

# Stress-Relaxation and Stress-Strain Behavior of Poly(ethylene-co-vinylacetate) at Varying Crosslink Density

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## Synopsis

The stress-relaxation modulus of an unfilled ethylene vinyl acetate polymer at three different degrees of crosslinking was measured at 15 temperatures over a temperature span of about 160°C. At each temperature, the time response was measured for at least 3 decades of time. From these data it was possible to construct a master curve for each degree of crosslinking. The time-temperature shift factors,  $a_T$ , were found to be related to temperature by the relation  $\log a_T = -A(T - 273)$ , where the parameter  $A$  has an average value of 0.234 for the three materials.

## INTRODUCTION

The mechanical behavior of a crosslinked ethylene-vinyl acetate copolymer (EVA) (30 wt % ethylene and 70 wt % vinyl acetate) has been investigated. EVA is a prime candidate for the pottant material for solar cell modules. A specific formulation, based on crosslinked EVA (denoted as A9918), has been developed which has been designed as a pottant for high speed encapsulation application to solar cell modules.\* During this phase of the effort, relatively little work on the mechanical behavior of the material, especially as a function of time and temperature, was carried out. The objective of the work reported here is to provide data on the mechanical behavior of this EVA system, and especially the long time response.

Solar cell arrays for the direct conversion of light into electricity will be economically feasible provided the useful lifetime of the array is sufficiently long, i.e., of the order of 25 years or so. This lifetime requirement implies that each of the components used in construction must also be able to carry out their individual functions for at least the required lifetime of the array. For components based on polymeric materials, one would like information about the mechanical response as a function of both time and temperature. It is obviously not possible to test each component for 25 years and some kind of accelerated testing must be carried out whereby the effects of both time and temperature can be substantially speeded up so that meaningful data with which to predict behavior over extended time and temperature regions can be obtained but over much shorter testing intervals.

For polymeric systems which do not undergo substantial amounts of deg-

\* This portion of work was carried out by Springborn Laboratories, Enfield, CT.

TABLE I  
 EVA Formulations

	Standard A9918	2X	4X
ELVAX 150	100	100	100
Lupersol 101	1.5	3	6
Naugard-P	0.2	0.2	0.2
Tinuvin 770	0.1	0.1	0.1
Cyasorb UV-531	0.3	0.3	0.3
Vulcanization time (min) at 150°C <i>in vacuo</i>	20	60	80

radation, a framework called viscoelastic analysis exists whereby the effects of time and temperature on the mechanical behavior can be assessed using a special type of accelerated testing. This is based on the fact that, for viscoelastic materials, the effects of time and temperature are directly related so that one can convert temperature data directly into corresponding time data and conversely.

In the work described here, the stress-relaxation behavior of EVA cross-linked to three levels has been measured over a very wide temperature range. The superposed stress-relaxation response has been obtained as well as the time-temperature shift factors. The stress-relaxation behavior was measured because it represents the basic time-dependent response from which other time-dependent responses such as creep can be obtained.

## EXPERIMENTS

### Materials

Three crosslinked EVA compositions were studied. These are listed in Table I where the entries denote parts by weight. Elvax 150 is the base polymer and is composed of 70 wt % vinyl acetate and 30 wt % ethylene. Lupersol 101 is the peroxide vulcanizing agent, and the remaining three ingredients are antioxidants and UV stabilizers which serve to decrease the rate of chemical degradation as promoted by oxygen and ultraviolet light. Vulcanization was accomplished at 150°C in vacuum bags for the times indicated in the Table. Material A9918 was compounded and vulcanized by Springborn Laboratory and was received in the form of vulcanized sheets.\* The 2X and 4X compositions were compounded and vulcanized by us using the same lots of ingredients furnished by Springborn which were used to prepare A9918.

 TABLE II  
 Sol Fraction and Network Chain Concentration for EVA

Material	Sol fraction	$\nu_e \times 10^6$ (mol/cc)
A 9918	0.45	0.77
2X	0.05	70
4X	0.08	180

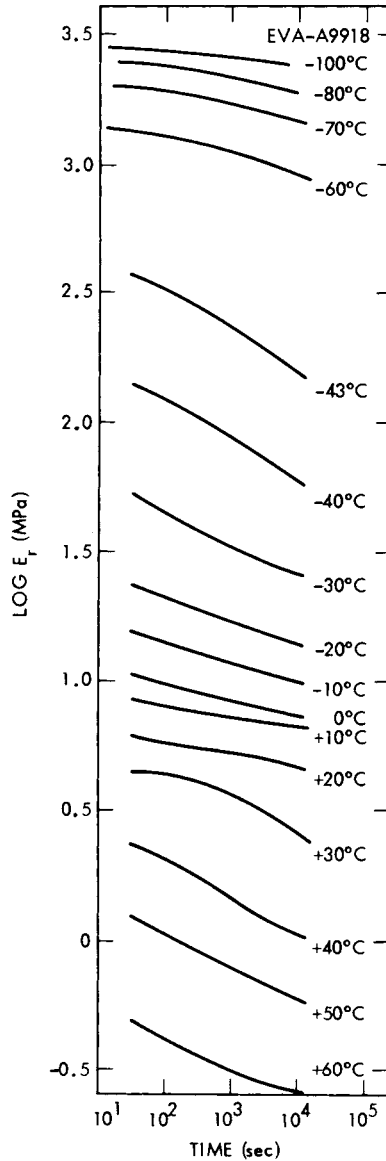


Fig. 1. Dependence of logarithm of reduced modulus  $E_r$ , on logarithm of time for A9918 at several temperatures from  $-100$  to  $+60^\circ\text{C}$ .

### Stress-Relaxation

Stress-relaxation experiments were carried out using an Instron testing machine fitted with a temperature chamber which could reach temperatures from  $-100$  to  $+60^\circ\text{C}$ . The vulcanizates in the form of strips 0.375 in. wide, about 0.060 in. thick and with a 4-in. gage length were mounted in the machine and strained to either 2% strain at low temperatures or 10% strain at higher temperatures using a crosshead speed of 10 in./min; after the appropriate strain was reached, the strain was held constant and the

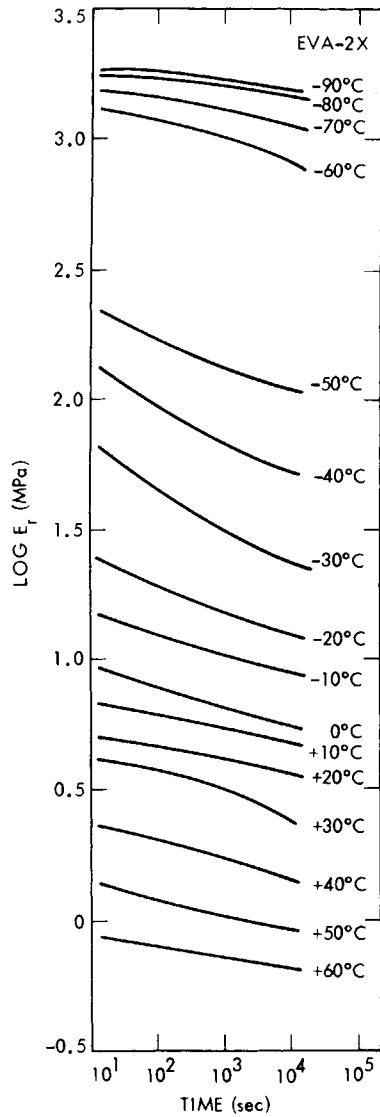


Fig. 2. Dependence of logarithm of reduced modulus  $E_r$ , on logarithm of time for JPL 2X at several temperatures from  $-100$  to  $+60^\circ\text{C}$ .

decay in stress was monitored for a time span covering about 3.5 decades. The stress value was converted to the corresponding modulus by dividing the stress by the appropriate strain. Log-log plots of the modulus vs. time were prepared for each test temperature. It should be noted that the modulus values are reduced modulus values corrected for temperature, i.e., the values plotted are  $E_r = E T_0/T$ , where  $E$  is the modulus measured at the temperature  $T$  and  $T_0$  is an arbitrarily chosen reference temperature taken to be  $273^\circ\text{K}$ . The necessity for the temperature correction factor is discussed by Ferry.<sup>1</sup>

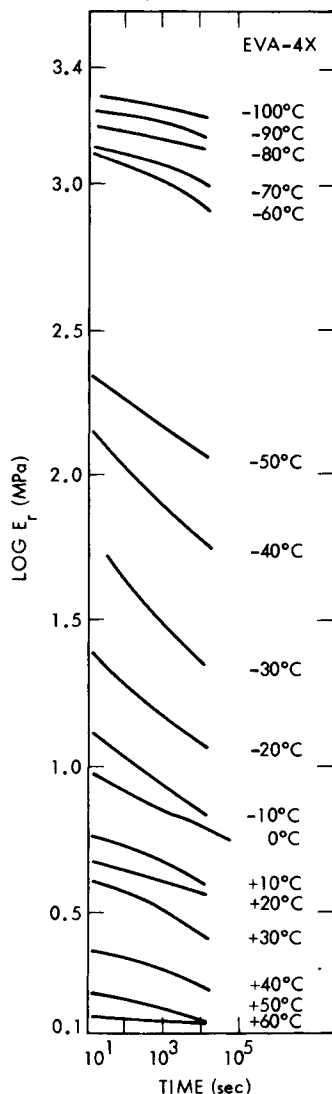


Fig. 3. Dependence of logarithm of reduced modulus  $E_r$ , on logarithm of time for JPL 4X at several temperatures from  $-100$  to  $+60^\circ\text{C}$ .

### Sol-Gel Studies

An important parameter affecting the mechanical behavior of a rubber vulcanizate is the concentration of network chains,  $\nu_e$ . A convenient method of estimating  $\nu_e$  is the use of equilibrium swelling measurements in a good solvent. It has been shown that the relationship between the equilibrium swelling and network chain concentration is given by<sup>2</sup>

$$\nu_e = \frac{-[\ln(1 - V_2) + V_2 + \chi_1 V_2^2]}{V_0 (V_2^{1/3} - V_2/2)} \quad (1)$$

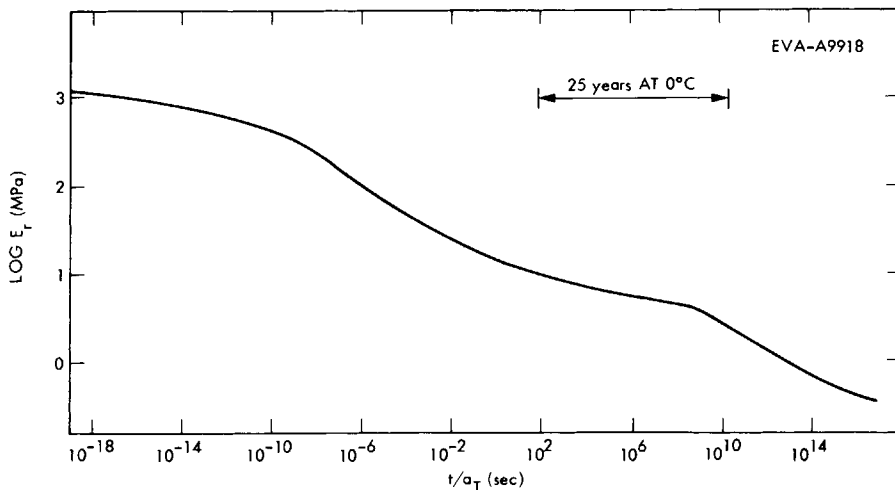


Fig. 4. Master curve for the logarithm of the reduced modulus and logarithm of reduced time (s) for A9918.

where  $V_2$  is the volume fraction of crosslinked EVA in the swollen gel at equilibrium,  $\chi_1$  is the solvent-polymer interaction parameter, and  $V_0$  is the molar volume of the solvent. For the work reported here, the solvent used was toluene; hence  $V_0 = 106.3$  cc/mol. The quantity  $V_2$  was estimated using

$$V_2 = \frac{W_p}{W_p + (\rho_p/\rho_s) W_s} \quad (2)$$

where  $W_p$  is the weight of polymer in the swollen gel,  $W_s$  is the corresponding weight of solvent, and  $\rho_p$  and  $\rho_s$  are the density of polymer and solvent, respectively. The value of  $\chi_1$  was estimated from solubility parameter values using<sup>3</sup>

$$\chi_1 = 0.34 + (V_0/RT)(\delta_p - \delta_s)^2 \quad (3)$$

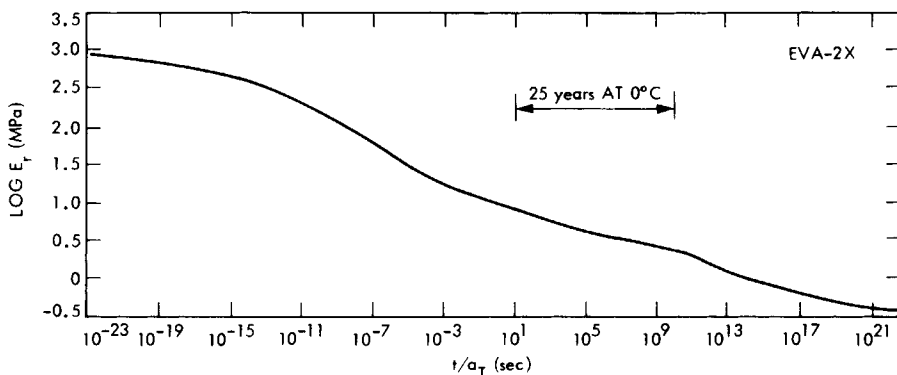


Fig. 5. Master curve for the logarithm of the reduced modulus and logarithm of reduced time (s) for JPL 2X.

where  $R$  is the gas constant in the appropriate units,  $T$  is the temperature (298 K), and  $\delta_p$  and  $\delta_s$  are the solubility parameters for the polymer and solvent, respectively.  $\delta_s$  has the value  $8.97 \text{ (cal/cm}^3)^{1/2}$  while the value of  $\delta_p$  of  $9.1 \text{ (cal/cm}^3)^{1/2}$  was estimated using the method described in Ref. 4. Using these data,  $\chi_1$  was calculated to have the value of 0.35.

In a typical experiment, a specimen about 0.07 in. thick and weighing about 1 g was dried to constant weight at room temperature in a vacuum oven. The specimen was then placed in a screw-cap jar containing about 200 mL of reagent grade toluene and tightly closed. The sample was allowed to swell and the weight of the swollen rubber was monitored weekly until a constant weight was obtained. During this time, the toluene swelling agent was replaced with fresh solvent 3–4 times. After the sample reached constant weight, it was removed and allowed to air dry and subsequently dried to constant weight at room temperature in a vacuum oven. The difference between the weight of the swollen gel (at equilibrium) and the final dry weight was taken to represent the weight of solvent in the swollen gel. The sol fraction was taken as the difference between the initial and final dry weight. The  $\nu_e$  values and corresponding sol fractions for the samples studied are listed in Table II.

## RESULTS AND DISCUSSION

### Stress-Relaxation

Figures 1–3 show the dependence of the logarithm of reduced modulus on logarithm of time (s) for the EVA vulcanizates as a function of test temperature. Figure 1 represents the data obtained using the sample prepared by the contractor containing 1.5 parts of peroxide. Figure 2 represents the 2X, and Figure 3 the 4X samples. At all test temperatures and for the three vulcanizates, the reduced modulus may be seen to decrease mono-

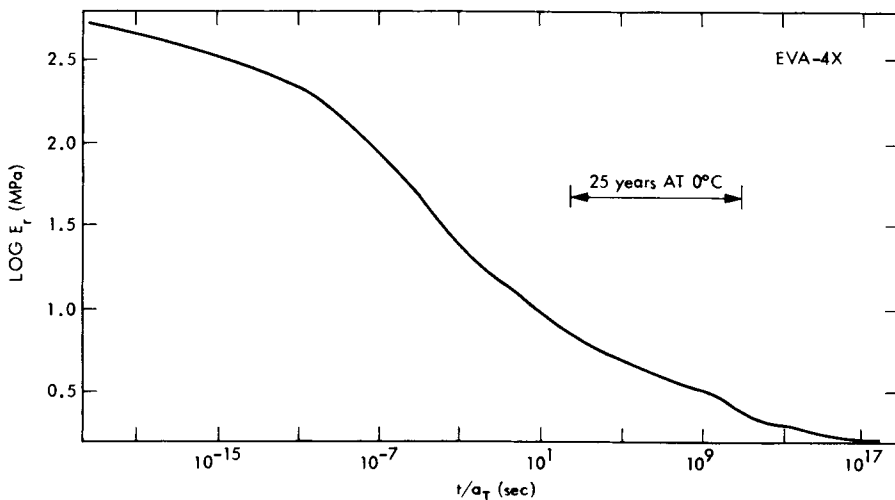


Fig. 6. Master curve for the logarithm of the reduced modulus and logarithm of reduced time (s) for JPL 4X.

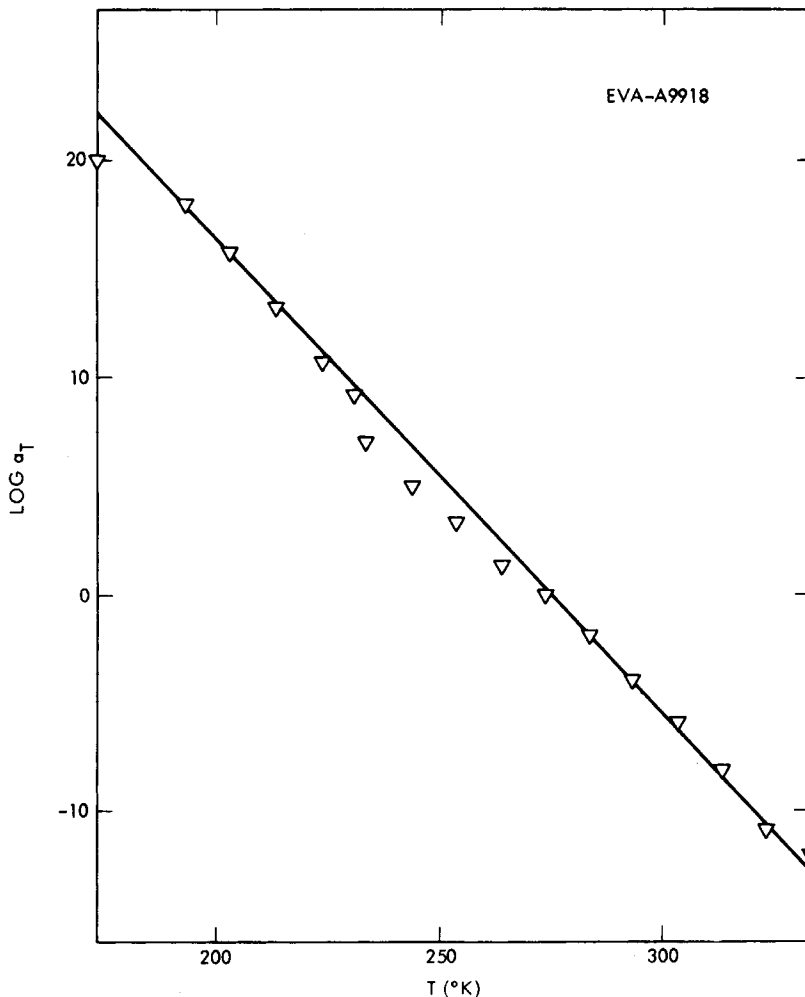


Fig. 7. Dependence of logarithm of the shift factor  $a_T$  on absolute temperature for sample A9918. The reference temperature is 273 K.

tonically with time. This is the expected behavior. For a viscoelastic material, it has been found that the isothermal responses for a given sample can be shifted horizontally to generate a master or superposed relaxation curve.<sup>1</sup> In practice, one temperature is taken as a reference, and the remaining isothermal responses are shifted horizontally until a smooth continuous curve is formed. The master curves constructed from the data in Figures 1-3 are shown in Figures 4-6. In all cases, the reference temperature was chosen to be 273 K. The horizontal shift denoted by the symbol  $a_T$  is then used to define the new variable  $t/a_T$  called the temperature reduced time or simply the reduced time.

It is apparent from the figures that there is insufficient overlap in the temperature range from about  $-43$  or  $-50$  to  $-60^\circ\text{C}$  to enable one to obtain a definitive value for  $a_T$ . The value of  $a_T$  used in this temperature interval for each sample is therefore approximate only. In addition, at the high test



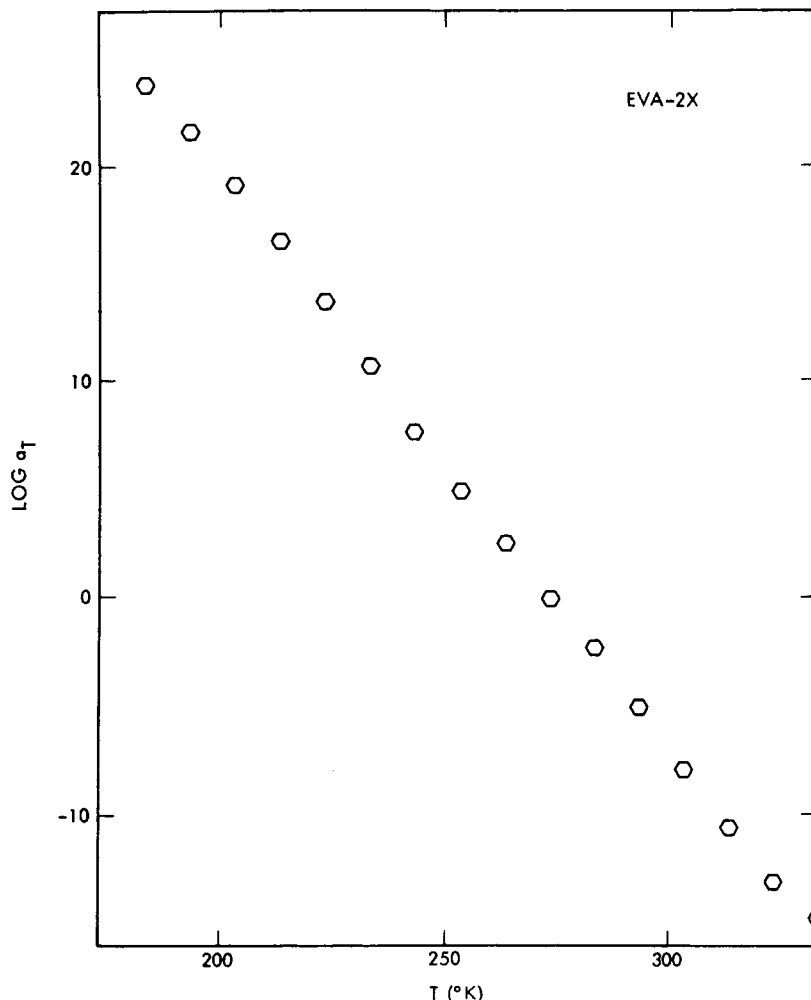


Fig. 8. Dependence of logarithm of the shift factor  $a_T$  on absolute temperature for sample JPL 2X. The reference temperature is 273 K.

temperatures, the overlap between the isothermal data is less than one would desire; however, there is still sufficient overlap to enable reliable values of  $a_T$  to be obtained.

The dependence of  $a_T$  on temperature is shown for each sample in Figures 7-9, where the logarithm of  $a_T$  is plotted as a function of the absolute  $T$ .  $\log a_T$  is zero in each case for  $T = 273$  K because this is the reference state. As may be seen, the response in all three cases is linear over the whole temperature range and hence the relationship between  $a_T$  and temperature can be represented simply by means of an equation of the form:

$$\log a_T = -A(T - 273) \quad (4)$$

where  $A$  is the slope of the response. For both A9918 and 4X,  $A$  has the value 0.221 while, for sample 2X,  $A$  has the value 0.261. These three  $A$

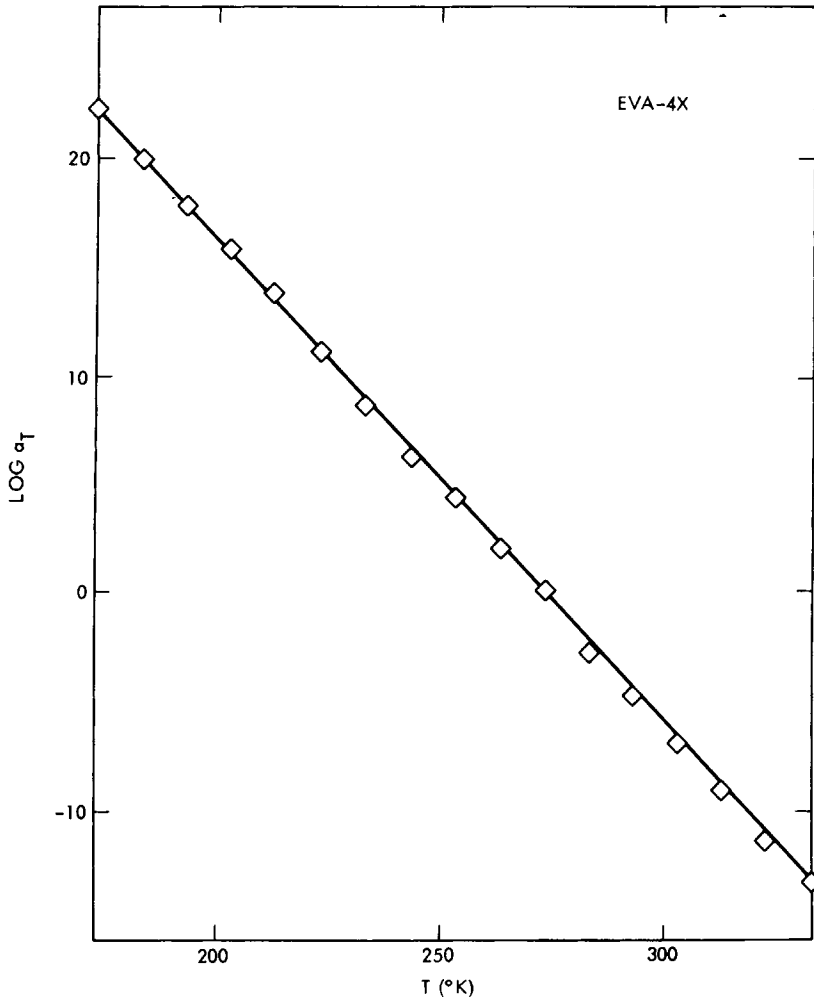


Fig. 9. Dependence of logarithm of the shift factor  $a_T$  on absolute temperature for sample JPL 4X. The reference temperature is 273 K.

values are numerically very close in value, and for all practical purposes one may use an average value of  $A$  equal to 0.234 to represent the three sets of data without serious error; this implies that  $A$  is independent of the concentration of network chains.

Returning to the stress-relaxation data (Figs. 4-6) the response shown by all these EVA vulcanizates resembles in a general way similar data for typical polymers. One should note the enormous time spans represented by these data as the time scale ranges over about 32 decades of time; stated in another way, the data in these figures represent the time dependence of the stress-relaxation modulus over 3.2 centuries of time. At short times, roughly for times less than about  $10^{-10}$  s, the three EVA materials are glassy and, consequently, have small breaking strains. In the range about  $10^{-10}$  to  $10^{-2}$  s, the materials are tough and leathery and have higher

breaking strains; for times greater than about  $10^{-2}$  s, they are rubbery, and, in this state, the breaking strains are largest.

An additional transition is evident at a time of about  $10^9$  s, which is particularly pronounced in the lightly crosslinked A9918 material. It is much less evident in the more highly crosslinked 2X and 4X materials. This transition is attributed to the onset of viscous flow.

In each figure, the horizontal bars represents 25 years of *elapsed* time assuming that the initial time represents 1 s, i.e., that the sample load was applied in 1 s after which the clock is started. A comparison of the length of the bar with the abscissa will give a better appreciation of the time dependence of the reduced stress-relaxation modulus. A question of interest in this connection is the following: If the EVA vulcanizate is deformed at, say, a temperature of 298 K (25°C) in 1 s what will be the stress-relaxation modulus 25 years later. The answer is readily obtained as follows: Since the reference temperature employed for reducing the data shown in the figure is 273 K, we use eq. (1) to calculate the  $a_T$  shift factor appropriate to 298 K. One then obtains  $\log a_{298} = -5.85$ . Thus, in order to get the time scale appropriate to a reference temperature of 298 K, this value of  $\log a_T$  must be subtracted from the time scale along the abscissa.

For a linear viscoelastic material, a knowledge of the time dependence of the reduced stress-relaxation modulus permits one to estimate other time-dependent material parameters such as the reduced creep,  $D_r(t)$ . Both exact and approximate methods of interconversion are available.<sup>1</sup> As a first approximation for times longer than those corresponding to end of the transition zone, the reduced creep compliance can be taken to be simply the reciprocal of the modulus. (This time scale coincides with that of practical interest so that this approximation is a relatively good one. Otherwise the methods described in Ref. 1 can be used to obtain a more accurate conversion.) The reduced creep compliance is defined as

$$D_r(t) = D(t)T_0/T \quad (5)$$

where  $D(t)$  is the compliance and  $T_0$  and  $T$  are an arbitrary reference temperature and the test temperature, respectively. The creep can be estimated by

$$\epsilon(t) = D(t)\sigma(t) \quad (6)$$

where  $\epsilon(t)$  is the time-dependent strain and  $\sigma(t)$  is the time-dependent stress. A particularly simple result is obtained when the stress is held constant; in this case the time dependence of the relative change in length is equal to the creep compliance itself multiplied by the magnitude of the constant stress.

Figures 10–12 show the dependence of the creep compliance, estimated as described above, on the reduced time for the three vulcanizates. In each figure, the horizontal bars represent the calculated change in  $D_r(t)$  for a 25-year time span for three temperatures, 0, 25, and 35°C. An examination of the figures shows, as expected, that the higher the temperature, the

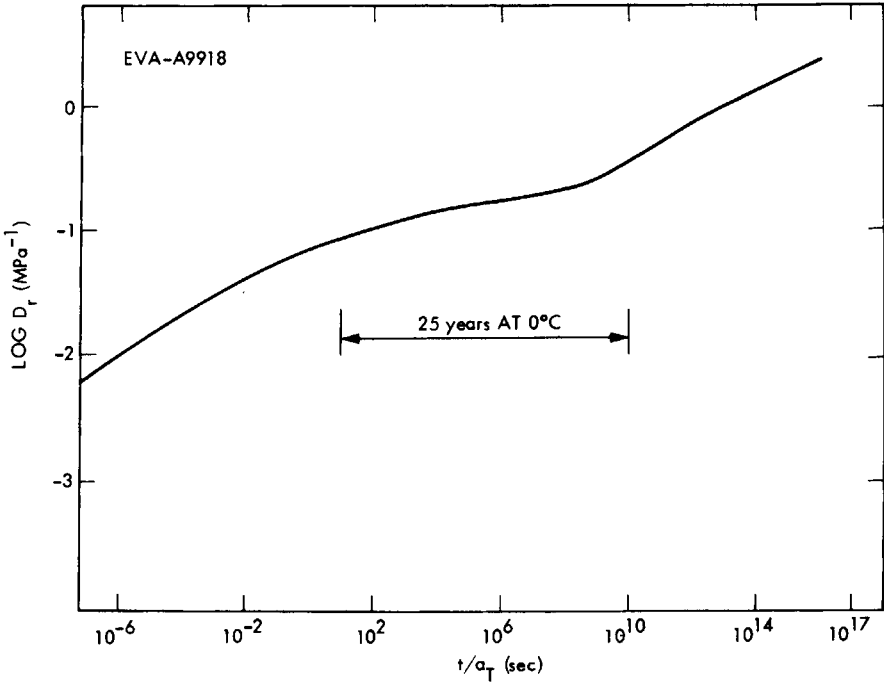


Fig. 10. Dependence of the logarithm of the reduced compliance  $D_r$  on reduced time for EVA A9918. The reference temperature is 273 K.

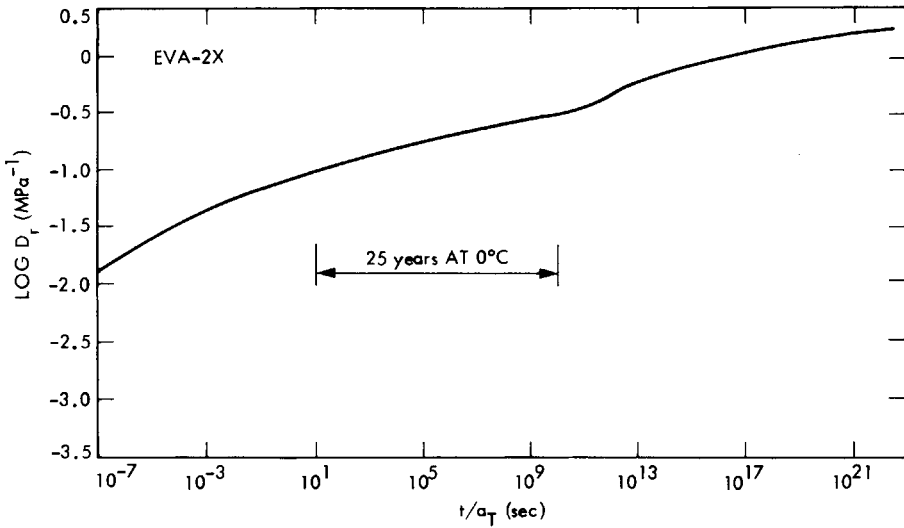


Fig. 11. Dependence of the logarithm of the reduced compliance  $D_r$  on reduced time for EVA JPL 2X. The reference temperature is 273 K.

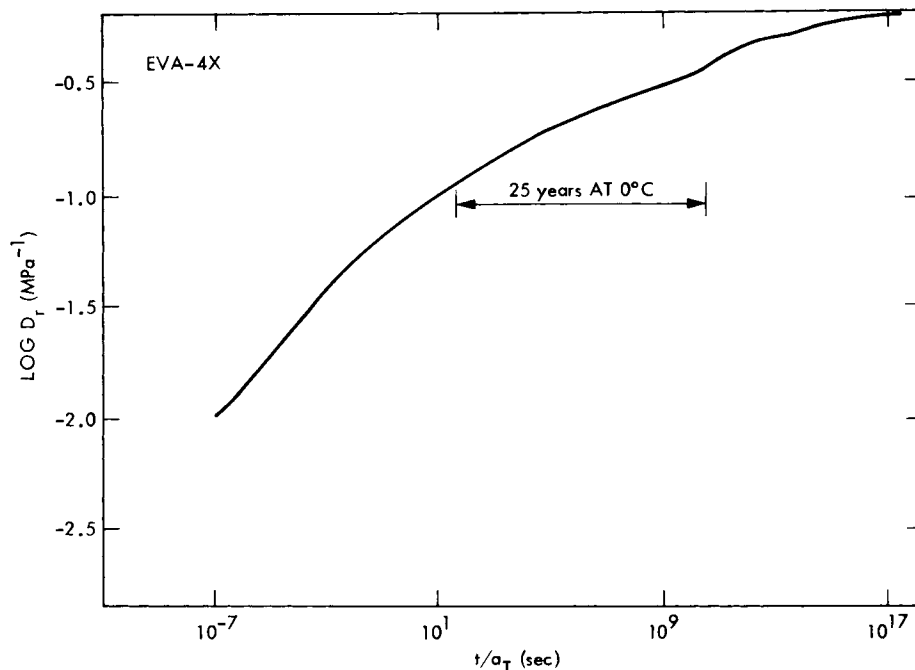


Fig. 12. Dependence of the logarithm of the reduced compliance  $D_r$  on reduced time for EVA JPL 4X. The reference temperature is 273 K.

greater is the change in  $D_r(t)$  and hence in the extent of increase in sample dimension due to creep. These plots can be used to calculate change in dimensions for other time spans and temperatures as well.

### CONCLUSIONS

It has been shown that gum vulcanizates of ethylene-vinyl acetate rubber obey time-temperature superposition; specifically it has been demonstrated that the isothermal stress-relaxation modulus measured over a temperature span of about 160°C can be superposed to yield master curves of modulus or of compliance over an extended time period. This kind of information is useful in design studies.

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