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Effects of Temperature, Strain Rate, and Swelling on the Stress-Strain Properties of Ethylene-Propylene Gum Vulcanizates of Varying Cross-Link Density

12 AUGUST 1963

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Prepared for COMMANDER SPACE SYSTEMS DIVISION
UNITED STATES AIR FORCE
Inglewood, California

LABORATORIES DIVISION • AEROSPACE CORPORATION
CONTRACT NO. AF 04(695)-169

⑱ ⑲ ⑤ 17 $.50 ⑭

SSD-TDR-63-176

④ $3.60

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EFFECTS OF TEMPERATURE, STRAIN RATE, AND SWELLING ON THE STRESS-STRAIN PROPERTIES OF ETHYLENE-PROPYLENE GUM VULCANIZATES OF VARYING CROSS-LINK DENSITY

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AEROSPACE CORPORATION
El Segundo, California

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ABSTRACT

The stress-strain properties and ultimate properties of EPR vulcanizates of varying cross-link density (swollen and unswollen) were determined at two temperatures and two strain rates. ~~The p~~roduct $\sigma v_r^{1/3}$ was found to ~~depend on v_r, contrary~~ to theory. A swell-deswell technique was employed to obtain "equilibrium" results at low v_r*. The Mooney-Rivlin constants were found to depend on temperature, strain rate, and cross-link density. The network structural parameters obtained from swollen stress-strain curves were always greater than values obtained from the Mooney-Rivlin constants, $2C_1$. Thermoelastic measurements showed that EPR undergoes a larger negative internal energy change on extension due to rotational energy levels within chains than polyethyene. A plot of the ultimate properties ~~as~~ log $(\sigma B/2C_1')$ vs log σ_B described a curve which was nearly independent of test conditions. The EPR curve was shifted in the direction of higher elongations, in comparison to a similar SBR curve.

* volume fraction of rubber

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FIGURES

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I. INTRODUCTION

The stress-strain curve for a vulcanized elastomer subjected to uniaxial tension can be approximated at low and moderate elongations by the Mooney-Rivlin equation[1]

$$\sigma/(\alpha - \alpha^{-2}) = 2C_1 + 2C_2/\alpha \tag{1}$$

where σ is the stress based on the original cross-sectional area of the sample; α is the extension ratio given by the ratio of the strained sample length to the unstrained length; and $2C_1$ and $2C_2$ are empirical constants. This equation has been developed from a phenomenological theory[1] of large elastic deformations. The statistical theory of rubber elasticity, which was developed from a molecular chain model, contains a single constant that is related to the structure of the polymer network. According to the molecular theory,[2] $2C_2$ should equal zero in Eq. (1), and $2C_1$ should be given by

$$2C_1 = \nu_e v_r^{1/3} RT(\langle r_i^2 \rangle / \langle r_0^2 \rangle) \tag{2}$$

where ν_e is the number of effective chains per unit volume in the network; v_r is the volume fraction of gel rubber; R is the gas constant; T is the absolute temperature; $\langle r_i^2 \rangle$ is the average mean-square end-to-end distance for the network chains in the undeformed isotropic state of the same volume as the strained sample and depends on the volume of the network and the orientation of the chains at the time of cross-linking; and $\langle r_0^2 \rangle$ is the average mean-square end-to-end distance for the chains in free space at the same temperature and diluent concentration and depends on bond lengths, bond angles, rotational energy levels within the polymer chain, and temperature. The ratio $\langle r_i^2 \rangle / \langle r_0^2 \rangle$ modifies the molecular theory for networks formed by cross-linking oriented chains[2] and for networks whose chain dimensions exhibit a temperature dependence due to rotational energy effects,[3] but it does not account for the positive C_2 term in the Mooney-Rivlin equation. Recent work of Roe and Krigbaum[4, 5] with natural rubber and Viton elastomer has shown that C_2 does not approach zero under equilibrium conditions, as has been suggested.[6] This study with ethylene-propylene rubber (EPR) and a similar study with styrene-butadiene rubber (SBR) also show that C_2 can be quite large even when equilibrium conditions are approached. Krigbaum and Kaneko[8] have attributed the C_2 term in Eq. (1) to rotational energy effects within individual chains. However, their theory predicts a negative C_2 term, which has not been found experimentally[5, 7] for elastomers such as SBR, Viton, and EPR, which exhibit a negative temperature coefficient for $<r_0^2>$. Recently, DiMarzio[9] has introduced an entropy correction into the statistical theory of rubber elasticity by considering the variations in the entropy of chain packing with elongation, which can explain the C_2 term in a qualitative manner. However, further modifications of the molecular theory appear necessary to explain the magnitude of the C_2 term. Ciferri and Flory[6] have pointed out that if C_2 is not zero under equilibrium conditions, one is not justified in equating C_1 of the Mooney-Rivlin equation to the network structural parameter in Eq. (2).

In this study, stress-strain measurements on EPR vulcanizates of varying cross-link density were made as a function of temperature, strain rate, and swelling to determine the effect of these variables on C_1 and to determine if C_1 is a consistent function of the effective number of chains in the network. Thermoelastic measurements and hysteresis studies were also made. A study of the stress-strain curves at high elongations where non-Gaussian[10] behavior becomes important and of the ultimate properties of EPR vulcanizates as a function of network structure, temperature, strain rate, and swelling was also undertaken, and the results were compared with results[7] obtained for SBR.

II. EXPERIMENTAL

Du Pont's Nordel, a terpolymer of ethylene, propylene, and a non-conjugated diene, was used in this study. The polymer contained about 53 mole % ethylene.[11] The compounding recipe was identical to that used in a previous study.[11] Various cross-link densities were obtained by varying the time of cure at 150°C. Ring test specimens were used in all experimental work in this report. The experimental procedures have been described previously.[7]

III. RESULTS

A. SWOLLEN AND EQUILIBRIUM STRESS-STRAIN CURVES

The stress-strain curves to failure for EPR vulcanizates of varying cross-link density swollen to their equilibrium extent in n-heptane were determined at two strain rates at 25°C. The results are shown in Fig. 1, plotted according to the Mooney-Rivlin equation, for data obtained at a rate of sample elongation of 0.98 in./min. The numbers on the curves indicate the sample cure time. In Fig. 1, $\sigma v_r^{1/3}/(\alpha - \alpha^{-2})$ is plotted against $1/\alpha$, where σ is the stress based on the original unswollen cross-sectional area of the sample; v_r is the volume fraction of polymer in the swollen sample at swelling equilibrium; and α is the extension ratio relative to the swollen unstrained length of the sample. The small correction[2, 12] for the decrease in v_r on extension was not made. A decrease in strain rate by a factor of 20 gave results which agreed with the data in Fig. 1 within the experimental error of ±8 percent. The swollen stress-strain curves were essentially time independent, but the ultimate properties decreased slightly as the strain rate decreased. All vulcanizates gave an initial horizontal curve, which indicated that the Gaussian statistical theory of rubber elasticity was obeyed. The upturns in the curves caused by the finite extensibility of the network chains were observed at lower elongations as cross-link density increased. The non-Gaussian effects that can be present in swollen unstrained samples of high cross-link density[13] were not observed for the highest cross-linked EPR vulcanizate used in this study.

In Table 1, the $2C_1'$ constants obtained for the EPR vulcanizates and the volume fraction of rubber, v_r, at swelling equilibrium are shown. The values of $2C_1'$ taken from the horizontal portions of the curves can be set equal to the network structural parameters, according to the statistical theory. By taking the dilation factor[2] of the structural parameter as unity, the polymer-solvent interaction parameter for the EPR-n-heptane system was computed; the results obtained were in good agreement with earlier results.[11]

Behavior close to the equilibrium response of a network was obtained by swelling the sample in heptane at each elongation and then deswelling the sample by the addition of acetone until a constant stress was attained.[7] The equilibrium volume swell of the vulcanizates in acetone was found to be 0.950. The results for the EPR vulcanizates are shown in Fig. 2, plotted in Mooney-Rivlin form. For the low cross-link density vulcanizates, the curves appear to approach a minimum value of $\sigma v_r^{1/3}(\alpha - \alpha^{-2})^{-1}$ at high elongations. For the high cross-link density EPR vulcanizates, rupture occurred before any leveling out of the curve was evident. Because of the high degree of curvature, it was not possible to obtain values for $2C_1$ and $2C_2$ of the Mooney-Rivlin equation. It is evident from Fig. 2 that there is a very rapid decrease in $\sigma v_r^{1/3}(\alpha - \alpha^{-2})^{-1}$ at low elongations. The slope of the curves at low α is about a factor of 4 higher than that observed for SBR.[7] A comparison of Figs. 1 and 2 shows that for each vulcanizate the product $\sigma v_r^{1/3}$ for the acetone-swollen state (high v_r) was much higher than the product observed for the heptane-swollen sample (low v_r) when the comparison was made at equal network strains. This is shown in Table 2, which gives the ratio, Φ, of $\sigma v_r^{1/3}$ in acetone to $\sigma v_r^{1/3}$ in heptane for the vulcanizates at various values of α.

Theory[2] predicts that $\sigma v_r^{1/3}$ should be invariant to dilution. The ratio in Table 2, which expresses the deviation from theory, increases as cross-link density decreases and for a particular vulcanizate decreases as α increases. The stress-strain curves obtained by the swell-deswell technique were reproducible and are thought to be a minimum estimate of the equilibrium behavior of the unswollen vulcanizates. The large discrepancies found can not be accounted for by the increase in swelling that occurs on extension or by experimental error. Similar results were found[7] for SBR vulcanizates, but the discrepancy was not as large as observed here for EPR.

B. UNSWOLLEN STRESS-STRAIN CURVES

The stress-strain curves for the unswollen EPR vulcanizates were obtained at two temperatures and two strain rates. Typical results obtained for the 25- and 21.5-min cures are shown in Fig. 3. The ordinate values for the 25-min cure have been shifted upward 10 units for clarity. The curves have very little resemblance to Gaussian theory curves, as large deviations are evident at low elongations. The long, almost flat portion of the stress-strain curves is characteristic of the EPR vulcanizates. The curves resemble more closely what is expected for a vulcanizate subjected to a two-dimensional extension[1] than the theoretical prediction for uniaxial tension. An increase in temperature or a decrease in strain rate leads to a stress-strain curve that lies below the curve obtained at a lower temperature or a higher strain rate. Strain rate and temperature effects become relatively more important for lower cross-link density vulcanizates. Permanent viscous flow was not responsible for the effects observed, since the samples would recover to their original lengths under suitable conditions. At 25°C, the upturns in the stress-strain curves appeared to occur at higher elongations at the lower strain rate. This has been attributed[14] to the non-affine deformation of the cross-link and entanglement points in the network at high elongations. At 78°C, the final upturn in the stress-strain curve was not observed for any of the EPR vulcanizates at the strain rates used here. In Fig. 4, the stress-strain curves obtained at 78°C at a strain rate of 0.060 min^{-1} for the 25- and 21.5-min cures are compared with the "equilibrium" curves obtained by the swell-deswell technique. The "equilibrium" curves lie considerably below the high-temperature, low-strain-rate curves. A large negative internal energy change contributes to the retractive force in EPR vulcanizates (as will be shown), so it is expected that the higher-temperature curve would lie above the lower-temperature curve when plotted as in Fig. 4. However, the effect is not large enough to account for the experimental results. It is possible that the high-temperature curves are still far from equilibrium curves, or that the small increase in volume in the acetone-swollen sample over the dry sample is responsible for the large discrepancy.

The stress-strain data obtained for the EPR vulcanizates were plotted in Mooney-Rivlin form, and the curves obtained for the 21.5-min cure are shown in Fig. 5. The constants $2C_1$ and $2C_2$ were evaluated by drawing the best straight line through the data points to the right of the minimum in the curves. The values of $2C_1$ and $2C_2$ obtained under different test conditions for the EPR vulcanizates are reported in Table 3.

The constants $2C_1$ and $2C_2$ depend significantly on the temperature and strain rate at which the sample was tested. Values of $2C_2$ for EPR are very high compared to those for other elastomers.[6, 7] Uncured EPR exhibits a significant stress-strain curve when tested at 25° in the same manner as the vulcanized samples. The $2C_1$ and $2C_2$ values obtained for the uncured sample tested at 78°C at a strain rate of 0.060 min^{-1} are included in Table 3. These constants could not be estimated for the other test conditions because of the large curvature of the Mooney-Rivlin plots. If the stress-strain curves for the unvulcanized samples are subtracted from the curves for the vulcanized samples, the curves obtained under different test conditions are brought more nearly into coincidence in the region of low elongations, as was found for SBR.[7] However, the values of $2C_2$ remain high. At 78°C and at the low strain rate, the effect of the entanglement network was small, so that the values of $2C_1$ and $2C_2$ in the last column of Table 3 can be considered to be unaffected by viscous effects due to the entanglement network. As was found for SBR,[7] $2C_2$ decreased with decreasing strain rate and increasing temperature and increased with increasing cross-link density. Values of $2C_1$ are always less than values of $2C_1'$ determined with swollen samples. The use of $2C_1$ to determine the number of effective chains in the network is not justified with EPR. Mooney-Rivlin plots for data obtained at 25°C possess definite minima. At 78°C, the sample ruptures prior to any upturn in the plot. In Table 4, the extension ratio at the minimum in the Mooney-Rivlin plots, α_m, and the value of $\sigma/(\alpha - \alpha^{-2})$ at the minimum are listed.

As cross-link density increases, the minimum in the curve shifts to lower elongations, as expected.[13] For the vulcanizates of low cross-link density, the elongation at the minimum is seen to shift to higher elongations as the strain rate is decreased. This is evidence for non-affine deformation.[14] For the higher cross-linked vulcanizates, the shift in the position of α_m with strain rate was not evident in this type of plot.

C. THERMOELASTIC MEASUREMENTS

Stress-temperature measurements at constant length were made on the 21.5- and 25-min EPR vulcanizates. The stress-temperature curve obtained for the 21.5-min EPR vulcanizate is shown in Fig. 6. All curves were non-linear and showed good reversibility. However, the stress-temperature curve appeared to be linear with temperature above about 35°C, and the procedure of Ciferri, Hoeve, and Flory[8] was used to obtain the contribution of the internal energy change, f_e, to the total retractive force, f, on stretching an EPR network. The slope of the stress-temperature curve was evaluated at 50°C, and the linear coefficient of thermal expansion was taken as 0.22×10^{-3} $\deg^{-1}$. The results, given in Table 5, show that for EPR there is a large negative internal energy contribution to the retractive force. At 50°C, about 45 percent of the retractive force arises from internal energy changes. Above 35°C, $d \ln \langle r_0^2 \rangle / dT$ was found to be -1.45×10^{-3} $\deg^{-1}$. Hence, $\langle r_0^2 \rangle$ for the ethylene-propylene copolymer has a larger negative temperature coefficient than that found for polyethylene.[3] Apparently the methyl side groups cause the trans conformation of the atoms in the backbone chain of EPR to be favored energetically over the trans form in polyethylene. The increase in the stress-temperature coefficient occurring below 35°C is probably a result of the more complicated potential energy diagram for rotation about backbone atoms due to the presence of the methyl group in EPR. Three unequal potential minima in the potential energy diagram for internal rotation about some of the bonds present in EPR might explain this result.[15]

D. HYSTERESIS EXPERIMENTS

In Fig. 7, the results of a cyclic stress-strain experiment are shown for the 21.5-min EPR vulcanizate at 25°C and a strain rate of 1.25 min^{-1}. After each cycle, the "permanent" set could be removed by swelling the sample in solvent vapor and removing the solvent in vacuo. The stress-strain curve obtained after this treatment was identical to the original stress-strain curve. The size of the hysteresis loop increased as the elongation to which a sample was cycled increased. Comparison of the hysteresis loops obtained for samples of different degrees of cross-linking for cyclic elongations to the same α showed the hysteresis loop to be smaller for higher degrees of cross-linking.

E. ULTIMATE PROPERTIES OF SWOLLEN AND UNSWOLLEN EPR VULCANIZATES

In Fig. 8, the stress-strain data for the swollen EPR vulcanizates are plotted as $(\sigma v_r^{1/3}/2C_1')$ vs α, where α is the extension ratio relative to the swollen unstrained state. The curves obey Gaussian theory at low elongations, but the upturns occur as predicted by non-Gaussian theory.[10] The ultimate properties of the swollen vulcanizates are given in Table 6 for two rates of elongation.

In Fig. 9, the stress-strain curves for four of the unswollen EPR vulcanizates are plotted as log $(\sigma/2C_1')$ against log ϵ, where ϵ is the strain equal to $\alpha - 1$. The effect of strain rate on the stress-strain behavior of four vulcanizates is shown in Fig. 9. The effect of temperature is shown for the 21.5-min cure. Large deviations from Gaussian theory occur at low elongations for all of the vulcanizates, with the deviations greater at low cross-link densities. Because of these large deviations, non-Gaussian theory could not be employed to evaluate N, the number of statistical segments in a network chain. This was also the case with SBR.[7]

The ultimate properties obtained for the unswollen EPR vulcanizates are reported in Table 7.

The final high elongation portions of the stress-strain curves in Figs. 8 and 9 for vulcanizates of different cross-link densities appear to describe a single curve within about 10 percent. In Fig. 10, log $\left[298\sigma_B v_r^{1/3}/(T2C_1')\right]$ is plotted against log $(\alpha_B - 1)$. This is a form of the Smith[16] failure envelope recently suggested by Landel and Fedors.[17] The failure points for all the vulcanizates, swollen and unswollen, define a single curve which appears to be independent of test conditions. This behavior was also found for SBR results.[7,17] The data points for tensile strengths at 78°C fall consistently to the left of the curve drawn in Fig. 10. The failure envelope for an EPR vulcanizate obtained by Bueche and Halpin[18] was shifted along the vertical axis to fit the curve in Fig. 10 and is shown as the dashed curve. A value of $2C_1'$, equal to 1.90 kg/cm^2, was calculated from the vertical shift required to fit the Bueche-Halpin vulcanizate in the high elongation region. A larger shift would be required to superpose the curves in the low elongation region. The Gaussian theory prediction is also shown. For swollen samples, Gaussian theory behavior is closely approached.

If log α_B is plotted as the abcissa in Fig. 10, a linear curve with a slope of 1.95 fits the data well. If the failure envelopes for vulcanizates of different cross-link density have the same shape in the region of the maximum elongation when plotted in the form of the reduced failure envelope,[17] the theory of Bueche and Halpin[18] predicts a slope of 2 for the envelope of the reduced failure curves. As the cross-link density of a vulcanizate decreases, the network would become more extensible, and the maximum elongation in the tensile failure envelope curve would be expected to shift upward along the reduced envelope in Fig. 10 to higher strain values.[17]

The low elongation portion of the EPR tensile failure envelope shown in Fig. 10 lies above the curve drawn through the ultimate property data. This portion of the failure envelope curve is obtained at high temperatures. At high temperatures and low elongations, it was shown (Fig. 5) that the effective number of chains in a network appears to be a strong function of α because of the high C_2 term for EPR vulcanizates. This can explain the deviation of the high-temperature portion of the reduced failure envelope from the curve shown in Fig. 10. The stress-strain curves at high temperature (Fig. 9) lead one to predict that the high-temperature part of the tensile failure envelope would also shift upward as the cross-link density decreases when plotted as in Fig. 10.

The tensile strength data show that at 25°C a maximum tensile strength occurs[19] at $\nu_e \approx 5 \times 10^{-6}$ mole/cm^3. At 78°C, or with swollen samples, the maximum is nonexistent. The tensile strength appears to be independent of chain density above a ν_e of 15×10^{-6} mole/cm^3 at high temperature and low strain rates.

IV. DISCUSSION

The stress-strain behavior of EPR vulcanizates swollen to their equilibrium swelling volume in heptane was adequately described by the Gaussian statistical theory of rubber elasticity up to elongations close to the ultimate elongation. The equilibrium stress-strain curves for vulcanizates slightly swollen in acetone obtained by a swell-deswell technique exhibited large deviations from theory (high C_2 term). The ratio of $\sigma v_r^{1/3}$ in acetone to that in n-haptane, which theoretically should equal unity,[2] was always greater than unity and was found to increase as cross-link density and elongation decreased. The ratio should equal the ratio of the unperturbed mean-square end-to-end length of the network chains in heptane to the unperturbed dimensions in acetone.[2, 12] The results indicate that the unperturbed chain dimensions of EPR increase on dilution. Specific solvent effects might be responsible for this effect;[12] however, these effects are usually not as large as indicated by the results for EPR. The ratio of $\sigma v_r^{1/3}$ obtained from the unswollen stress-strain curves obtained at high temperatures and slow strain rate, where viscous effects were small, to $\sigma v_r^{1/3}$ for the acetone-swollen curves obtained by the swell-deswell method, was also high for EPR vulcanizates (1.35 to 2.0) and increased as cross-link density decreased. The high-temperature results are close to equilibrium results, which indicates that a small change in volume causes a large change in elastic behavior. The fundamental assumption of the molecular theory[2, 3] that intermolecular interactions are independent of strain appears to be invalid for EPR. The effect of dilution on $<r_0^2>$ may be related to the number of entanglement cross-links in a network, as EPR of high initial molecular weight contains about 2.4 times as many entanglements[11] at the same number of chemical cross-links as SBR networks and also shows the largest effect of dilution on stress-strain properties.[7]

The constants $2C_1$ and $2C_2$ of the Mooney-Rivlin equation were found to depend on temperature, strain rate, and cross-link density for unswollen EPR vulcanizates. The highest C_2 term of any commonly used elastomer is exhibited by EPR. The number of network chains computed from $2C_1$ is lower than the number that would be obtained if results on swollen samples were used. The upturn in the stress-strain curves at elongations approaching the ultimate elongation, which was caused by the finite extensibility of the network chains, was shifted to higher elongations at lower strain rates. This, and the results of hysteresis experiments,[7] were evidence for non-affine deformation. Because of the large deviations from theory occurring at low elongations, which are probably related to entanglement cross-links, and the non-affine deformation which comes into play at high elongations, it was not possible to employ non-Gaussian theory[10] to determine the number of statistical segments in a network chain.

Stress-temperature measurements on two EPR vulcanizates showed that there is a large negative internal energy contribution to the retractive force for these vulcanizates. The nonlinear stress-temperature curve obtained for EPR might be a result of a complicated potential energy diagram for rotation about backbone chain atoms. Another possibility is that the C_2 term in the equation of state for EPR could invalidate the stress-temperature equations[2,3] if it is a function of temperature. The theory of Krigbaum and Kaneko,[8] which relates the C_2 term of the Mooney-Rivlin equation to rotational energy effects, predicts a negative C_2 term for elastomers such as EPR, which display a negative internal energy contribution; however, experimental results showed that C_2 values for EPR are positive and larger than normal.

As was the case with SBR,[7,17] a plot of the ultimate properties of the swollen and unswollen vulcanizates as $\log(\sigma_B/2C_1')$ vs $\log(\alpha_B - 1)$ defined a curve which was nearly independent of test conditions. As cross-link density decreases, the maxima in the failure envelope curves would shift to higher elongations[17] along the curve in Fig. 10. The data of Fig. 10 show that

σ_B/v_e is proportional to α_B^2. According to the theory of Bueche and Halpin,[18] the maximum elongations in the tensile failure envelopes of vulcanizates of varying cross-link density are proportional to $N^{1/2}$, where N is the number of statistical segments in a network chain. If the reduced failure curves for vulcanizates of different cross-link density have the same shape in the vicinity of the maximum elongations where they curve upward[17] from the reduced failure envelope, then a curve through the maximum elongations would be parallel to the reduced failure envelope. Hence, σ_B/v_e at the maximum elongations reached by the different vulcanizates would also be proportional to α_B^2. This is indicated by the Bueche-Halpin theory, since N is proportional to α_B^2.

The low elongation portion of the reduced failure curve in Fig. 10 does not agree with the stress-strain results (Fig. 9) at high temperature, particularly for vulcanizates of low cross-link density. This means that the high-temperature, low-elongation portion of the tensile failure envelopes would probably not fall on the envelope of the reduced failure curve, but would be shifted to positions above the curve as cross-link density decreased.

A comparison of the EPR reduced failure curve for data at 25°C with the curve obtained for SBR[7] shows that both curves have the same shape, with the EPR curve shifted slightly to the right toward higher elongations. Comparison of results for vulcanizates containing equal numbers of network chains shows that the EPR networks possess higher extensibilities. Since α_B is proportional to $N^{1/2}$, this is consistent with the expectation that the molecular weight of a statistical unit is less for EPR than for SBR.[14] The ultimate elongations of swollen EPR vulcanizates were greater than those obtained for SBR vulcanizates of equivalent cross-link density. This is no longer true for unswollen EPR vulcanizates at 78°C, and the tensile strengths and ultimate elongations of EPR vulcanizates agreed with equivalent networks of SBR. At 78°C the tensile strengths of both EPR and SBR were nearly independent of cross-link density, indicating that the number of network chains is not an important variable in the breaking mechanism at higher temperatures.

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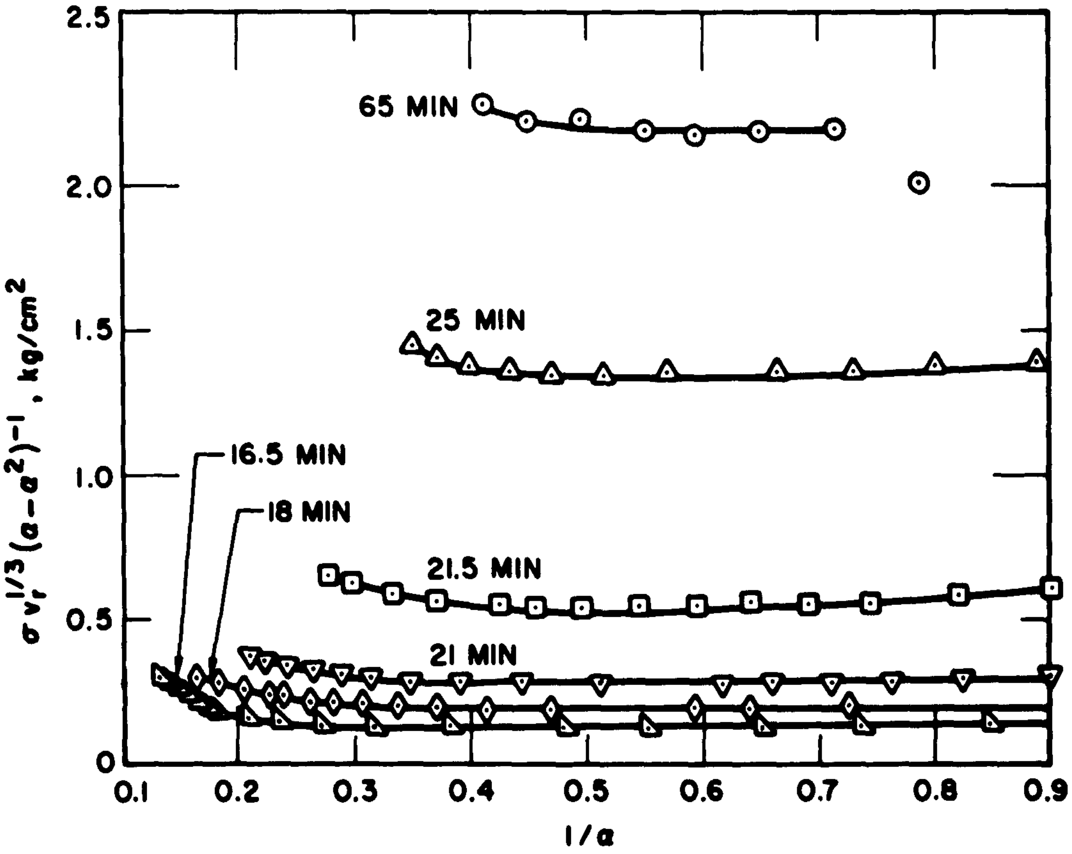

Fig. 1. Mooney-Rivlin Plots for EPR Gum Vulcanizates Swollen to Equilibrium Extents in n-Heptane at 25°C

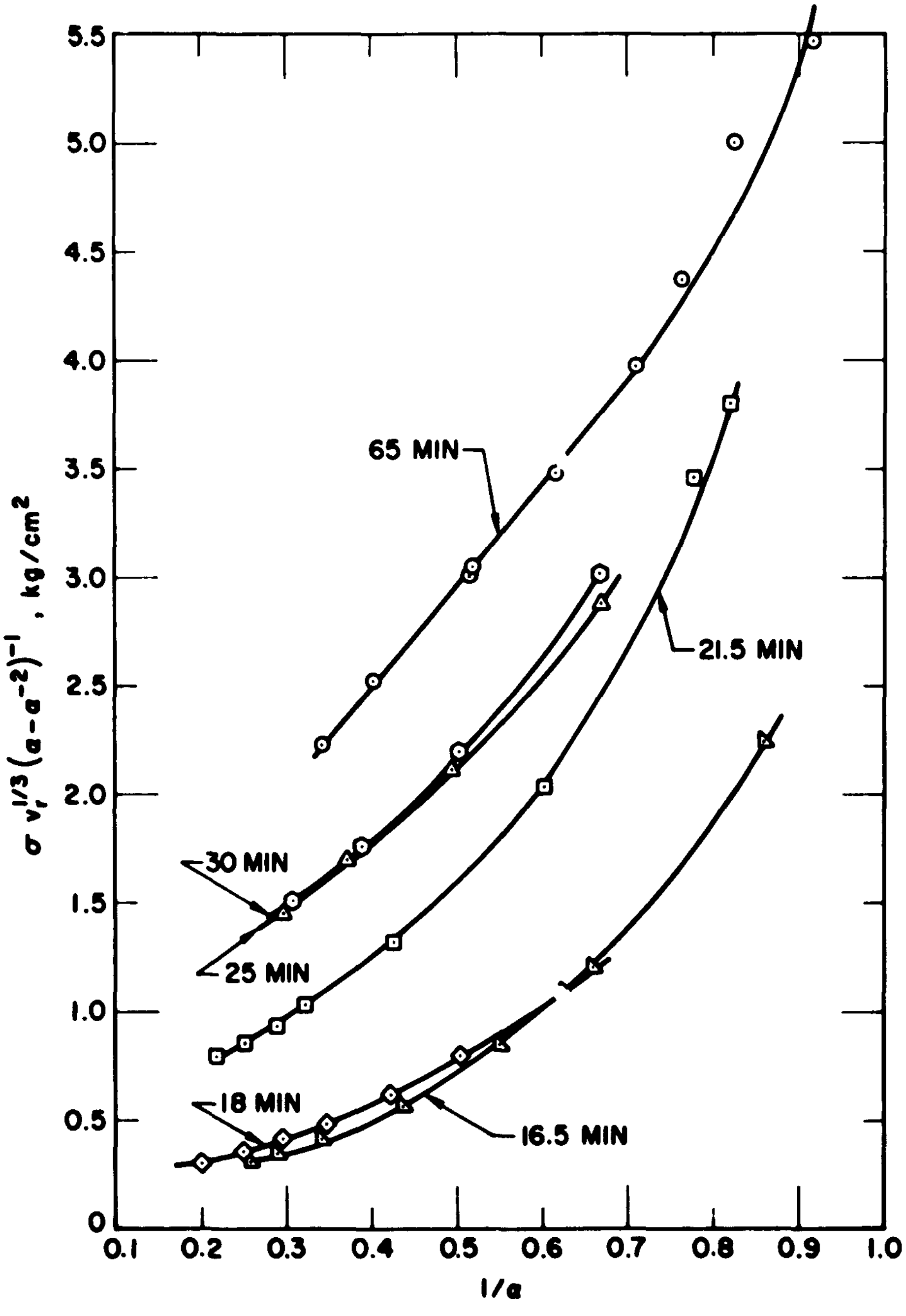

Fig. 2. Mooney-Rivlin Plots for Data Obtained by the Swell-Deswell Technique for EPR Vulcanizates at 25°C

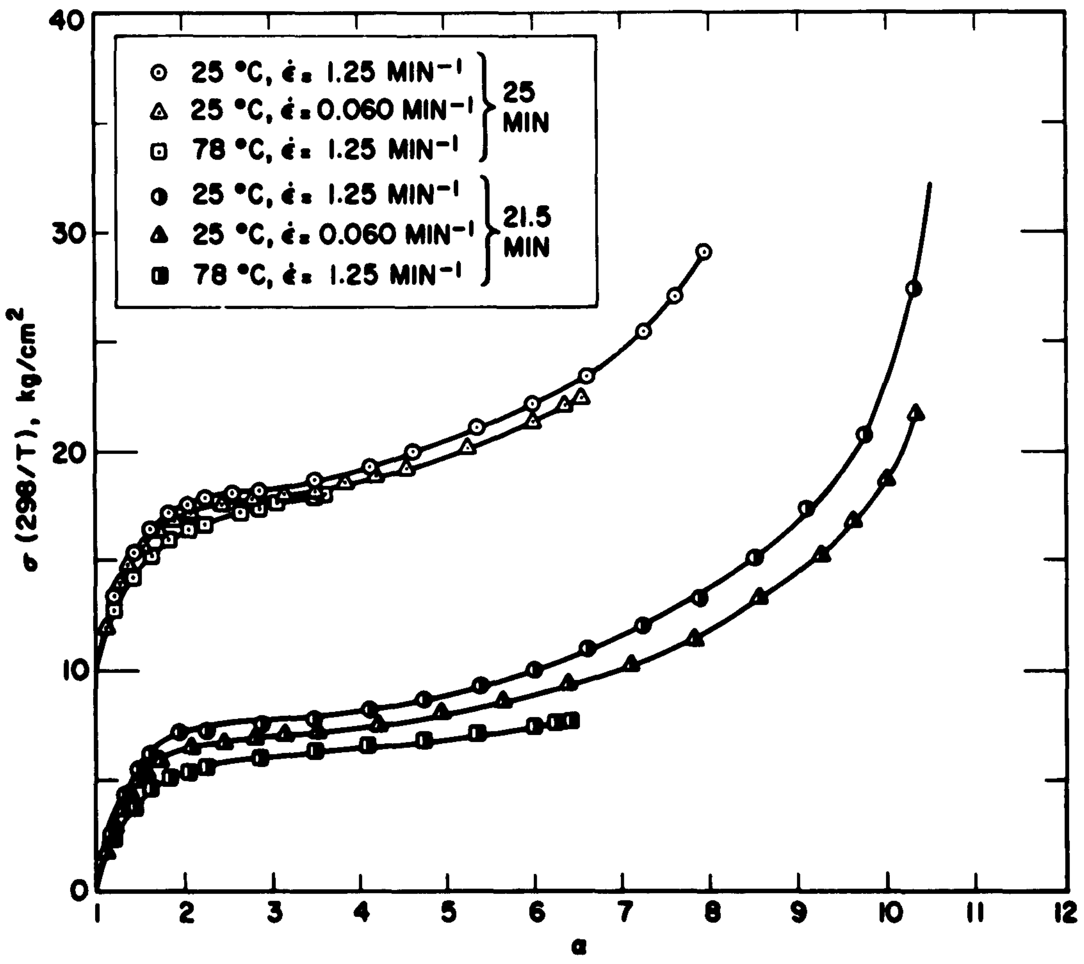

Fig. 3. Effect of Temperature and Strain Rate on the Stress-Strain Curves of Two EPR Vulcanizates

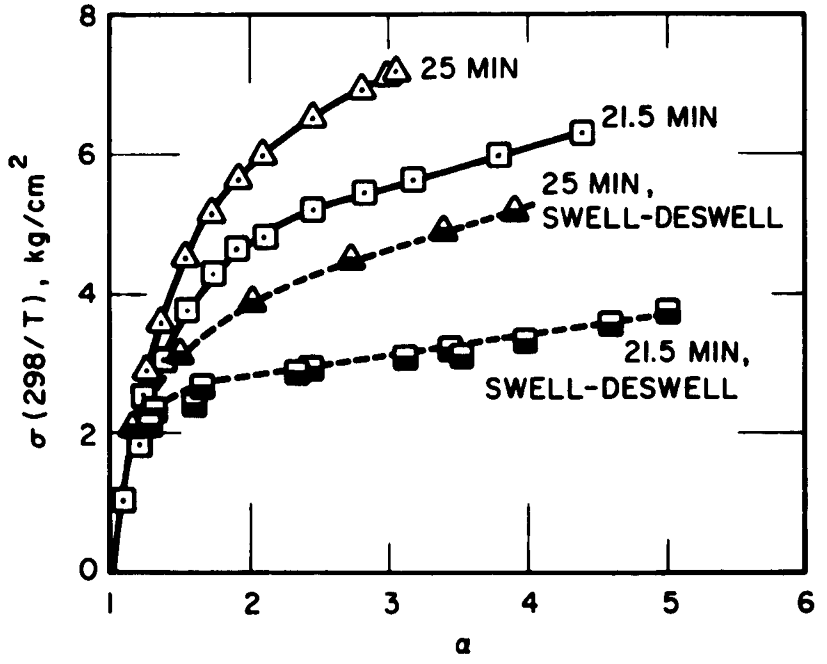

Fig. 4. Stress-Strain Curves at 78°C at a Strain Rate of 0.060 Min^{-1} Compared to Curves Obtained by the "Equilibrium" Swell-Deswell Method

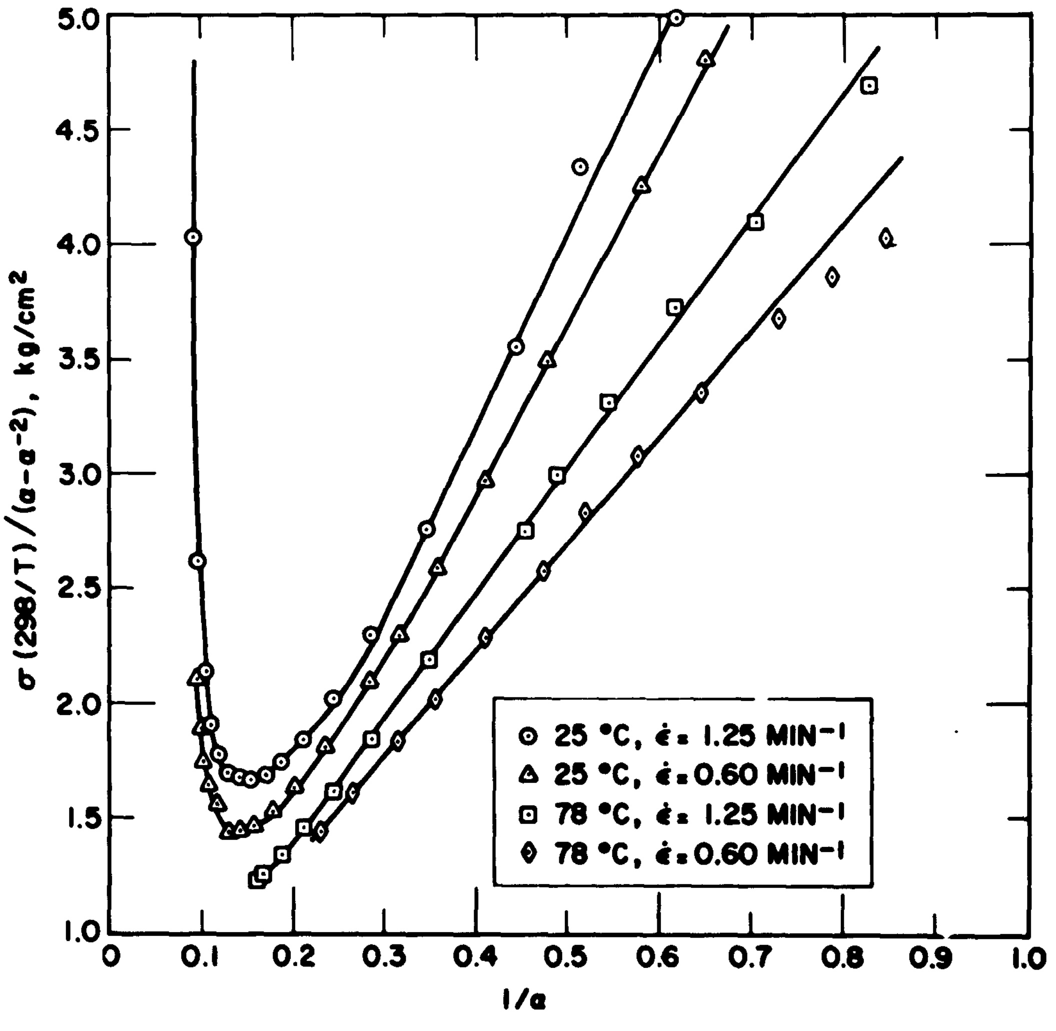

Fig. 5. Mooney-Rivlin Plot of Stress-Strain Data Obtained for the Unswollen 21.5-Min EPR Vulcanizate

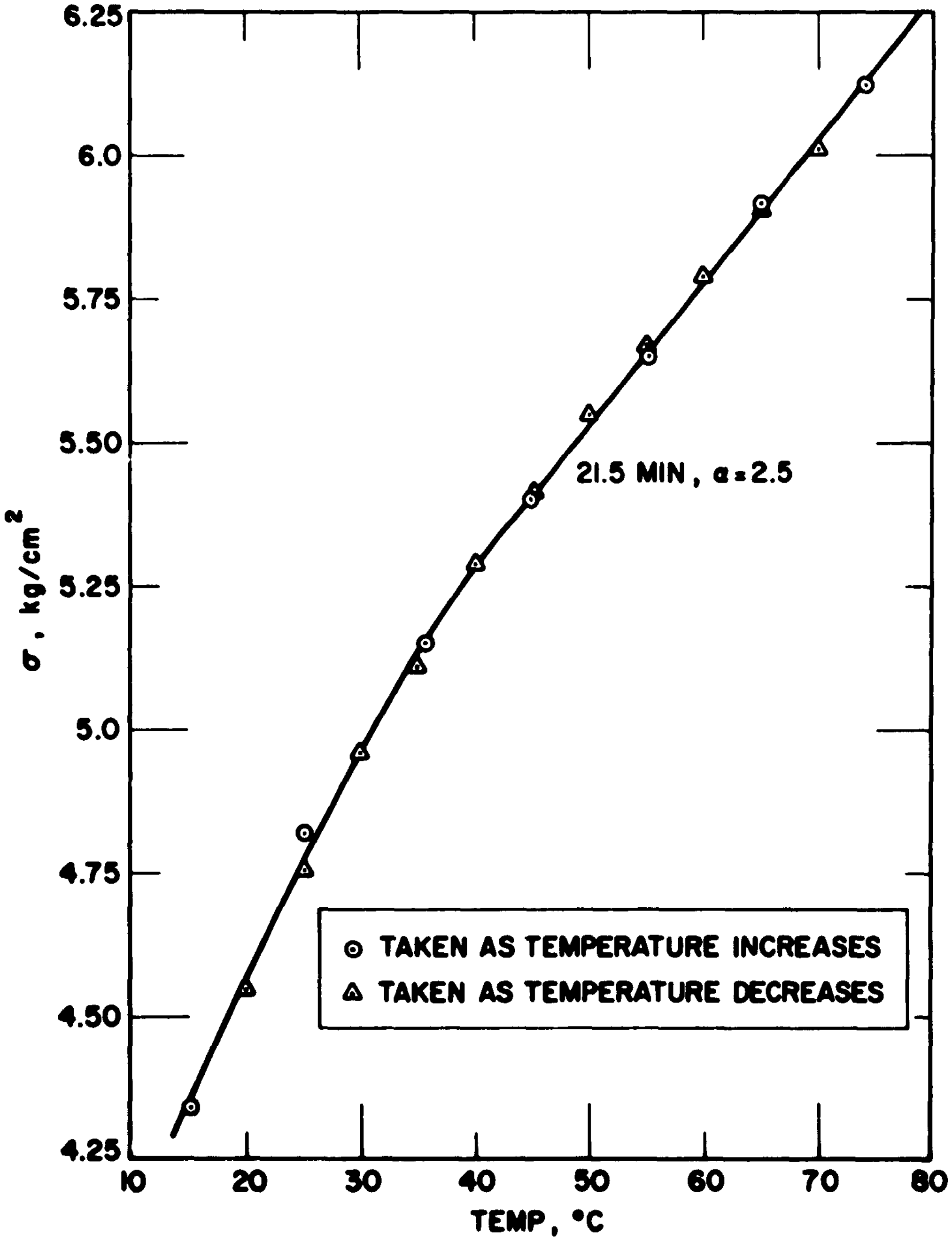

Fig. 6. Stress-Temperature Curve at Constant Length for 21.5-Min EPR Vulcanizate

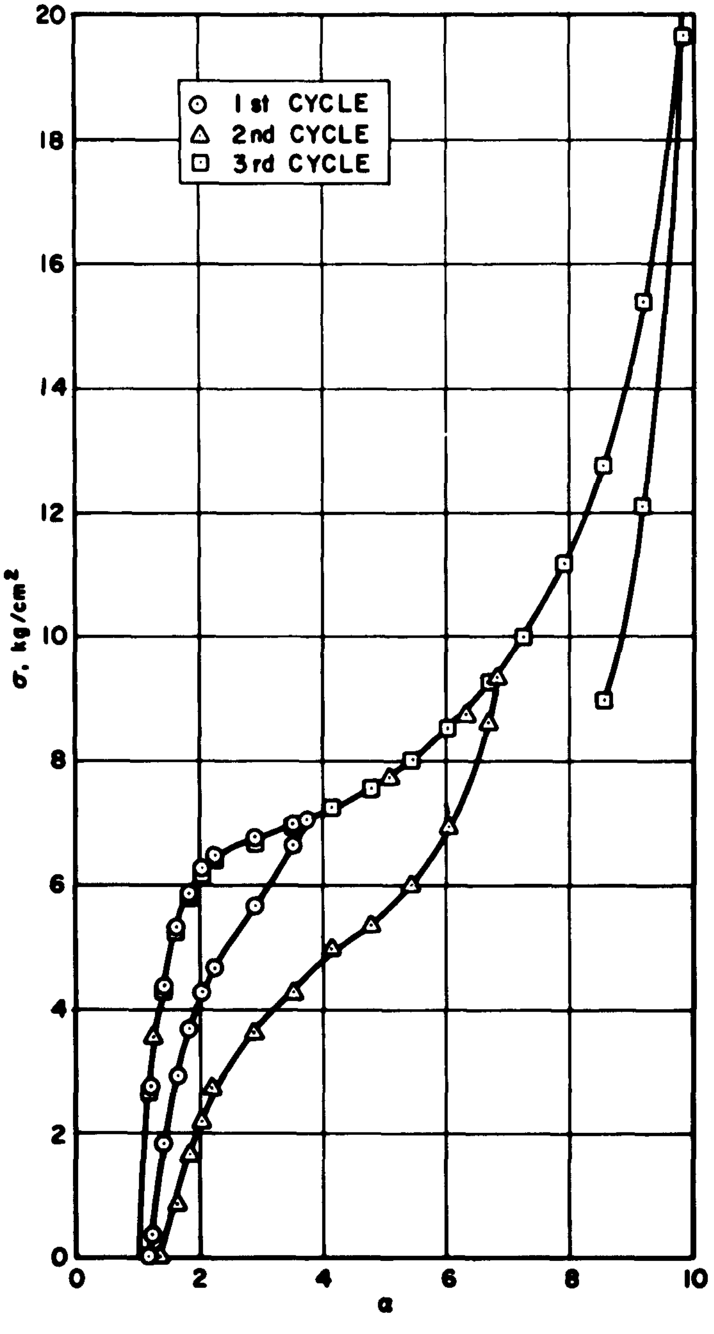

Fig. 7. Hysteresis Exhibited by 21.5-Min EPR Vulcanizates at 25°C

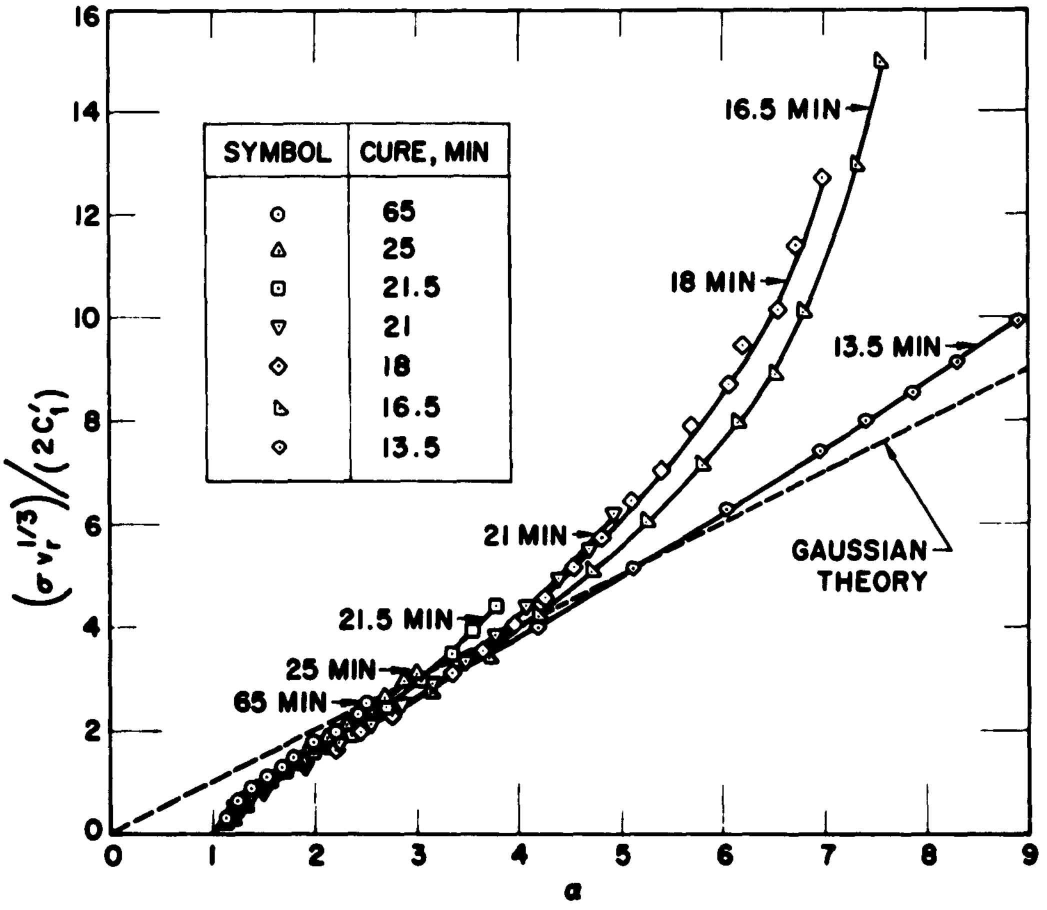

Fig. 8. Stress-Strain Data at 25°C for EPR Vulcanizates Swollen in Heptane

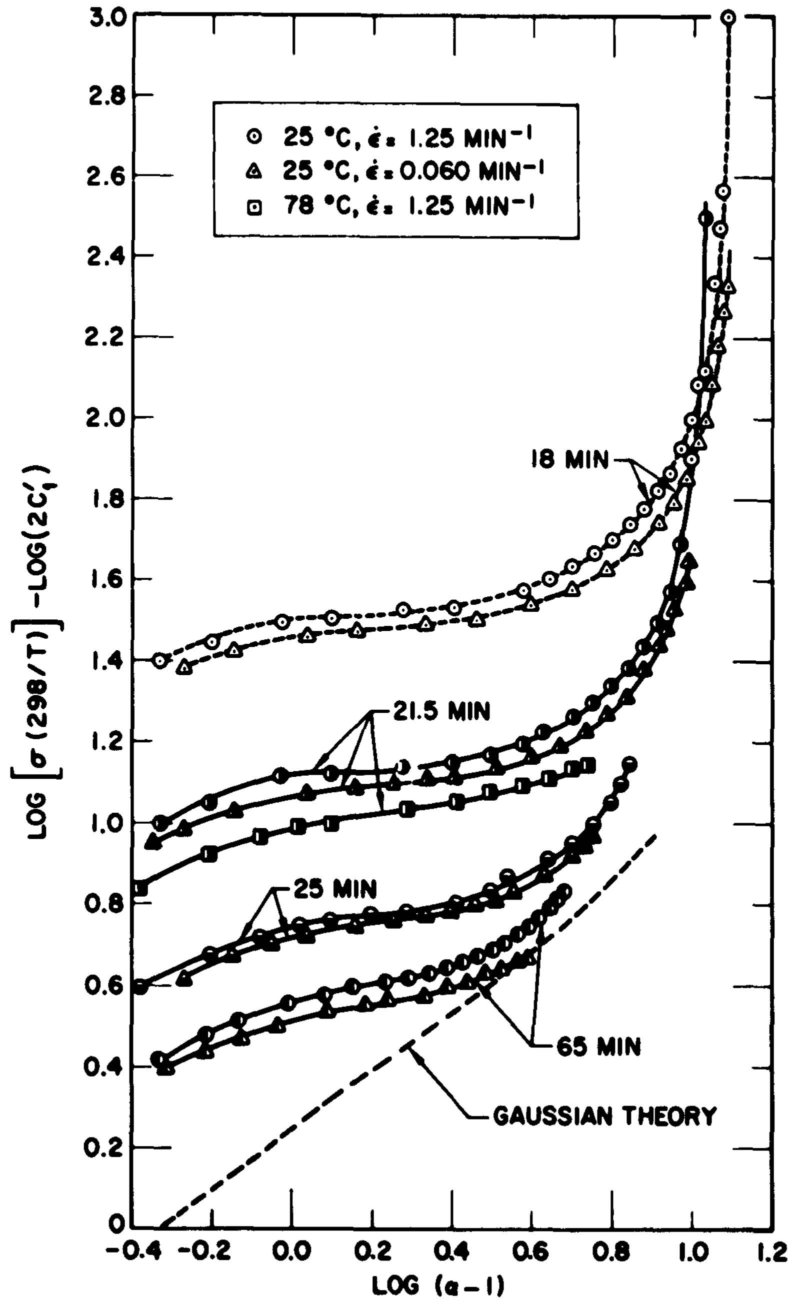

Fig. 9. Stress-Strain Curves at High Elongations for Unswollen EPR Vulcanizates

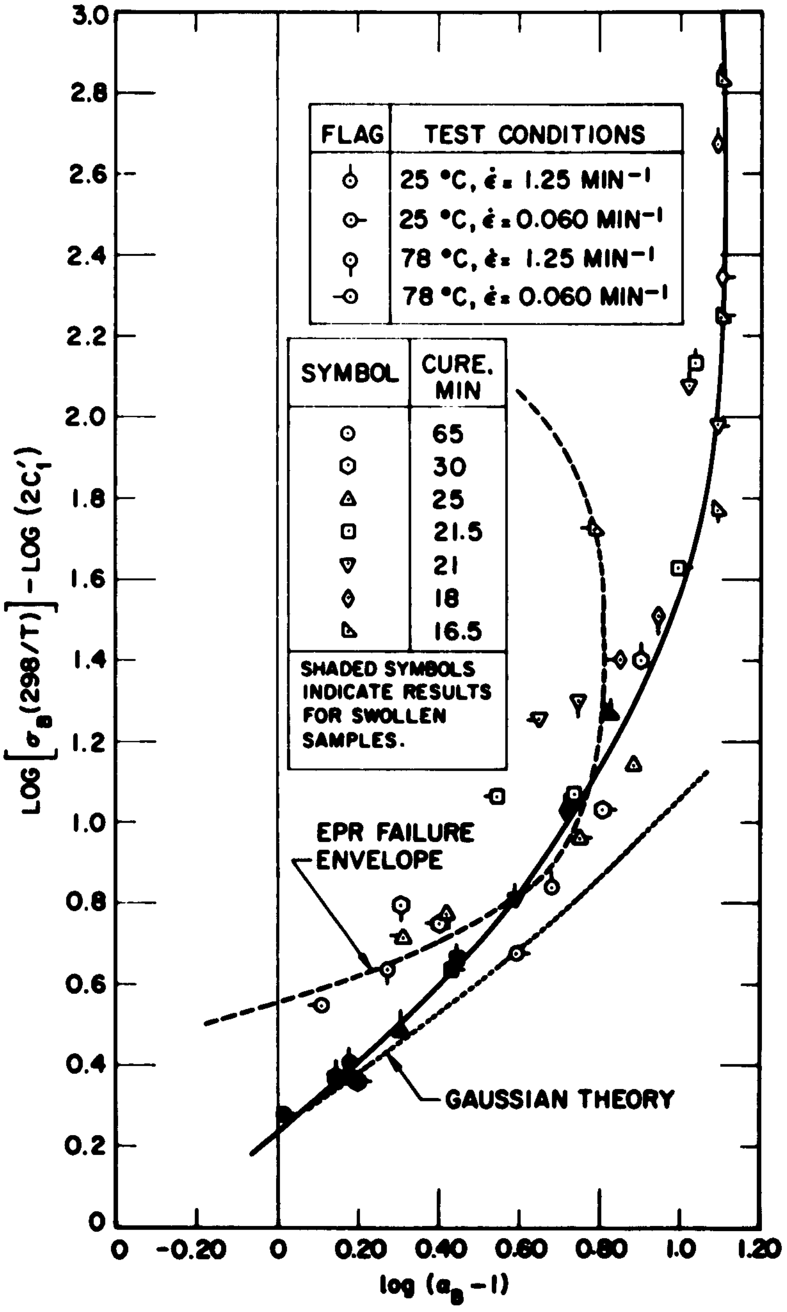

Fig. 10. Reduced Failure Envelope for EPR Vulcanizates

Table 1. Values of $2C_1'$ Obtained for EPR Vulcanizates at Swelling Equilibrium with Heptane at 25°C

Cure, min	v_r	g[a]	$2C_1'$
13.5	0.0185	0.320	0.011
16.5	0.0435	0.581	0.13
18	0.066	0.670	0.21
21	0.075	0.713	0.30
21.5	0.096	0.720	0.55
25	0.167	0.831	1.36
30	0.171	0.839	1.38
65	0.203	0.864	2.20

[a] Volume fraction of gel rubber in sample

Table 2. The Ratio $\sigma v_r^{1/3}$ (Acetone) to $\sigma v_r^{1/3}$ (Heptane)

Evaluated at equal network extension ratios relative to the swollen unstrained length in the two solvents for EPR gum vulcanizates

	Φ				
α	65 min	30 min	21.5 min	18 min	16.5 min
1.25	2.0	—	6.5	—	—
1.54	1.6	2.0	4.4	5.5	10.7
2.00	1.3	1.5	2.9	3.7	6.5
2.50	—	1.2	2.3	2.7	4.5
3.33	—	—	1.6	2.0	3.2

Table 3. The Effect of Temperature and Strain Rate on the Mooney-Rivlin Constants for EPR Vulcanizates of Varying Cross-Link Density

Cure, min	$25^{o}C, \epsilon = 1.25\ min^{-1}$		$25^{o}C, \dot{\epsilon} = 0.060\ min^{-1}$		$78^{o}C, \epsilon = 1.25\ min^{-1}$		$78^{o}C, \epsilon = 0.060\ min^{-1}$	
	$2C_1$, kg/cm^2	$2C_2$, kg/cm^2	$2C_1$, kg/cm^2	$2C_2$, kg/cm^2	$2C_1$, kg/cm^2	$2C_2$, kg/cm^2	$2C_1$, kg/cm^2	$2C_2$, kg/cm^2
Uncured	—	—	—	—	—	—	-0.20	0.53
13.5	-0.59	7.65	-0.12	5.44	-0.53	3.78	-0.47	2.84
16.5	0.05	7.40	-0.19	6.78	-0.04	4.60	0.11	3.83
18	-0.19	7.83	-0.19	7.25	0.08	4.85	0.11	4.05
21	0.25	7.06	-0.10	6.56	0.10	5.00	0.00	4.30
21.5	-0.13	8.38	-0.07	7.46	0.31	5.41	0.39	4.63
25	0.21	8.13	0.24	7.55	0.68	5.85	0.77	5.05
30	0.40	7.45	0.20	7.13	0.71	5.60	0.98	4.85
65	1.00	6.94	0.58	7.04	1.45	6.10	1.45	5.10

Table 4. Stress and Extension Ratio at the Minimum Point of the Mooney-Rivlin Plots for EPR Vulcanizates at 25°C

Cure, min	$\dot{\epsilon} = 1.25$ min^{-1}			$\dot{\epsilon} = 0.060$ min^{-1}
	α_m	$\sigma(\alpha - \alpha^{-2})^{-1}$, kg/cm^2	α_m	$\sigma(\alpha - \alpha^{-2})^{-1}$, kg/cm^2
13.5	8.7	1.14	10	0.85
16.5	8.0	1.37	9.1	1.09
18	7.7	1.46	8.0	1.23
21	6.7	1.64	8.0	1.22
21.5	6.6	1.68	7.4	1.45
25	6.0	2.04	6.0	1.90
30	5.9	2.00	5.9	1.93
65	4.9	2.49	4.9	2.04

Table 5. Stress-Temperature Results for EPR Vulcanizates

Cure, min	α	$(d\sigma/dT)^a \times 10^3$ P, L, kg/cm^2/deg	$-\left[\frac{\partial \ln(f/T)}{\partial T}\right]^a \times 10^3$ P, L, deg^{-1}	$\frac{f_e}{f}^a$
21.5	2.50	24.9	-1.40	-0.47
21.5	2.65	21.4	-1.39	-0.46
25	2.05	26.6	-1.35	-0.47
25	2.15	23.7	-1.19	-0.41
				-0.45 Average

[a] Evaluated at 50°C.

Table 6. Ultimate Properties of Swollen EPR Vulcanizates

Cure, min	0.98 in./min		0.047 in./min	
	$\sigma_B v_r^{1/3}$ (kg/cm^2)	α^a	$\sigma_B v_r^{1/3}$ (kg/cm^2)	α^a
65	5.65	2.51	4.20	2.03
30	3.25	2.41	3.40	2.55
25	4.25	3.01	3.25	2.49
21.5	2.55	3.78	2.40	3.70
21	1.95	4.94	—	—
18	2.38	6.47	—	—
16.5	2.45	7.70	—	—
13.5	0.12	8.84	—	—

[a] Extension ratio relative to the swollen unstrained length

Table 7. Ultimate Properties of Unswollen EPR Vulcanizates

Cure, min	Temp, °C	$\dot{\epsilon} = 1.25\ \text{min}^{-1}$		$\dot{\epsilon} = 0.060\ \text{min}^{-1}$	
		σ_B, kg/cm^2	α_B	σ_B, kg/cm^2	α_B
65	25	15	5.80	10	4.95
30	25	35	9.00	15	7.43
25	25	19	7.94	12	6.60
21.5	25	75	11.8	24	10.8
21	25	36	11.5	29	13.2
18	25	80	13.3	47	13.6
16.5	25	89	13.7	23	13.5
13.5	25	70	15.2	40	16.5
65	78[a]	9.6	2.87	7.6	2.28
30	78	8.8	3.03	7.8	3.51
25	78	8.1	3.61	7.2	3.05
21.5	78	8.0	6.44	6.4	4.47
21	78	6.0	6.55	4.8	5.45
18	78	6.8	9.64	5.4	8.10
16.5	78	7.8	13.3	4.6	6.96
13.5	78	2.7	2.44	2.0	1.94

[a] For results at 78°C, σ_B has been multiplied by the kinetic theory factor, 298/351.

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(Contract AF 04(695)-169) Unclassified report

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