Stress Relaxation Studies of Model Silicone RTV Networks

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Synopsis

The stress relaxation behavior of model silicone room temperature vulcanizing (RTV) elastomers has been used to examine the chemistry of the cured silicone network. It has been shown that the tin crosslinking catalyst, together with water, produces siloxane bond rearrangement which results in chemical stress relaxation. The measurement of the rate of stress relaxation of unfilled model elastomers at various temperatures gave an apparent activation energy of 10.3 kcal/mole^{-1} for the relaxation process. In addition, the effects of some of the constituents of the RTV on relaxation behavior have been examined.

INTRODUCTION

The chemistry of cure of silicone RTVs has been studied using techniques such as nuclear magnetic resonance (NMR) and infared (IR); however, the chemistry of the cured system has been largely overlooked due to experimental difficulties. Many analytical techniques are unable to distinguish between reactants and products in the cured system. For example, bond interchange in a polymer network results in products that are chemically indistinguishable from the reactants. However, the mechanical behavior of an interchanging network is quite different than that of a static one.

In order to examine the chemistry of cured RTV formulations, we have determined the stress relaxation behavior of unfilled model RTV elastomers. Using the technique, the physical and chemical relaxation of the silicone networks may be examined. In addition, bond cleavage and bond recombination may be differentiated. Furthermore, rate constants and activation energies may be obtained. For background information on the theory and principles of stress relaxation, several sources are available.[1]

EXPERIMENTAL

Materials

Dialkyltin salts were obtained from Eastman Kodak. All other materials were obtained from General Electric Silicone Products Business Division and were used without further purification. One component moisture cure model RTV formulations consisted of polydimethylsiloxane with hydrolyzable endgroups, silicone plasticizing fluid, crosslinker, adhesion promoter, stabilizers, and a dialkyltin salt (vulcanizing agent). The uncured RTV formulations were dispensed into a Teflon mold machined by Kintz Plastics, which held three
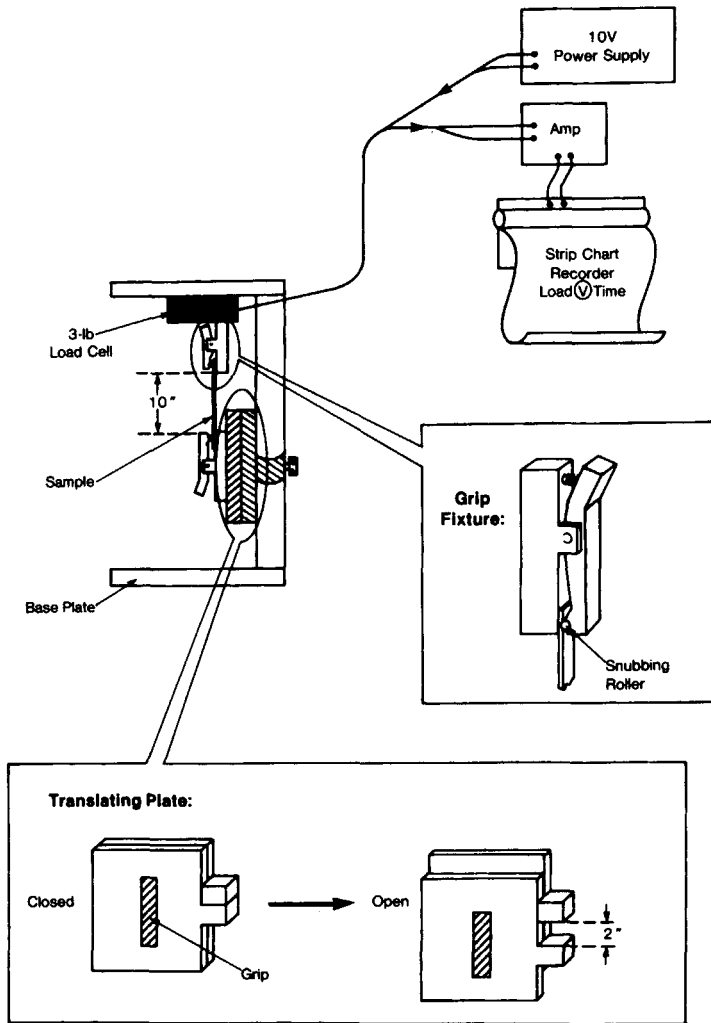
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Fig. 1.   The stress relaxation tester.

samples 12 inches × 0.5 inches × 0.075 inches. After one or two days of cure, the samples were removed from the mold and allowed to cure for a total of 14 days at 50% relative humidity (RH). Samples not used within 28 days of cure were discarded.

Stress Relaxation Instrumentation

The instrument was designed to mimic an Instron (Fig. 1). The framework was constructed from optical components ordered from the Newport Corporation. The 3 lb. load cell was obtained from Interface, Inc. The grips were designed and built utilizing a roller bar to grip the sample rather than a more severe "knife edge" type grip (see detail).

The top grip was attached to the load cell, with which load could be monitored with time on a strip chart recorder. The bottom grip was attached

to a translating plate. The back of the plate was attached to the framework, and the front section of the plate was than free to move downward to a full length of 2 inches through a series of grooves and springs (see detail). The gauge length was 10 inches before elongation and 12 inches at full elongation of the translating plate (strain = 20%).

Temperature was controlled by means of an elongating glass condenser attached to a constant-temperature water bath. Temperature was maintained to ±1°C. In addition, the atmosphere surrounding the sample was controlled by enclosing the entire apparatus in a glove bag.

Continuous Stress Relaxation Technique

Before testing, the thickness of each sample was measured. Then, approximately 1/2 inch was trimmed from each end of the length of the sample, where material defects were found to be the greatest. The sample was then placed between the upper and lower grip such that there was no measurable residual stress. It was then allowed to equilibrate in the desired atmosphere and at the desired temperature for a period of not less than 20 minutes.

The test was begun by quickly and smoothly bringing the translating plate down to the full length. After the elongation, a 2 inch length of aluminum block was paced between the stops of the translating plate.

The sample was then left in this condition for approximately 48 hours. This technique provided information on both chemical and physical relaxation. In particular, chain scission can be quantified since any bond recombination occurring during the duration of the experiment would not contribute to the stress.

Permanent Set Technique

The test procedure used for permanent set was the same as for the continuous test. However, the test was terminated at several different times during the 48-h test period and the sample allowed to rest for a period of time equal to the length of the test prior to measuring the deviation in gauge length from the original 10 inch length between grips.[2]

Permanent set provided information about bond recombination. After removing the sample from the tester, any chains that were not cut would cause the elastomer to recover. Bonds that have undergone scission followed by recombination in the relaxed state, would cause the sample to recover incompletely; the amount of permanent set can be directly related to the amount of chain recombination in the network.

Intermittent Stress Relaxation Technique

A sample was allowed to remain in an unelongated state, in the desired environment, for most of the 48-h test period. At appropriate intervals during the test period, the sample was loaded onto the tester as previously described and quickly elongated; the load reading was taken and the sample quickly returned to the unelongated state.[3]

Intermittent measurements provided information on both chain scission and recombination. As the material remains largely in an unstressed state,
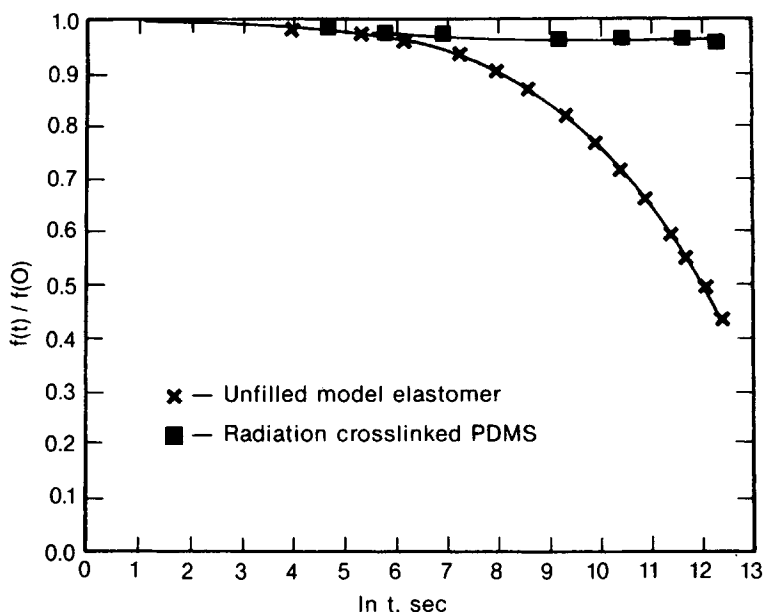
Fig. 2.   Physical (x) vs. chemical (■) relaxation for polydimethylsilicone elastomers.

relative reaction rates for scission and recombination in an unperturbed system may be observed. For example, scission in excess of recombination would result in a decay of stress over the period of the test.

RESULTS AND DISCUSSION

Physical vs. Chemical Relaxation

The stress relaxation spectrum of the model elastomer is shown in Figure 2. Comparison with the purely physical stress relaxation spectrum of a radiation crosslinked polydimethylsiloxane rubber[4] indicates that the rate of stress relaxation is much greater for the tin catalyzed sample; this is attributed to chemical stress relaxation.

The equation of state for a rubber states:[5]

$$f_{(0)} = n_{(0)}RT(\alpha^2 - 1/\alpha)$$ (1)

where:

$f_{(0)}$ = stress

$n_{(0)}$ = moles of network chains/unit volume

R = gas constant

T = temperature in Kelvin

$\alpha = \dfrac{\text{stretched length}}{\text{unstrectched length}}$

The initial stress on a sample is proportional to the number of loadbearing chains in the network. This equation is applicable at any time during the test, or[6]

$$f_{(t)} = n_{(t)}RT(\alpha^2 - 1/\alpha) \tag{2}$$

Thus,

$$\frac{f(t)}{f(0)} = \frac{n_{(t)}}{n_{(0)}} \tag{3}$$

The normalized stress at any time is equal to the ratio of loadbearing chains in the system to the original number of loadbearing chains. For instance, the model elastomer sample in Figure 2 has approximately 43% of the loadbearing original chains in the system still actively bearing load at the end of the test.

Kinetics

Observed rate constants for the composite relaxation were obtained from stress relaxation measurements of 30, 40, 50, and 60°C. The stress relaxation measurements were found to obey the following rate equation, where $\alpha = 1/2$:

$$\frac{f}{f_{(0)}} = e^{-kt^{\alpha}} \tag{4}$$

where:

$$f_{(t)}/f(0) = \text{normalized stress}$$

$$T = \text{time}$$

$$k = \text{observed rate constant}$$

$$\alpha = \text{fractal}$$

See Table I and Figure 3.

The rate constants were found to obey the Arrhenius equation with a correlation coefficient of 0.98, yielding an apparent activation energy of approximately 10.3 kcal for the composite relaxation.

TABLE I
Observed Rate Constants for Stress Relaxation

Temp. (°C)	k_{obs} (s^{-1})	Correlation coefficient
30	2.22×10^{-7}	> 0.9
40	3.33×10^{-7}	> 0.99
50	4.94×10^{-7}	> 0.99
60	1.08×10^{-6}	> 0.99
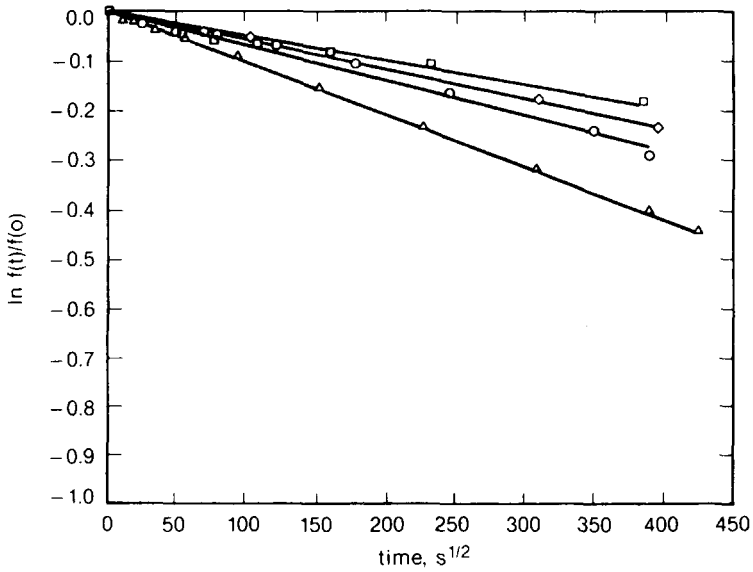
Fig. 3.   Stress relaxation functions at various temperatures. (□) 30°C/N_2; (◇) 40°C/N_2;(○) 50°C/N_2; (△) 60°C/N_2.

Cause of Chemical Relaxation

The chemical reaction responsible for stress relaxation was determined by comparison of the relaxation spectra obtained under various environmental conditions. In the first case (see Fig. 4), the experiments were performed under argon (~ 18% RH) thus eliminating most of the water and oxygen. Faster
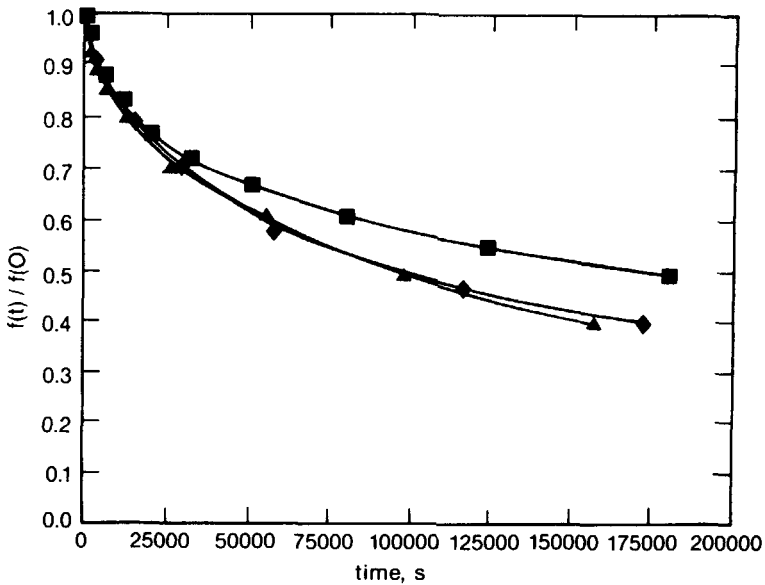

Fig. 4.   Stress relaxation functions obtained in various atmospheres. (◆) au, 40% RH; (■) argon, 18% RH; (▲) argon + H_2O, 40% RH.
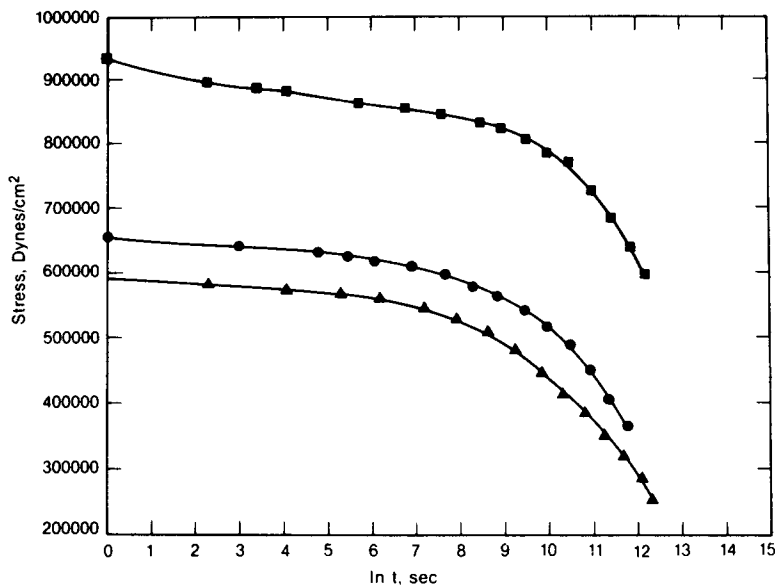
Fig. 5. The effect of plasticizer level on stress relaxation measurements. (■) 0%; (●) 7%; (▲) 14% plasticizer.

relaxation was observed when the experiment was performed under ambient conditions (~ 40% RH). The same relaxation rate was obtained when the experiment was performed under argon with a water content corresponding to a relative humidity of ~ 40%. These results clearly indicate that water is at least partly responsible for the chemical stress relaxation.

Two ways in which water may affect relaxation rates were postulated. First, water may cleave Si—O—Si bonds, thereby reducing the number of loadbearing chains. Alternatively, water may insert itself within the network, producing a plasticizing effect. In order to determine which mechanism was operative, the stress relaxation spectra of three samples with different levels (0%, 7%, and 14% by weight) of an inert silicone plasticizing fluid were obtained (Fig. 5). The plasticizer level had no effect on the shape of the curve, but did affect the stress at 20% elongation throughout the experiment. These results indicate that if water is acting to plasticize the matrix, then exposure to water should decrease the stress; however, the stress at 20% elongation of a sample remained at the value obtained under ambient conditions even after soaking in water for 24 hours. Thus, although water may cause some plasticization, the amount is negligible.

The above results suggest that water is involved in a bond cleavage reaction. It was found that in addition to water, the tin condensation catalyst is necessary to facilitate this cleavage. A sample swollen in toluene to remove the catalyst was found to exhibit no chemical relaxation. Therefore the proposed mechanism of chemical stress relaxation for the model network is:

$$Si—O—Si + H_2O \xrightarrow[\text{catalyst}]{} 2Si—OH \tag{5}$$

An activation energy of 10.3 kcal/mole is reasonable for acid catalyzed silox-
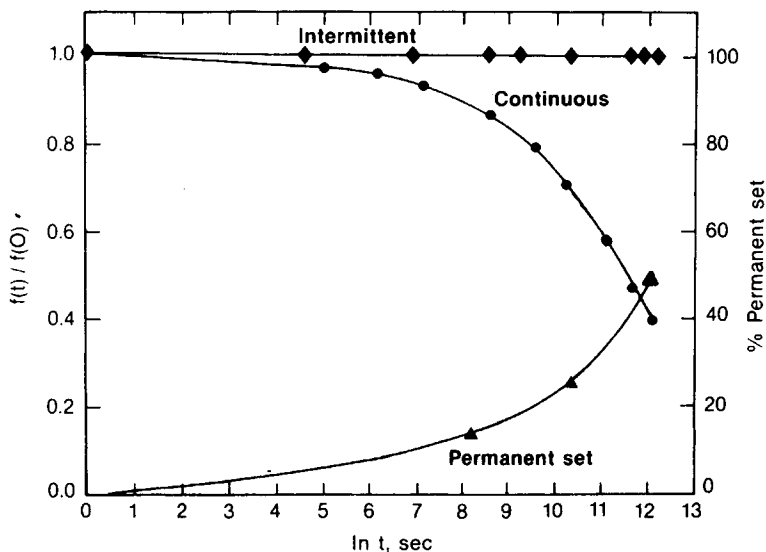
Fig. 6. Continuous (●) stress relaxation measurements vs. intermittent (◆) stress decay measurements and % permanent set (▲).

ane cleavage and is consistent with activation energies obtained by other workers[7] for chemically crosslinked polydimethylsilicone networks.

Bond Scission and Bond Recombination

Continuous stress relaxation tests provide information regarding chain scission; however, they yield no information regarding bond recombination since reformed chains are made at the new equilibrium length and therefore contribute nothing to the measured stress. On the other hand, in intermittent stress relaxation experiments, the sample is largely maintained in its un-strained state, so that any newly formed bonds do contribute to the stress. If only bond breaking is occurring, the intermittent and continuous tests would yield identical results; however, if more bond making than bond breaking were occurring (as in an incompletely cured system), the intermittent stress relaxation would give an increase in stress with time. Intermittent stress relaxation of the model elastomer showed a constant stress (see Fig. 6) indicating that bond scission and recombination are occurring at nearly equal rates.

The permanent set experiment provides information about bond recombina-tion and results obtained from intermittent stress relaxation experiments. In this experiment, the sample is elongated on the tester for an interval of time and then allowed to relax in the unelongated state for a period of time equal to or greater than the test time. The incomplete recovery of the sample is determined by measurement of the set length and corresponds to the amount of bond reformation at the elongated length. Without any bond recombina-tion the sample would eventually recover to its original length provided a proportion of the original load-bearing network chains are still intact. Re-formed bonds apply a force opposing the retractive force in the sample. The permanent set curve for the unfilled model elastomer is shown in Figure 6. The theoretical permanent set curve, calculated from the intermittent and
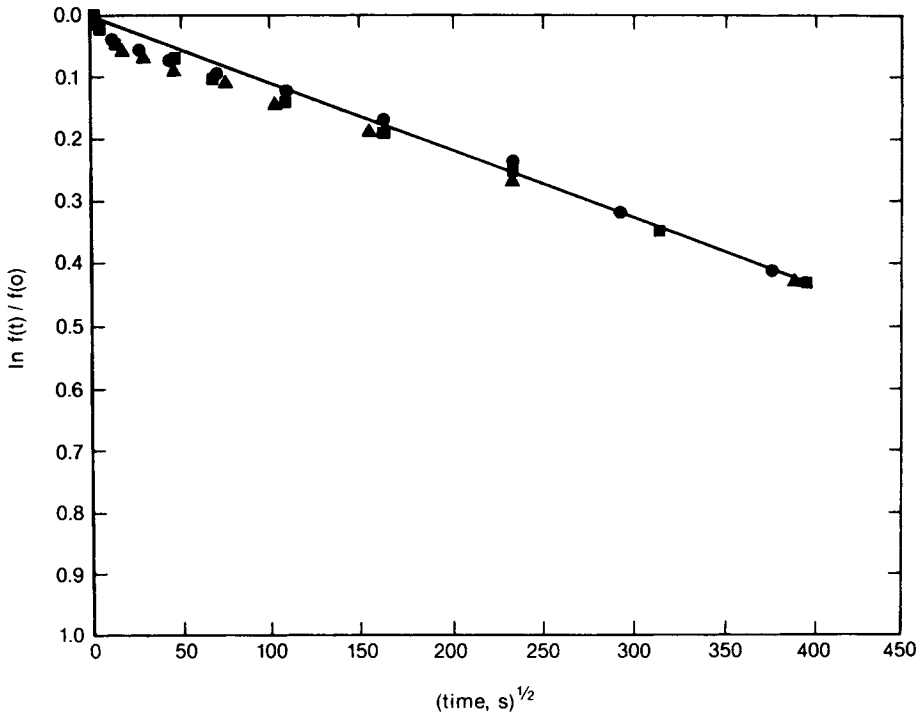
Fig. 7.   The effect of different strains on the observed rate of stress relaxation. (▲) 15% e; (■) 10% e; (●) 5% e.

continuous relaxation measurements according to equations in Ref. 2, overlays the experimental curve. This provides additional evidence that bond making and bond breaking proceed at nearly equal rates.

Effect of Different Strains

In order to ascertain that the observed processes are not strain-induced, three identical samples were subject to continuous testing with different strains, holding all other variables constant. In Figure 7, one can see that changing the amount of strain on the sample does not affect the stress relaxation behavior. All the samples showed the same rate of relaxation. This result is further supported by the findings of other workers,[8] who concluded that up to very large strains, chemically crosslinked PDMS systems behave independently of strain.

Effect of Cure Time

Four samples were dispensed and allowed to cure at 25°C, 50% RH for 7, 14, 32 and 76 days, respectively. At the appropriate time, each of the samples was subjected to continuous testing with all other variables held constant (Fig. 8). It was found that the rate of stress relaxation decreased with cure time. Identical relaxation rates were found for samples cured between 14 and 32 days. After 76 days of cure, the sample showed a marked decrease in the rate of relaxation due to either catalyst deactivation or a very slow rate of
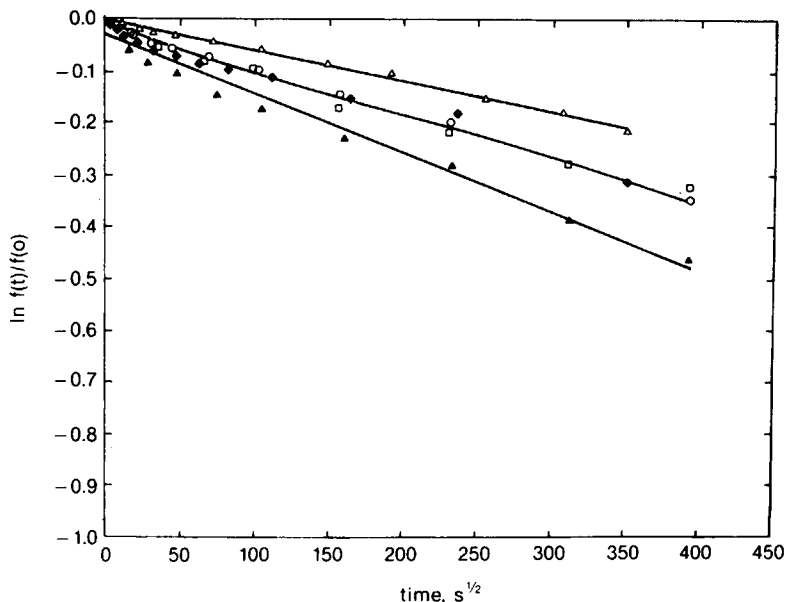
Fig. 8. The effect of varying cure time on the observed rate of stress relaxation. (▲) cured 7d/50% RH; (□) cured 14d/50% RH; (◆) cured 21d/50% RH; (○) cured 32d/50% RH; (△) cured 76d/50% RH.

crosslinking between 32 and 76 days. The latter theory is supported by calculation of the actual stress, in dynes/cm^2, at time zero for each of the tests: the stress at 20% elongation is found to increase between 7 and 14 days of cure, and again between 32 and 76 days. Therefore, all other tests were performed sometime between 14 and 28 days of cure in order to assure reproducibility.

CONCLUSIONS

Although the PDMS network was crosslinked when stress relaxation tests were performed, the material was still a dynamic, "living" system. Both bond scission and bond recombination were found to occur at nearly equal rates over the time scale of the experiment. Water in conjunction with tin cure catalyst was determined to cause the stress relaxation behavior via cleavage and recombination of siloxane linkages.

Stress relaxation has proven to be an excellent method for the study of the chemistry of the cured PDMS network. Further studies are planned to examine the effect of chemical constituents of the formulation (catalyst, fillers, crosslinkers, etc.), and of different cure systems, such as PDMS with acetoxy endgroups, on the stress relaxation behavior. Additionally, the site of bond cleavage (crosslink vs. random) will be determined.

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