

Physical and Chemical Stress Relaxation of Elastomers

JOHN G. CURRO and EDWARD A. SALAZAR, *Sandia Laboratories, Albuquerque, New Mexico 87115*

Synopsis

In this paper we have developed a method whereby physical and chemical relaxation processes can be distinguished, using stress relaxation experiments as a function of temperature. We assumed that there exists some temperature range above the glass transition temperature over which the chemical effects can be neglected for the time scale of the experiments. The data in this low temperature range were then used to determine the WLF constants and other physical relaxation parameters. The physical component of the stress relaxation could then be subtracted from high temperature experiments in order to extract chemical kinetic information. Based on certain reasonable assumptions, an equation was developed for the relaxation modulus of a chemically reacting system. This equation could be used to determine the time dependence of the crosslink density, or conversely could be used to predict the long term relaxation modulus from an assumed kinetic mechanism. These calculations were demonstrated for ethylene propylene and butyl elastomers.

INTRODUCTION

The long term properties of elastomers can result from two fundamentally different processes. First, there can be physical relaxation processes such as the flow of chains, the movement of entanglements, etc. Second, there can be chemical processes such as scission of covalent bonds at the crosslinks or along the main chain. The purpose of this investigation is to present a method whereby these two processes can be distinguished, using stress relaxation data at different temperatures.

Tobolsky¹ was probably the first to recognize that stress relaxation could be caused by chemical processes. The chemical component was identified by Tobolsky and others by performing the stress relaxation experiments at temperatures sufficiently high that the physical contribution to the relaxation process could be neglected. Other workers were able to separate physical and chemical processes under certain conditions where details about the chemical processes were known. For example, Bueche² attributed the chemical relaxation processes in poly(dimethylsiloxanes) to rearrangements caused by the presence of acid or base impurities. By performing stress relaxation experiments on purified samples, Bueche was able to subtract out the physical relaxation processes of the ordinary impure elastomers. Murakami³ and co-workers used experiments in a nitrogen atmosphere to subtract the physical part of the stress relaxation of ethylene propylene rubber (EPR) cross-linked with sulfur. These workers assumed that the chemical process in-

volved in the reaction was caused by the presence of oxygen and that no chemical processes occurred in the nitrogen experiment.

In this work we do not need to assume any details concerning the chemical reactions involved except that there exists some temperature range above the glass transition temperature where chemical processes can be neglected over the time scale of the experiment. From experiments in this temperature range, the WLF constants and other physical relaxation parameters are determined. The physical contribution to the stress relaxation is then calculated for the higher temperature experiments. Using this procedure, we were able to calculate the overall reaction kinetics occurring at temperatures where both physical and chemical relaxation processes are important. We have demonstrated this technique with the use of data obtained on EPR and butyl rubber. We also present equations that can be used to predict the long term viscoelastic properties of elastomer undergoing chemical reaction.

EXPERIMENTAL

Samples of EPR and butyl rubber were obtained from the Parker Seal Company. These materials were standard formulations crosslinked with both sulfur and peroxide. The stress relaxation experiments were performed in glass cylinders. The stress was monitored by load cells that were calibrated prior to the experiment. The temperature was controlled by heating tapes around the glass tubes. The temperature variation over the sample length was not greater than 2°C. The load cells were read by a PDP 8 computer that was programmed to take readings at specified intervals. The samples were fixed at approximately 20% strain. The Young's modulus was obtained from the stress and elongation, with the use of the well-known equation from rubber elasticity:⁴

$$E = \frac{3\sigma}{[\lambda - (1/\lambda^2)]} \quad (1)$$

where λ is the stretch ratio.

Swelling measurements were made on the sulfur- and peroxide-cured EPR in order to determine their crosslink densities. The solvent used was benzene and the procedure used was identical to that used by Bueche.⁵ The data were analyzed through use of the swelling formulae obtained by Flory.⁶

THEORY

We assume that the elastomer has a constitutive equation characteristic of a modified linear viscoelastic material:

$$\sigma(t) = \frac{[\lambda - (1/\lambda^2)]}{3(\lambda - 1)} \int_{-\infty}^t E_v(t-s) \frac{d\epsilon}{ds} ds \quad (2)$$

where σ is the stress, ϵ is the strain, and E_v is the relaxation modulus. The factor involving the stretch ratio is to account for small nonlinearities. E_v is considered to be parametric in the temperature and crosslink-density histories. The relaxation modulus can be written as an integral over the relaxation spectrum:

$$E_i(t) = E_i(\nu) + \int_{-\infty}^{\infty} H(\tau) \exp\{-t/\tau\} d \ln \tau \quad (3)$$

where E_i is the equilibrium modulus and H is the relaxation spectrum.

We now introduce the well-known time-temperature shift factor (a_T) and assume that it is given by the WLF equation⁷

$$\log(a_T) = -C_1(T - T_0)/(C_2 + T - T_0) \quad (4)$$

where C_1 and C_2 are constants and T_0 is the reference temperature. We also introduce an analogous shift factor for the crosslink density defined by a_ν .

$$a_\nu = \tau_n(T, \nu) / \tau_n(T, \nu_0). \quad (5)$$

This crosslink-density shift factor was first introduced by Plazek.⁸ Its use essentially assumes that all the relaxation times are shifted the same amount by a change in crosslink density. Experimental evidence, as pointed out by Plazek, indicates that a_ν has a power law dependence on the crosslink density:

$$a_\nu = (\nu_0 / \nu)^x \quad (6)$$

where ν_0 is the reference crosslink density and x is an experimentally determined exponent. Figure 1 shows data on several materials determined by Plazek,⁸ by Chasset and Thirion,⁹ and by the authors of this paper. It can be seen from this figure that a wide variety of elastomers obey the power law relationship with the same exponent $|x|$.

In using these two shift factors, we are assuming a specific type of temperature and crosslink-density history dependence of the viscoelastic processes. We can now write the relaxation modulus at any crosslink density or temperature as

$$\tilde{E}(t, T) = \tilde{E}_e(\nu) + \int_{-\infty}^{\infty} \tilde{H}(\tau) \exp\{-t/\tau a_T a_\nu\} d \ln \tau \quad (7)$$

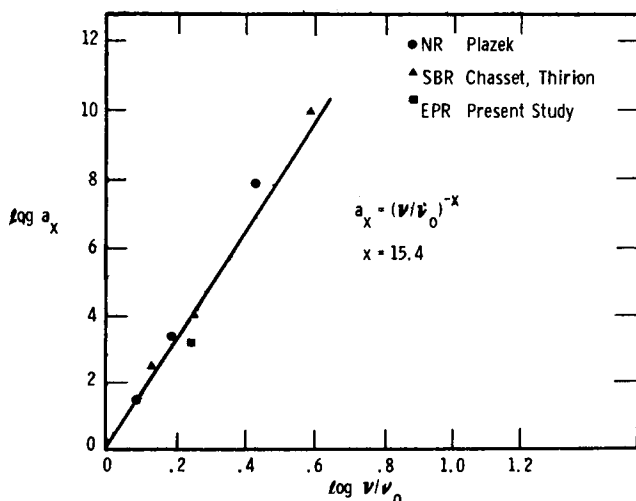


Fig. 1. Crosslink-density shift factor vs. crosslink density.

where the variables are reduced by the density-temperature product

$$\tilde{F} = F\rho_0 T_0 / \rho T. \quad (8)$$

In this work we will be primarily concerned with the long term behavior of the relaxation modulus. This corresponds to the terminal region of the relaxation spectrum. Experimental data indicate that the terminal region of the relaxation spectrum is approximately linear with a small slope. We thus approximate \tilde{H} by

$$\tilde{H} \propto \tau^{-m} \quad \text{large } \tau. \quad (9)$$

If eq. (9) is introduced into eq. (7), the integral can be performed for long times to give

$$\tilde{E}_v(t, T) = \tilde{E}_e [1 + (\tau^0 a_v a_T / t)^m] \quad \text{large } t \quad (10)$$

where τ^0 is a characteristic relaxation time. An empirical equation of this form was proposed by Chasset and Thirion⁹ to represent long term creep data. The equilibrium modulus can be expressed in terms of the crosslink density using the theory of rubber elasticity⁴

$$\tilde{E}_v(t, T) = 3 \left(\frac{V}{V_0} \right) G \nu k_B T [1 + (\tau^0 a_v a_T / t)^m] \quad (11)$$

where V is the volume and G is the so-called front factor. Both sides of this equation are now divided by the equilibrium modulus at a reference crosslink density to give

$$\frac{\tilde{E}_v(t, T)}{\tilde{E}_e(\nu_0)} = \frac{\nu}{\nu_0} [1 + (\tau^0 a_T / t)^m (\nu / \nu_0)^{-m\alpha}]. \quad (12)$$

This equation can be used to calculate the relaxation modulus of a chemically reacting system, provided of course that the time dependence of the crosslink density is known. Conversely, eq. (12) can be used to determine the kinetics of the reaction from experimental data for the relaxation modulus. A very similar approach was used recently by Moacanin, Aklonis, and Landel^{10,11} with a different constitutive assumption.

APPLICATION

We assume that in the temperature range 300° to 350°K that the chemical reaction is not significant over the time scale of the stress relaxation experiments (about 100 hr). From these low temperature data, the constants in the WLF equation [eq. (4)] were determined for EPR and butyl rubber cross-

TABLE I
Physical Relaxation Parameters

	m	τ^0 , hr	$E_e(n/m^2)$	C_1	C_2
Butyl	0.07294	0.0522	3.18×10^6	3.62	5.14
EPR	0.06526	0.0273	2.03×10^6	11.20	123.00

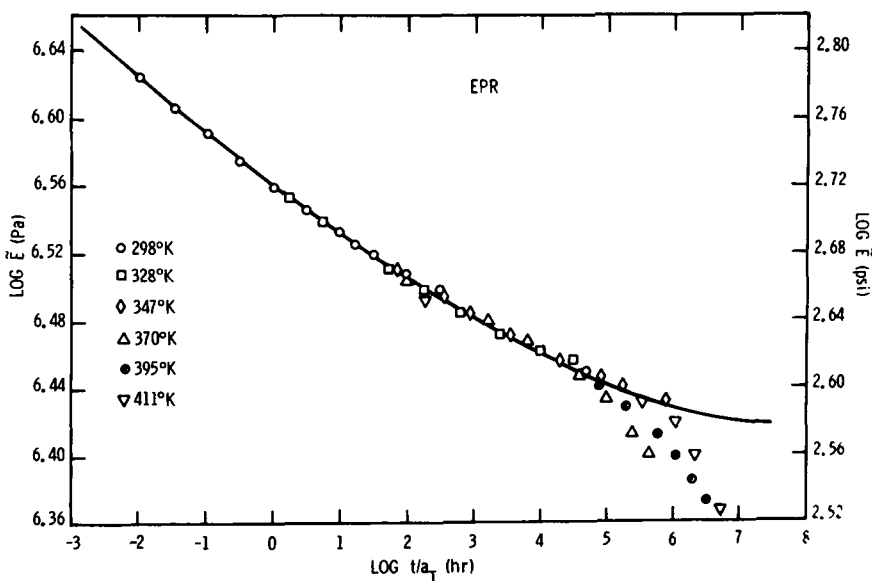


Fig. 2. Stress relaxation of EPR.

linked with sulfur. A least-squares technique was used to determine the constants from the observed shift factors, and the results are presented in Table I. The WLF equation was then used to compute the shift factors for the stress relaxation data above 350°K. The data on these two elastomers are plotted in Figures 2 and 3 as a function of $\log(t/a_T)$. It can be seen from these figures that superposition is not obtained at the higher temperatures. This deviation from time-temperature superposition is caused by chemical reaction effects.

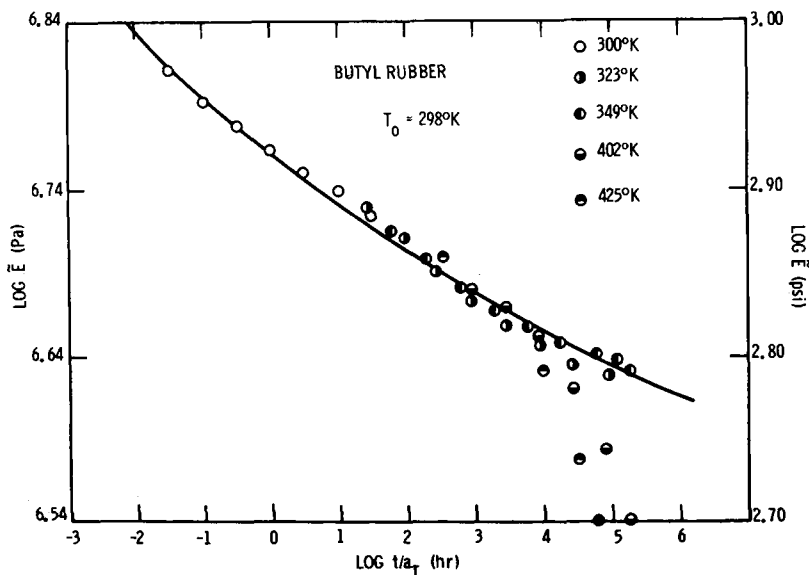


Fig. 3. Stress relaxation of butyl rubber.

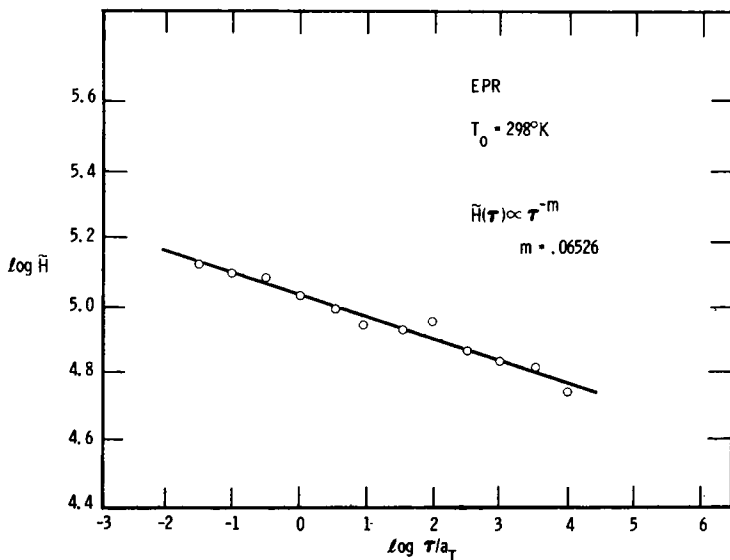


Fig. 4. Relaxation spectrum of EPR.

The physical relaxation parameters (m, τ^0, \bar{E}_e) can now be found. The relaxation spectrum was determined from the stress relaxation data in Figures 2 and 3 in the low temperature range. A second derivative approximation was used^{1,7} in this calculation. These results are shown on a log-log plot in Figures 4 and 5. It can be seen that straight lines are obtained for these two materials and that the slope of the lines is the parameter (m). With this value of m , the parameters τ^0 and \bar{E}_e were varied to get the best fit to the low temperature stress relaxation data. The solid lines in Figures 2 and 3 are calculated from eq. (10) with these parameters which are also given in Table I.

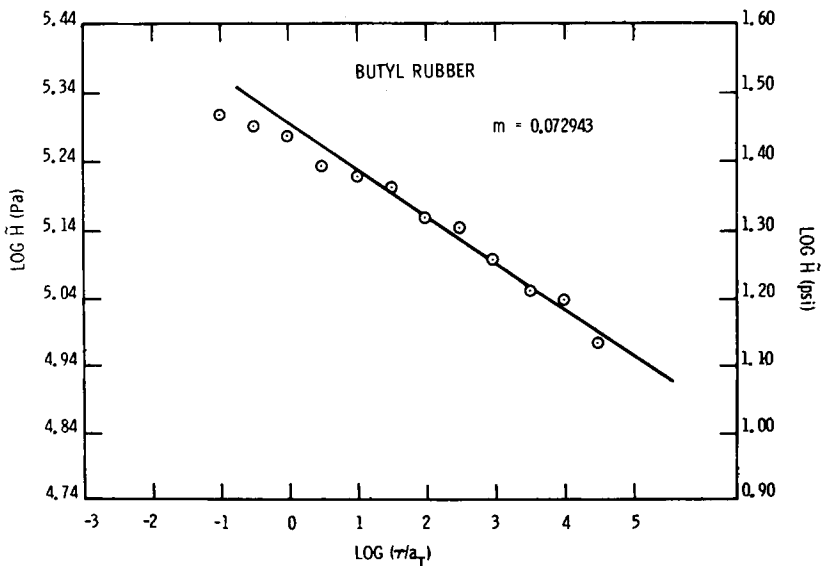


Fig. 5. Relaxation spectrum of butyl rubber.

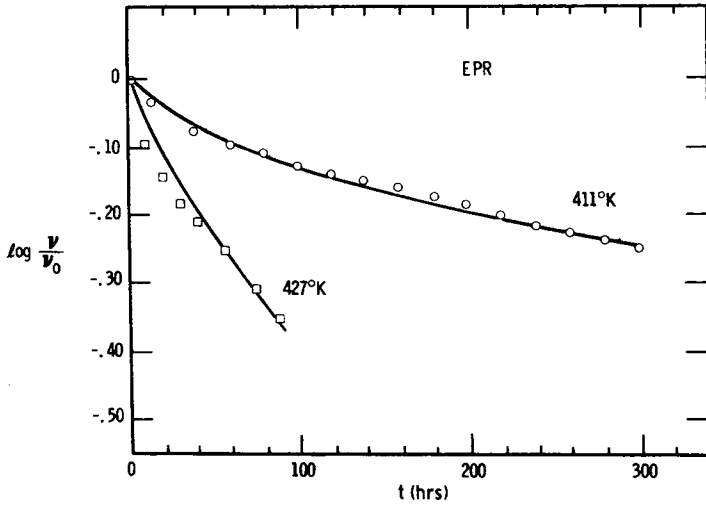


Fig. 6. Kinetics of EPR.

We are now in a position to calculate the time dependence of the crosslink density. Equation (12) can be expanded in a power series about $(1 - \nu/\nu_0)$. Neglecting terms higher than quadratic is permissible for small conversions. Equation (12) can then be approximately written as:

$$\frac{\tilde{E}_\nu(t, T)}{\tilde{E}_l(\nu_0)} = \frac{\nu}{\nu_0} \left[1 + \left(\frac{\tau^0 a_{T\nu}}{t} \right)^m (1 + mx) \right] - \left(\frac{\nu}{\nu_0} \right)^2 mx \left(\frac{\tau^0 a_{T\nu}}{t} \right)^m. \quad (13)$$

This quadratic equation can then be solved for ν/ν_0 to give

$$\frac{\nu}{\nu_0} = \frac{F}{2mx} \left\{ 1 - \left[1 - \frac{4mx\tilde{E}_\nu}{\tilde{E}_e} \left(\frac{t}{\tau^0 a_{T\nu}} \right)^m F^{-2} \right]^{1/2} \right\} \quad (14)$$

$$F = \left(\frac{t}{\tau^0 a_{T\nu}} \right)^m + 1 + mx.$$

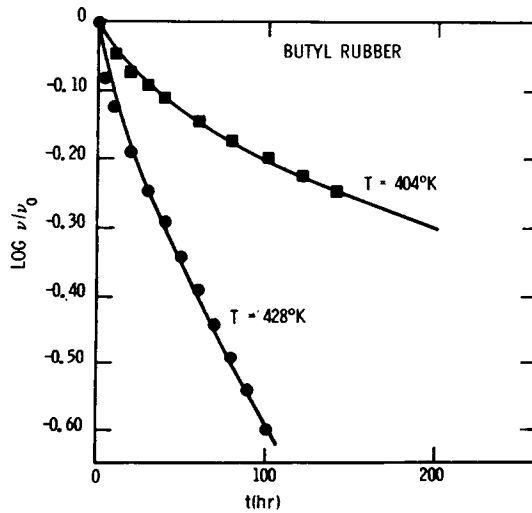


Fig. 7. Kinetics of butyl rubber.

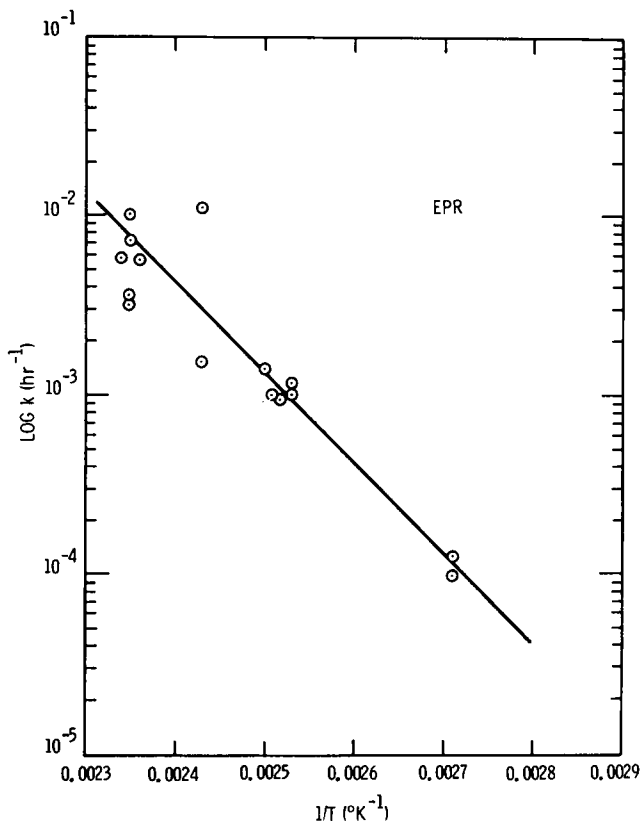


Fig. 8. Arrhenius plot for EPR.

Equation (14) was used together with the high temperature stress relaxation data to determine the time dependence of the crosslink density in EPR and butyl rubber. The results are shown in Figures 6 and 7.

KINETICS

We feel that because of the relative stability of the backbone chains in EPR and butyl rubber, that the reduction in crosslink density in these materials is primarily caused by scission at the sulfur crosslinks. In the butyl compound, there is a small amount of unsaturation present (about 2%) which could lead to some main-chain scission. If random scission at the crosslinks was occurring, then a first-order reaction would be expected.¹ From Figures 6 and 7 it can be seen that there is some curvature in the lines, which indicates that the reaction is not first order. This curvature could be caused by the existence of a distribution of sulfur chain lengths in the crosslinks and, also, by different rate constants for the scission of (C—S) bonds and (S—S) bonds. The effect of chain length can be seen by letting P_n be the number of sulfur chains having n units. The rate of change of this number is given by the rate expression

$$(-dP_n / dt) = nkP_n. \quad (15)$$

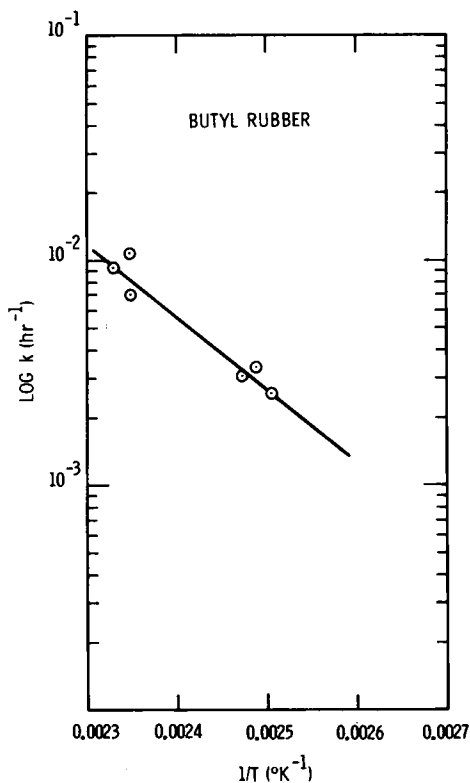


Fig. 9. Arrhenius plot for butyl rubber.

This equation can be easily solved for P_n . The crosslink density is the sum over all chain lengths n .

$$\nu = \frac{1}{V} \sum_n P_n = \frac{1}{V} \sum_n P_n^0 \exp\{-nkt\}. \quad (16)$$

An equation of this form can account for the curvature in the lines in Figures 6 and 7. Of course, a knowledge of the chain distribution is required in order to use eq. (16).

For engineering purposes, the reaction kinetics can be approximated by a first-order process. The first-order rate constants obtained are shown on Arrhenius plots in Figures 8 and 9. The activation energies are 20.0 and 16.9 kcal/mole for the sulfur-cured EPR and butyl elastomers, respectively. This information can be used to make predictions of the long time behavior of these materials from eq. (12). Log-log plots of the predicted relaxation modulus, as a function of time, are shown in Figures 10 and 11 for various temperatures. The kinetic parameters used in these predictions are shown in Table II. The physical relaxation parameters used appear in Table I.

CONCLUSIONS

In this paper we have described a method that can be used to differentiate between physical and chemical processes in long term experiments. The assumptions made were:

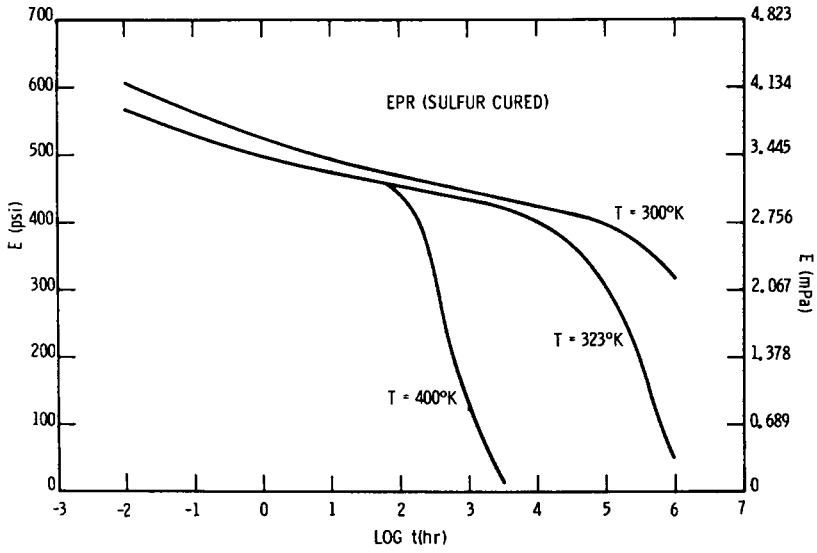


Fig. 10. Projected relaxation modulus of EPR.

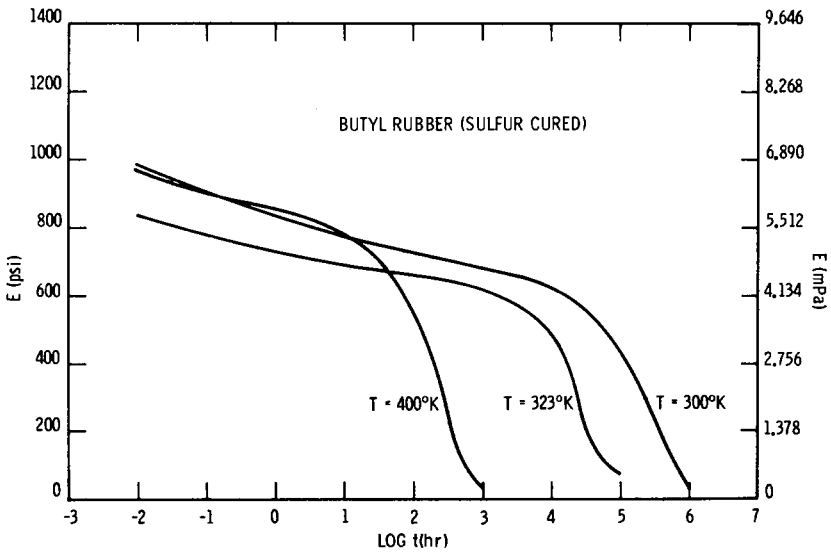


Fig. 11. Projected relaxation modulus of butyl rubber.

TABLE II
Kinetic Parameters

	S, 1/hr	H, kcal/mole
Butyl	4.287×10^6	16.9
EPR	4.940×10^8	21.4

1. There exists some temperature range above the glass transition over which chemical effects can be neglected over the time scale of the stress relaxation experiment (about 100 hr).

2. The material is thermorheologically simple, that is, time-temperature superposition can be used.

3. A crosslink-density-time shift factor can be applied, and the form of this shift factor is a power law dependence of the crosslink density.

4. The relaxation spectrum in the terminal relaxation zone is proportional to the reciprocal of the relaxation time raised to some small power (m).

These assumptions have been verified experimentally for EPR and butyl rubber. With the required physical relaxation parameters, eq. (12) can be used to extract chemical kinetic information on the change of crosslink density.

Equation (12) can also be used to predict the long term relaxation modulus of elastomers, once the time and temperature dependence of the crosslink density are established.

The authors would like to thank Dr. L. A. Harrah of Sandia Laboratories for his assistance in interfacing the PDP 8 computer to our stress relaxation equipment. The authors would also like to thank Dr. J. J. Aklonis for bringing reference 8 to their attention.

This work was supported by the U.S. Atomic Energy Commission.

References

1. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960.
2. R. C. Osthoff, A. M. Bueche, and W. I. Grubb, *J. Amer. Chem. Soc.*, **76**, 4659 (1954).
3. K. Murakami and S. Tamura, *J. Polym. Sci. A-1*, **9**, 423 (1971).
4. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford Univ. Press, London, 1958.
5. T. J. Dudek and F. Bueche, *J. Polym. Sci. A-2*, **2**, 811 (1964).
6. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953.
7. J. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1970.
8. D. Plazek, *J. Polym. Sci. A-2*, **4**, 745 (1966).
9. R. Chasset and P. Thirion, *Proc. Int. Conf. on Noncrystalline Solids*, North-Holland Publishing, Amsterdam, 1965, p. 345.
10. J. Moacanin, J. J. Aklonis, and R. Landel, *Amer. Physical Soc. Bull.*, **16**, 342 (1971).
11. J. Moacanin, J. J. Aklonis, and R. Landel, private communication.

Received May 28, 1974