

Viscoelastic Properties of Sulfonated Ethylene-Propylene Terpolymer Neutralized with Zinc Cation

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Synopsis

Stress-relaxation measurements in uniaxial extension, in the terminal zone, were made of sulfonated ethylene-propylene terpolymer (EPDM), neutralized with zinc cation. The sulfonation levels were 15 to 20 meq/100 g polymer (0.47 and 0.62 mol %), and for each level the effect of the ionic plasticizer, zinc stearate, was investigated. For all the polymers, the decay of the modulus with elapsed time was gradual and featureless, reflecting a broad distribution of relaxation times. Sensitivity of the ionomers' structures to thermal history before an experiment was suggested by irreproducibility in the magnitudes, but not the distribution, of relaxation times at a given temperature. For polymers containing zinc stearate measured at 80°C, the amount of permanent set was low for relaxation up to about 20 h, but increased rapidly with additional hours of stretch. Time-temperature superposition did not apply. Composite curves were constructed by matching the stress-relaxation response at short times; moduli measured at long times fell above the composite curve. The shapes of the composite curves were similar, regardless of the level of EPDM sulfonation or the presence of zinc stearate. The apparent Arrhenius activation energy for short-time relaxation at similar levels of the modulus was about 35 kcal/mol at 140°C for the unplasticized polymers and about 70 kcal/mol at 90°C for the polymers containing zinc stearate, in contrast to the usual effect of plasticizer on the rate of relaxation of amorphous polymers except near the glass transition temperature.

INTRODUCTION

Copolymers whose major component is a nonionic backbone, usually hydrocarbon, and whose minor component is pendant ionic groups neutralized in whole or in part to form salts, have come to be called ionomers.¹ The ionic moieties are thought to form microdomains inside the hydrocarbon matrix, and long-range molecular motion is presumably dominated by the kinetics of dissociation and association of a transient network of ionic moieties.

The viscoelastic relaxation of ionomers has apparent transition, plateau, and terminal zones; qualitatively, the distribution of relaxation times is reminiscent of that characteristic of an amorphous linear polymer² above the critical molecular weight for the onset of entanglements. However, viscoelastic studies at constant temperature of ionomers have been limited mostly to the transition and plateau zones, because for many ionomers the terminal zone appears only at very high temperatures. Relaxation in the terminal zone has been reported for ionomers of butadiene-methacrylic acid and butadiene-2-methyl-5-vinylpyridine,³ of ethylene-methacrylic acid,⁴ of styrene-methacrylic acid,⁵⁻⁸ of butadiene-styrene-4-vinylpyridine,⁹ and of perfluoroethylene with an ionic comonomer.¹⁰ Interpretation has generally been in terms of the applicability of time-temperature superposition. In extensive measurements of ionomers of different ion contents, Eisenberg^{5-8,11} observed that time-temperature super-

TABLE I
Characterization of the Zinc-Sulfonate EPDM Copolymers

Polymer code	Sulfonate content (meq/100 g polymer)	Zinc stearate content (g/100 g polymer)	Number sulfonate groups per polymer chain
15-0	15	—	7-8
15-10	15	10	7-8
20-0	20	—	10
20-10	20	10	10

position applied to ionomers with less than a critical ion content, which depended on the polymer backbone. For ionomers with higher ion content, composite relaxation curves could be constructed by matching relaxation curves at short times, the moduli measured at longer times falling below the composite curve. The fast relaxation at long times was interpreted as the effect of a new relaxation mechanism associated with the presence of large ion clusters.

The synthesis and properties of sulfonated ethylene-propylene terpolymer (EPDM) containing about 1 mol % salt groups have recently been reported by Lundberg and co-workers.¹²⁻¹⁹ EPDM has a glass transition temperature at about -50°C , so EPDM-based ionomers might be expected to relax substantially at relatively low temperatures. Accordingly, stress-relaxation measurements in the terminal zone were undertaken of sulfonated EPDM ionomers neutralized with zinc cation.

EXPERIMENTAL

Materials

Samples of sulfonated ethylene-propylene terpolymer (sulfonated EPDM) neutralized with zinc cation, all prepared from the same parent EPDM, were generously donated by Dr. Robert D. Lundberg of the Exxon Research and Engineering Co. Two levels of sulfonation were provided, 15 and 20 meq/100 g polymer (0.47 and 0.62 mol %, respectively). For each level of sulfonation, one sample was undiluted and another contained the ionic plasticizer, zinc stearate,^{16,17} at the level of 10 g/100 g of the neutralized sulfonated polymer. The parent EPDM copolymer contained about 50% ethylene, 46% propylene, and 4% 5-ethylidene-2-norbornene by weight. \bar{M}_n was estimated to be 40,000-50,000 and \bar{M}_w/\bar{M}_n was about 2. The polymer was manufactured by the Uniroyal Corp. under the trademark Royalene 521. From the polymer \bar{M}_n , and assuming an average monomer repeat molecular weight of 31 corresponding to the EPDM composition, the average number of sulfonate groups per chain of sulfonated polymer was estimated. Table I summarizes the polymer sulfonate and zinc levels and the approximate numbers of sulfonate groups per polymer chain.

A slight degree of crystallinity was probably the cause of anomalous features of the parent EPDM copolymer. The degree of crystallinity was too small to be confirmed in calorimetric measurements on a DuPont Model 2-IIC Differential Calorimeter, but crystallinity was suggested by several observations. During storage at 4°C over the space of 6 months, the polymer did not flow,

TABLE II
Heat Treatment of the Zinc-Sulfonate EPDM Copolymers

Polymer code	Treatment
15-0	150°C for 8 h
15-10	150°C for 8 h 150°C for 70 h
20-0	170°C for 20 h; then 150°C for 20 h
20-10	150°C for 20 h

though flow was expected from the relatively low molecular weight and T_g in the neighborhood of -50°C . In subsequent stress relaxation, the retractive force did not decay to zero even at 100°C , though the polymer did dissolve completely in toluene, showing that it was not crosslinked to a gel. That these results were caused by crystallinity, rather than branching, is suggested by observations of the birefringence. The polymer possessed a small residual birefringence in the unstretched state. And during stress relaxation, the time-dependent birefringence decayed somewhat more slowly than the stress, in violation of the semi-empirical law²⁰⁻²² that, for amorphous polymers above the glass transition temperature, the ratio of the birefringence to the stress (stress-optical coefficient) is constant.

Heat Treatments

In order to prepare samples for stress-relaxation, it was necessary to mold the polymers. Molding was performed in dry nitrogen atmosphere, at 150°C or (when necessary to shape the polymer) 170°C . Cooling was allowed to take place slowly, by equilibration of the molding oven with the surrounding air. The molded samples were about 1 mm thick. Although all the polymers showed degradative darkening at the edges after molding, little darkening occurred in the inner portions from which strips for stress relaxation were cut. Since polymers 15-0 and 20-0 did not flow to assume the shape of the mold, for these polymers the heat treatments were more properly annealing than molding. Before and after molding, the polymers were stored *in vacuo* at room temperature. Isolated solubility tests verified that the polymers were not crosslinked to a gel. Table II summarizes the heat treatments.

Stress Relaxation

For measurements of stress relaxation, carried out in dry nitrogen atmosphere, strips were cut from the networks 0.40 cm wide and usually 5 cm long. For measurements at 100°C or less, they were glued to steel clamps with cyanoacrylate glue, but for measurements at higher temperatures they were glued with epoxy glue. The temperature was usually stable within 0.2°C . The instrument configuration has been described previously.²³ The force was measured directly to 0.01 g by a PL-1200-02 Mettler Balance and recorded digitally vs. time by a separate printer. The stretch ratio λ was determined from the distances between circular fiducial marks measured before and during the experiment with a traveling microscope. Four marks were used to ensure that the stress ratio was

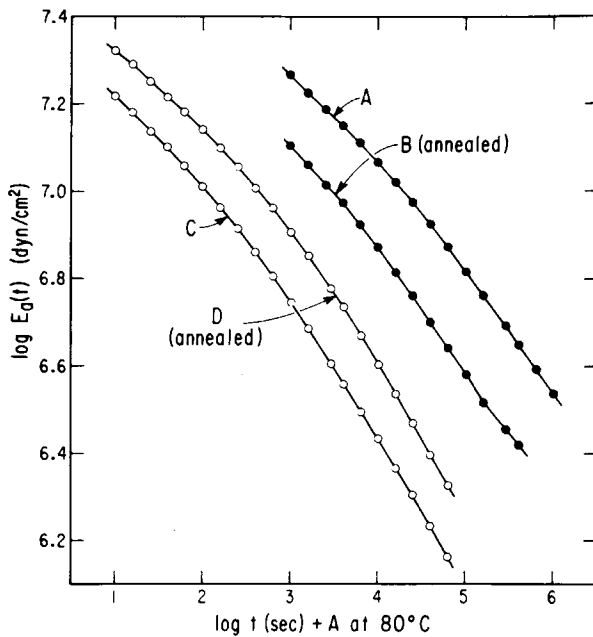


Fig. 1. Effects of annealing on logarithmic $E_a(t)$ of polymer 15-10 measured at 80°C: (○) stretched without prior annealing (curve A) and annealed at 100°C before stretch (curve B); (●) stretched without prior annealing (curve C) and annealed at 95°C before stretch (curve D). $A = 0$ for curves A and B; $A = 2$ for curves C and D.

uniform within 0.01 (or sometimes 0.02). The stretch ratio was usually between 1.22 and 1.26. The results were calculated in terms of the apparent Young's modulus (apparent because deviations from neo-Hookean elasticity are neglected), defined to be

$$E_a(t) = 3f(t)/A_0(\lambda - \lambda^{-2}) \quad (1)$$

where $f(t)$ is the time-dependent force and A_0 is the original cross-sectional area, determined from the known width and the thickness measured with a micrometer at the strip's two ends and middle. If the stress-strain relation is neo-Hookean, this provides the Young's relaxation modulus of linear viscoelasticity; deviations at this magnitude of strain are expected to be small. The unstretched dimensions away from room temperature were estimated with a linear thermal expansion coefficient of 2.5×10^{-4} per degree.

RESULTS

Effects of Thermal History

In extensive measurements on polymers 15-10 and 20-0, irreproducibility in the positions, but not the shapes, of the modulus decay curves on the logarithmic time scale was apparently associated with differences in thermal history. In measurements of polymer 15-10 (containing zinc stearate) at 80°C, annealing usually speeded up relaxation but in one case it slowed relaxation down. In Figure 1, the two rightmost curves illustrate that annealing polymer 15-10 could

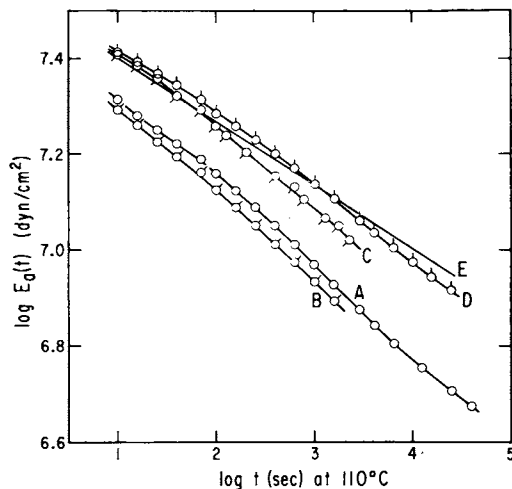


Fig. 2. Effects of thermal history on logarithmic $E_a(t)$ of polymer 20-0 measured at 110°C: (A) 2 months after molding; (B) 14 months after molding; (C) annealed in dry nitrogen atmosphere at 150°C; (D) annealed *in vacuo* at 150°C; (E) annealed as for curve D and then soaked in water.

speed up relaxation. (These curves are shifted to the right by two logarithmic units of time to avoid clutter in the graph.) Curve A shows the relaxation of a polymer strip stretched without special annealing and curve B the relaxation of a strip kept at 100°C in dry nitrogen atmosphere before measurement at 80°C. The curves have the same shape, but the effect of annealing was apparently to speed up relaxation by 0.80 logarithmic units of time (a factor of 6.3). Additional evidence that annealing could speed up relaxation is that polymer 15-10 relaxed more rapidly, by up to 0.20 logarithmic units (a factor of 1.6), the longer the molding heat treatment it had sustained (cf. Table II).

An instance where annealing slowed down relaxation is shown in the two leftmost curves in Figure 1. Curve C shows the relaxation of a strip stretched without special annealing and curve D the relaxation of a strip kept at 95°C *in vacuo* before measurement at 80°C. (No weight loss was detected.) Again the curves have the same shape, but here annealing apparently slowed down relaxation, by 0.60 logarithmic units (a factor of 4). It should be noted that polymers containing zinc stearate are known to absorb less moisture than polymers which do not contain it^{12,16} and that experiments described below suggest that absorbed moisture did not materially influence the measurements of polymer 20-0.

Irreproducibility in the time scale of relaxation occurred even for polymer 15-10 which did not sustain special annealing before stretch at 80°C. Differences of up to 0.15 logarithmic units in the locations of the modulus decay curves on the logarithmic time scale (a factor of 1.4) were not correlated with time at room temperature after molding, nor did they disappear if the polymer was annealed *in vacuo* at 60–80°C for 2 days after molding, as suggested in Ref. 17; they were probably associated with small, uncontrolled differences in time at 80°C before stretch, between 30 min and 2 h.

Relaxation of polymer 20-0 (not containing zinc stearate) at 110°C was not affected by annealing at 110°C before stretch. However, stress relaxation at 110°C was apparently speeded up by long storage at room temperature and

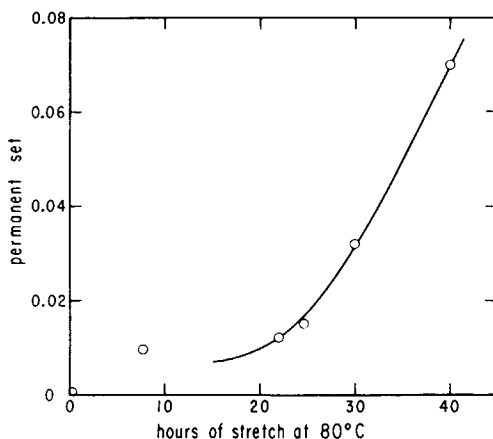


Fig. 3. Permanent set plotted vs. hours of stretch at 80°C, for polymer 15-10.

slowed down by annealing at 150°C just before an experiment. Figure 2 illustrates this. First (curve A) the polymer was stretched 2 months after molding. Next (curve B) it was stretched 1 year later; the relaxation was 0.20 logarithmic units faster, a factor of 1.6. Then (curve C) it was stretched after annealing in dry nitrogen atmosphere at 150°C for 2 h; the relaxation was 0.60 logarithmic units slower than for curve A, a factor of 4. The shapes of curves A, B, and C are the same within experimental accuracy. Suspecting loss of absorbed moisture during annealing at 150°C, the polymer was annealed *in vacuo* at 150°C for 19 h; the relaxation afterwards (curve D) was nearly the same as the earliest measurement times as that represented by curve C, but the subsequent relaxation was more gradual. Finally, polymer which had been annealed *in vacuo* at 150°C for 24 h was soaked in water until it regained the 1% weight lost during annealing; 19 h were required. The relaxation (curve E) does not differ greatly from that represented by curves C and D. This result, and the very slow rate of water absorption, suggest that the results reported in this section are indeed principally effects of thermal history, not to a great extent of the uptake or loss of absorbed moisture.

Irreversible change of structure was not associated with the stress relaxation of polymers 15-10 and 20-0. When polymers were restretched after annealing until the length no longer shortened with time, the decay of the modulus was the same as for previously unstretched strips which had undergone the same annealing history.

Permanent Set of Strips of Polymer 15-10 Stretched at 80°C

The permanent set of strips of polymer 15-10, stretched at 80°C for differing lengths of time, was determined from their lengths after recovery at 95°C for 24 h. The results are plotted in Figure 3 as a function of hours of stretch. The amount of permanent set was low after relaxation less than about 20 h, in agreement with the oft-cited finding of Cooper²⁴ for a variety of metal salts of butadiene-methacrylic acid and butadiene-acrylic acid copolymers, seeming to indicate the existence of a stable structure whose reference undeformed state

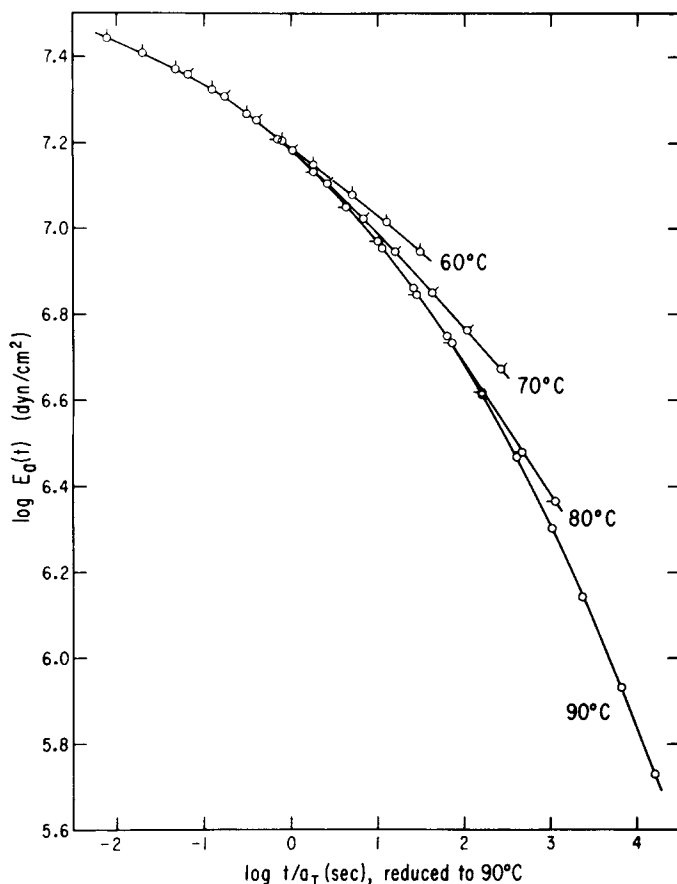


Fig. 4. Composite stress-relaxation curve, reduced to 90°C by match at short times, for polymer 15-10.

was the unstretched length.²⁴ But the permanent set increased rapidly with additional hours of stretch.

Composite Curves Describing Stress Relaxation at Several Temperatures

The modulus decay curves at different temperatures for a given polymer were matched at short times to generate composite curves, following the example of Eisenberg.^{5-7,10,11} The individual curves typically matched over only 1-2 decades of logarithmic time. Before the curves were matched, the moduli were multiplied by $T_0\rho_0/T\rho$, where ρ is the density at the absolute temperature T of measurement and ρ_0 refers to the reference temperature T_0 . For polymer 15-10, the composite curve, reduced to 90°C, is shown in Figure 4. For polymer 15-0, the composite curve, reduced to 110°C, is shown in Figure 5. At each temperature, the moduli at long times deviate from the composite curve, being greater in magnitude. For polymer 20-0, deviations from the composite curve are much more severe than for polymer 15-0.

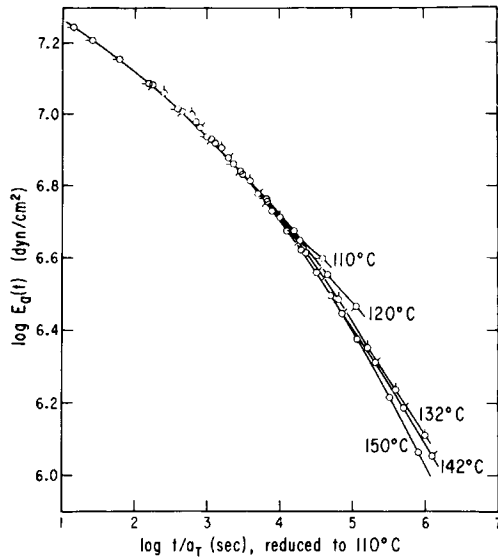


Fig. 5. Composite stress-relaxation curve, reduced to 110°C by match at short times, for polymer 15-0.

The composite short-time relaxation curves are compared for the polymers containing zinc stearate ionic plasticizer in the left portion of Figure 6, and for the polymers not containing zinc stearate in the right portion. To avoid clutter, smooth lines rather than data points are plotted, and deviations from the composite curves are omitted. The shapes of the curves are similar, but, for polymers 20-10 and annealed 20-0, relaxation to a given modulus is slower than for polymers 15-10 and 15-0, respectively. Since polymers 20-10 and 20-0 have a higher sulfonate content, this is a reasonable finding. The shapes of the curves for the polymers not containing zinc stearate resemble the shapes of the curves for the polymers containing zinc stearate. As described above, for polymer 20-0 the time scale of relaxation at 110°C depends on the thermal history, being faster for polymers not annealed just before stretch; the coincidence of time scales of relaxation at 110°C for unannealed polymer 20-0 and for polymer 15-0 is an ac-

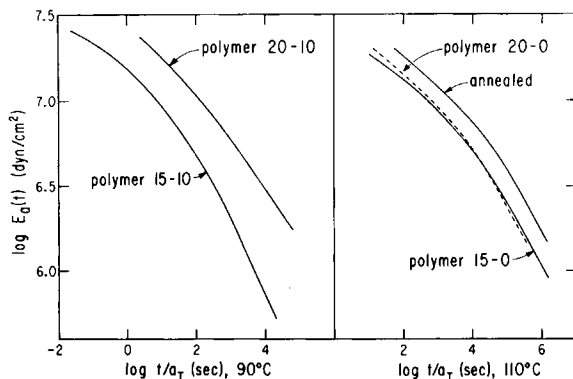


Fig. 6. Comparison of composite stress relaxation curves at short times. Left: polymers 15-10 and 20-10, reduced to 90°C. Right: polymers 15-0 and 20-0, reduced to 110°C.

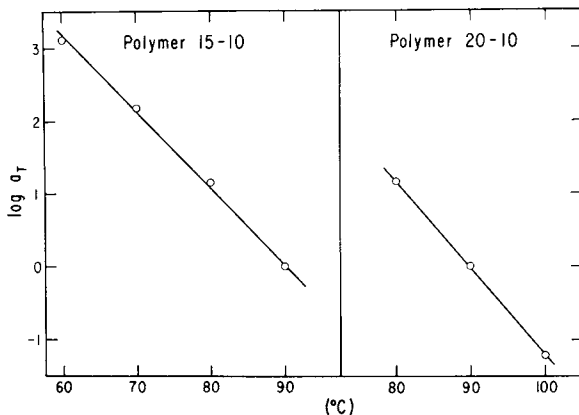


Fig. 7. Logarithmic shifts in time to reduce stress-relaxation curves to 90°C, for polymers 15-10 and 20-10.

cidental outcome of the choice of reference temperature, as is evident from the discussion of activation energies which follows.

Figures 7-9 show plots of the logarithmic shifts in time needed to piece together the modulus decay curves. The designation $\log a_T$ is not intended to imply a WLF²⁵ dependence on temperature. Linear relations seem to hold, except for unannealed polymer 20-0 at the lower measurement temperatures. For polymers 15-10 and 20-10, the reason that scatter is not great is that the time at the measurement temperatures before stretch was always the same.

Apparent Arrhenius activation energies ΔH_a were calculated, for the straight line regions drawn in Figures 7-9, from plots against inverse absolute temperature; they are tabulated in Table III. The activation energies are twice as high at similar values of the modulus for the polymers containing zinc stearate plasticizer as for those which did not, but there is no apparent dependence on the sulfonate content. For polymers 15-10 and 20-10 (containing zinc stearate), $\Delta H_a \approx 70$ kcal/mol at 90°C; for polymers 15-0 and 20-0 (not containing zinc stearate), $\Delta H_a \approx 35$ kcal/mol at 140°C. These activation energies are considerably higher than the values which can be calculated² from WLF parameters reported in Ref.

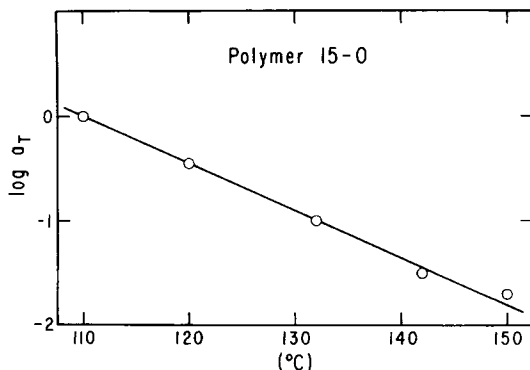


Fig. 8. Logarithmic shifts in time to reduce stress relaxation curves to 110°C, for polymer 15-0.

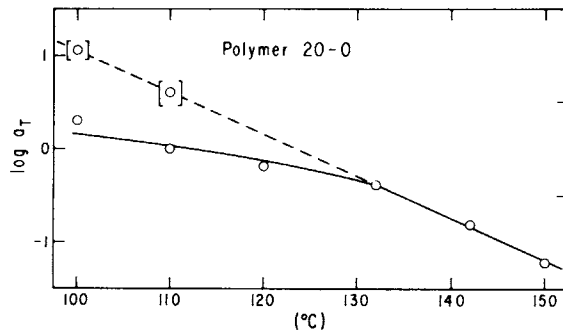


Fig. 9. Logarithmic shifts in time to reduce stress-relaxation curves to 110°C, for polymer 20-0. Bracketed points represent strips annealed at 150°C soon before stretch.

17 for similar EPDM ionomers (of slightly lower molecular weight) neutralized with zinc (the comparisons are included in Table III), and are somewhat lower than the values which can be calculated from WLF parameters reported in Ref. 6 for the sodium salt of styrene-methacrylic acid copolymers. In Ref. 17, most measurements were made below room temperature, at frequencies above 0.01 Hz.

Figure 9 illustrates that, for strips of polymer 20-0 stretched after annealing at 150°C, the shift factors to 110°C fall on the extrapolated line from the very highest measurement temperatures. By contrast, for strips stretched without special annealing, the apparent activation energy is less, the lower the temperature. For polymer 15-0, the shift factors in Figure 8 all fall on the same line regardless of the measurement temperature. Whether this reflects a profound difference between polymers 15-0 and 20-0 or merely their different molding treatments (cf. Table III), is not known.

DISCUSSION

In the terminal zone stress-relaxation experiments on zinc-sulfonated EPDM copolymers described above, the decay of the modulus with elapsed time was gradual and featureless, reflecting a broad distribution of relaxation times. The shapes of the composite modulus decay curves in Figure 6 are remarkably similar in character, regardless of the level of EPDM sulfonation or the presence or absence of zinc stearate. These results are in general agreement with previous

TABLE III
Apparent Arrhenius Activation Energies for Stress Relaxation at Short Times

Polymer	ΔH_a (kcal/mol)
15-10	64 at 90°C
20-10	71 at 90°C
15-0	36 at 140°C
20-0	32 at 140°C
48-A in Ref. 17 ^a	7 at 140°C
Parent EPDM in Ref. 17 ^b	10 at 140°C

^a Sulfonate content similar to polymer 20-0 but molecular weight slightly lower.

^b Composition similar to parent EPDM in present study but molecular weight slightly lower.

findings.³⁻¹¹ However, the nature of the large deviations from time-temperature superposition contrasts with the findings of Eisenberg for styrene-methacrylate⁵⁻⁷ and ethyl acrylate¹¹ ionomers, where the modulus decay curves measured at long times fell below the composite curve for short-time relaxation. The deviations found in the present study are in the opposite sense; the postulated two relaxation mechanisms^{5-7,11} to describe those results do not describe the present results. The deviations do not appear to be caused by crystallinity, since they persisted above the melting temperatures of polyethylene crystallites.

Strong and unexpected sensitivity of the ionomers' structures to thermal history is suggested by the observed dependencies of the rates of relaxation on the temperature of measurement and on the thermal history before measurement. Annealing before an experiment usually speeded up relaxation of polymer 15-10 (containing zinc stearate), but slowed down relaxation of polymer 20-0, without altering the distributions of relaxation times. Long storage at room temperature speeded up relaxation of polymer 20-0. These results raise the question whether the ionomers' structures also changed during the course of a long experiment at constant temperature. In comparing the apparent Arrhenius activation energies for short-time relaxation, it is striking that, at similar values of the modulus, the activation energy was twice as high for the polymers containing zinc stearate as for those which did not, in contrast to the usual effect of plasticizer on the behavior of amorphous polymers, except near T_g .² In dynamic viscoelastic experiments by Lundberg and co-workers¹⁷ at room temperature and below, the apparent activation energy for a polymer similar to polymer 20-0 was lower still (cf. Table III). It is evident that the processes responsible for relaxation in zinc-sulfonated EPDM are more temperature-dependent at high temperatures, long times, and in the presence of ionic plasticizer, than at lower temperatures, relatively high frequencies, and in the absence of plasticizer.

Although there are no obvious indications that either absorbed moisture or the apparent slight degree of crystallinity in the parent EPDM random copolymer materially influenced the above findings, their generality will remain unclear until experiments on this complicated system can be repeated with ionomers of better characterized structure. No molecular interpretation of these findings is offered at the present time.

This work was supported by the National Science Foundation, Grant Nos. DMR 78-16954 and DMR 81-15462, Polymers Program, to Professor John D. Ferry. I am indebted to Dr. Robert D. Lundberg and Dr. Pawan K. Agarwal, both of the Exxon Research and Engineering Co., for the gift of materials and for helpful discussions, and to Professor Stuart L. Cooper and Dr. Carl Wang for the use of the differential scanning calorimeter and for assistance in using it. I am particularly grateful to Professor Ferry for suggesting the project and for many helpful suggestions.

References

1. For recent reviews, see A. Eisenberg and M. King, *Ion Containing Polymers, Physical Properties and Structure*, Academic, New York, 1977; W. J. MacKnight and T. R. Earnest, Jr., *Macromol. Rev.*, **16**, 41 (1981).
2. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, 1980.
3. E. P. Otocka and F. R. Eirich, *J. Polym. Sci., A-2*, **6**, 921 (1968).
4. K. Sakamoto, W. J. MacKnight, and R. S. Porter, *J. Polym. Sci., A-2*, **8**, 277 (1970).
5. A. Eisenberg and M. Navratil, *J. Polym. Sci. B*, **10**, 537 (1972).
6. A. Eisenberg and M. Navratil, *Macromolecules*, **6**, 604 (1973).

7. A. Eisenberg and M. Navratil, *Macromolecules*, **7**, 84 (1974).
8. E. Shohamy and A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1211 (1976).
9. C. T. Meyer and M. Pineri, *Polymer*, **17**, 382 (1976).
10. S. C. Yeo and A. Eisenberg, *J. Appl. Polym. Sci.*, **21**, 875 (1977).
11. A. Eisenberg, H. Matsuura, and T. Tsutsui, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 479 (1980).
12. H. S. Makowski, R. D. Lundberg, L. Westerman, and J. Bock, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **19**(2), 292 (1978); R. D. Lundberg and H. S. Makowski, *ibid.*, **19**(2), 287 (1978); R. M. Neumann, W. J. MacKnight, and R. D. Lundberg, *ibid.*, **19**(2), 298 (1978); H. S. Makowski and R. D. Lundberg, *ibid.*, **19**(2), 304 (1978).
13. A. Eisenberg, Ed., *Ions in Polymers*, Am. Chem. Soc., Washington, D.C., 1980.
14. H. S. Makowski, R. D. Lundberg, L. Westerman, and J. Bock, in Ref. 13.
15. R. D. Lundberg and H. S. Makowski, in Ref. 13.
16. H. S. Makowski and R. D. Lundberg, in Ref. 13.
17. P. K. Agarwal, H. S. Makowski, and R. D. Lundberg, *Macromolecules*, **13**, 1679 (1980).
18. R. D. Lundberg and H. S. Makowski, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1821 (1980).
19. P. K. Agarwal and R. D. Lundberg, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **23**(1), 58 (1982); R. D. Lundberg and P. K. Agarwal, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **23**(1), 61 (1982).
20. H. Janeschitz-Kriegl, *Adv. Polym. Sci.*, **6**, 170 (1969).
21. J. W. Noordermeer and J. D. Ferry, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 509 (1976).
22. K. Osaki, S. Kimura, and M. Kurata, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 517 (1981).
23. O. Kramer, R. Greco, J. D. Ferry, and E. T. McDonel, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1675 (1975).
24. W. Cooper, *J. Polym. Sci.*, **28**, 195 (1958).
25. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

Received September 23, 1982

Accepted December 15, 1982