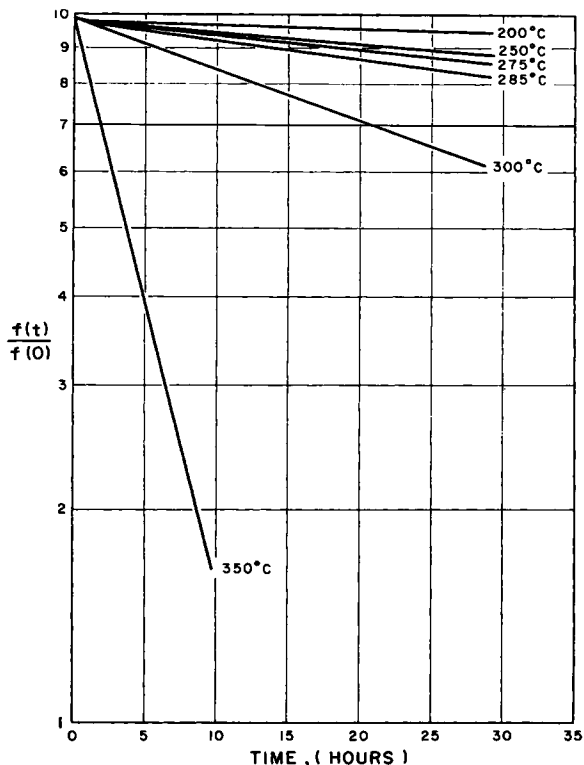
Fig. 2. Stress relaxation of ethylene–propylene terpolymer. Note straight lines after initial physical relaxation.

elastomers, e.g., natural rubber. More promising results have been obtained with the use of EPT and the apparatus described above.

The results of stress relaxation experiments in the temperature range 200–350°C. are shown in Figure 2. The plots of ln $f(t)/f(0)$ versus time are linear over the time scale of the experiments, except for an initial time portion, usually less than 30 min. This initial rapid relaxation is primarily due to molecular slippage.[3] However, the final rate was always constant for a particular temperature.

The polymer network exhibits remarkable stability, considering the high temperatures involved. Three important features were observed.

(1) The rate of relaxation was independent of sample thickness. This indicates that the rate of relaxation under the best conditions is not controlled by the surrounding atmosphere (i.e., traces of oxygen).

(2) Slow rates of relaxation in this system, at these high temperatures, are obtained only if the nitrogen is flowing into the inner chamber. Also, without the outer chamber the rate of relaxation is very rapid.

(3) A small amount of oxidative degradation of EPT networks causes the samples to turn brown. During these experiments, with the double chamber, the samples remained virtually colorless. A slight cloudiness did

TABLE II
Effect of Temperature on Rate of Stress Relaxation

Temperature T, °C.	$1/T \times 10^3$	$d[\ln f(t)/f(0)]/dt,$ $\text{min.}^{-1} \times 10^5$
200	2.12	1.9
250	1.91	6.03
275	1.82	7.23
285	1.79	10.8
300	1.74	24.9
350	1.61	318

develop, and after a long time the samples became limp and tacky. This indicates again that the stress relaxation is occurring by a mechanism other than oxidation.

The slopes of plots of $\ln f(t)/f(0)$ versus time are shown in Table II. This gives an activation energy in the temperature range 280–350°C. of 53 kcal./mole. Below 280°C. the temperature dependence falls off to an activation energy of 9 kcal./mole. Recent work by Yu and Wall[9] on the thermal degradation of an enthylene–propylene copolymer gave an activation energy of 42 kcal./mole over the temperature range 230–322°C. This was obtained by using rates of scission calculated from an equation which assumes random scission along the backbone of the polymer and an average chain length between crosslinks greater than 100.

Yu and Wall also studied the stress relaxation of crosslinked polyethylene. It is interesting to note that with polyethylene measurable stress relaxation started at 280°C., the temperature that we observed for the transition to the more rapid relaxation of EPT. From the present data and the Yu equation our rates of scission were found to be considerably lower than those estimated by Yu and Wall for their copolymer.

Discussion

Above, an apparent activation energy of 35 kcal./mole was deduced for the silicone elastomer. Whether this represents the activation of the Si—O bond interchange or the degradation of the vinyl polymer connecting the polydimethylsiloxane chains, or a combination of the two is not known. Likewise, the apparent activation energy of 53 kcal./mole for the stress relaxation of EPT may represent the overall activation energy of a complex series of reactions. However, the straight lines obtained suggests that only one mechanism is important in each case.

Because of the extreme sensitivity of the relaxations to moisture and oxygen, the present apparent activation energies must be viewed with caution. Perhaps a still better atmosphere would tend to reduce the relaxation rates still further, yielding significantly different values. Work on this problem is continuing in this laboratory.

References

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Résumé

On a effectué des expériences tension-relaxation dans une atmosphère d'azote sèche sur de polydiméthylsiloxane et des terpolymères éthylène-propylène.   Des temps de relaxation beaucoup plus longs qu' attendus ont été observés et les diagrammes du logarithme $f(t)/f(0)$ en fonction du temps étaient linéaires dans tous les cas.

Zusammenfassung

Spannungsrelaxationsversuche wurden an Polydimethylsiloxan und an einem Äthylen-Propylenterpolymeren unter trockener Stickstoff-atmosphäre ausgeführt.   Die beobachteten Relaxationszeiten waren viel länger als erwartet und in allen Fällen wurde eine lineare Abhängigkeit von ln $f(t)/f(0)$ von der Zeit erhalten.