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Viscoelastic Behavior of Concentrated Oil Solutions of Sulfo Polymers. 2. EPDM and Zinc Sulfo-EPDMs

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ABSTRACT: The viscoelastic behavior of semidilute solutions of metal-neutralized sulfonated EPDM polymers in a paraffinic oil is described. The results are compared to those of the base EPDM solutions. The data of the bulk behavior of these two polymer systems as well as those of another comparable molecular weight polyisobutylene polymer are also described for comparative purposes. The detailed solution studies of zinc-neutralized sulfonated EPDM polymers demonstrate the changes in the permanence and strength of physical associations as a function of diluent concentration. At 5 wt % zinc sulfo-EPDM, the behavior of this solution at high frequencies resembles that of a covalently cross-linked elastomer, while at low frequencies the behavior is that of a typical Newtonian fluid. In contrast, the base EPDM dissolved at 5 wt % concentration displays virtually no indication of entanglements. A range of polymer concentrations of zinc sulfo-EPDM was investigated from 1 to 12.5 wt % polymer at a sulfonate level of 20 mequiv/100 g of polymer. At polymer concentrations near 1 wt %, a slight entanglement plateau was evident. Similar studies were conducted on polymers having a range of sulfonate levels of 10, 20, and 30 mequiv/100 g, all at 5 wt % polymer concentrations. As sulfonation level increases, the entanglement plateau is extended and the modulus increases. These findings are consistent with a dynamic interaction of metal sulfonate groups whose degree of clustering is widely variable in nonpolar media. These results contrast markedly with those of the magnesium sulfonated EPDM which, under comparable conditions, exhibits a much more persistent network. The viscoelastic data are analyzed following conventional linear viscoelastic theories. Monomeric friction coefficients of various systems are calculated with the modified Rouse model, and relationships of viscoelastic parameters, the entanglement plateau $G_N{}^0$, recoverable compliance $J_e{}^0$, and zero-shear viscosity, η_0, as a function of concentration are established for the zinc salt solution of sulfo-EPDM. The following relations for the sulfonated EPDM were obtained: $G_N{}^0 \propto C^{2.5}$, $J_e{}^0 \propto C^{-1}$, and $\eta \propto C^{6.0}$, and for the unsulfonated EPDM polymer $G_N{}^0 \propto C^{2.0}$, $J_e{}^0 \propto C^{-1}$, and $\eta \propto C^{1.7}$ and $\eta \propto C^{4.5}$ below and above the breakpoint. In summary, these studies demonstrate how metal sulfonate interactions alter the solution behavior of this class of ionomers as a function of polymer concentration, sulfonate level, and cation type and explain how some ionomers simply behave as higher molecular weight analogues of EPDM, while others can act as if they were highly cross-linked systems simply by changes in the cation or sulfonate level.

Introduction

The effect of diluent concentration on the viscoelastic properties of conventional polymers has been examined in a number of cases, and a summary of such investigations has been described by Ferry and Graessley in some detail.[1,2] The bulk of prior efforts were concerned with linear amorphous, narrowly distributed polymers, with particular emphasis on polystyrenes dissolved in a variety of diluents. Part of this paper is concerned with the effect of diluents on the viscoelastic behavior of ethylene–propylene–ethylidenenorbornene or EPDM terpolymer; the diluent of choice is a paraffinic oil.

This system is of interest for several reasons. First, EPDM is often extended with such oils in practical applications, and, therefore, its viscoelastic behavior in diluted form is relevant. Second, EPDM is especially suited for certain functionalization reactions, especially substitution with metal sulfonate groups. The resulting ionomers can form extremely persistent ionic networks of practical significance.[3,4] Such ionomers are readily extended by paraffinic oils to form a class of ionomer gels with unusual viscoelastic effects. Since the sulfonation of EPDM to yield such metal sulfonate ionomers appears to occur with few side reactions and with apparently no significant effect on the degree of polymerization, a direct comparison of oil-extended EPDM with oil-extended sulfo-EPDM offers an opportunity to investigate the concentration, shear rate, and temperature effects of such ionic networks. The second and major thrust of this paper deals with these aspects.

During the past few years, a number of studies of sulfonated polymers demonstrated that the properties of these materials arise from a high degree of physical association. In such polymers the metal sulfonate groups aggregate to form strong ionic cross-links. Above certain levels of sulfonation in some systems, for example, the barium salt of a sulfonated EPDM at sulfonate contents >20 mequiv/100 g of polymer, the overall physical behavior of the polymer approaches that of a covalently cross-linked polymer. Viscoelastic studies[3] have confirmed that in bulk systems the physical cross-links of these sulfonate ionomers maintain their integrity to very high temperatures, yet polar additives can be very effective in dissociating these cross-links.[5] In this respect the viscoelastic properties of these sulfonated ionomers are different from those observed with carboxylated ionomers. Similarly, dilute solution[5] studies have demonstrated that sulfonated ionomers are very effective viscosifiers for nonpolar diluents even when employed at levels of ~1% or less. Under dilute solution conditions the presence of various polar cosolvents can give rise to different levels of polymer association and, therefore, different apparent molecular weights. In all these cases it has become evident that in low-polarity media each metal sulfonate group exists as an undissociated ion pair and that these two ion pairs aggregate to provide the physical cross-links.

While these studies have shown that metal sulfonate groups associate in a dilute environment, there have been few corresponding studies conducted in concentrated polymer solutions, i.e., about 2–15% polymer. This region is of practical interest, and the resultant ionomer gels can also offer substantial insight into the relaxation processes that these ionomers undergo.

Viscoelastic studies conducted on bulk sulfo-EPDM have shown a substantial difference in the degree of ionic association at high temperature, that is especially dependent on the cation employed. For example, compared to other monovalent or divalent cations, zinc sulfo-EPDM

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Table I

	M_n	M_w/M_n	$M_{z+1}M_z/M_w^2$	T_g, °C	log η, P	[η], dL/g
EPDM[a]	40 000	2.1	26.6	−55	7.46 (25 °C)	1.25,[c] 1.36[d]
polyisobutylene	14 000	6.9	15.3	−68	6.00	
100N oil[b]	200	3.0		−85(?)	−0.44	

[a] Ethylene and ENB content 55 and 4.4 wt %, respectively; at 25 °C $\rho_p = \rho_s = 0.856$ g/cm^3. [b] A petroleum hydrocarbon fraction, mostly paraffinic (average carbon number ~35; 9% aromatic). [c] In TCB at 147 °C. [d] In THF at 25 °C.

exhibits a lower melt viscosity at sulfonate levels of 10–30 mequiv/100 g and evidence of decreased network perfection.[3] Zinc sulfo-EPDM provides an ionomer with the viscoelastic behavior that should be markedly altered as a function of diluent concentration. Its behavior can then be compared to that of the base EPDM, similarly diluted. When possible we shall also attempt to compare the behavior of the base EPDM and zinc sulfo-EPDM to another high molecular weight polymer, polyisobutylene. A subsequent paper[6] in this series will be concerned with the viscoelastic behavior of magnesium sulfo-EPDM, a system that displays a more permanent network than is observed for the zinc cation.

Experimental Section

Solutions of the zinc-neutralized sulfonated EPDM in 100N oil solvent were prepared. For comparative studies various solutions of the precursor EPDM polymer were also prepared in the same solvent. In the case of sulfonated polymers the solutions covered a concentration range of ~1–15 wt % while the concentrations of solutions of the base EPDM ranged from 1% to 100%. Because of the rather strong ionic associations prevailing in the sulfonated polymers,[3] the dissolution of these polymers in various types of solvents is extremely sluggish and at times very difficult. Satisfactory homogeneous samples of higher concentrations (>15 wt % in 100N oil) could not be prepared in a reasonable desired period of time (100 days). The homogeneity of the samples used for final measurements was determined by visual observation and by reproducible viscoelastic measurements made as a function of time.

The characterization data for the base EPDM and 100N oil are given in Table I. Measurements were made on a commercial polyisobutylene sample manufactured by Exxon Chemical Co. and sold uner the trademark Vistanex LM. This polymer was chosen because some of its bulk properties are similar to those of EPDM. The weight-average molecular weight of this sample is similar to the EPDM used for the present studies. Other characterization data of Vistanex LM are listed in Table I.

The sulfonation chemistry of the EPDM polymer has been discussed in detail previously.[3,7] Zinc salts of sulfonated EPDM of varying levels of sulfonation were prepared. Extensive data are reported on a sample having sulfonation level of 20 mequiv.[22] On a mole basis, this concentration of sulfonate groups corresponds to about 7 groups per molecule. Using the average molecular weight of a repeat unit, 38 of the EPDM terpolymer, the average molecular weight between sulfonate groups, for the sulfo-EPDM(20) sample is about 5400. Characterization of these polymers in terms of MW, MWD, or [η] has not been practical (so far) because of the strong ionic associations that prevail in these systems even in very dilute solutions.[5] However, various physical characterizations such as NMR, viscoelasticity, etc., of these polymer systems indicate that at low sulfonate levels ($\lesssim$1.0 mol %) the sulfonation chemistry does not alter the structure of the base polymer (other than by sulfonating the unsaturated sites on the backbone). The overall process of sulfonation is straightforward, and over a number of years it has yielded reproducible products.

The solutions were prepared in covered beakers using a magnetic stirrer. In some cases, especially at high polymer concentrations, the beakers were mildly heated (50–60 °C) in a water bath to facilitate dissolution. Quite often complete dissolution of the polymer took as long 4 weeks. As pointed out in the introduction, at room temperature most of the concentrated solutions of sulfo-EPDM polymers were gels. Although 100N oil solvent has an extremely low vapor pressure (<0.01 mmHg at 40 °C) and its boiling point is above 350 °C, the preparation of solutions at higher temperatures was not attempted in order to avoid the possibility of the polymers being irreversibly affected. The various solutions studied in this report are listed in Table II.

Table II
Composition of Various Solutions

sample no.	nominal concn, (wt % polymer)	sulfonation level, mequiv	counterion
1-0-1 EPDM	1		
1-0-2 EPDM	3		
1-0-3 EPDN	5		
1-0-4 EPDM	15		
1-0-5 EPDM	35		
1-0-6 EPDM	60		
1-0 EPDM	100		
1-1 sulfo-EPDM	1	~20[a]	Zn
1-2 sulfo-EPDM	2	~20	Zn
1-3 sulfo-EPDM	5	~20	Zn
1-4 sulfo-EPDM	12.5	~20	Zn
1-9 sulfo-EPDM	5	~10	Zn
1-3 sulfo-EPDM	5	~20	Zn
1-10 sulfo-EPDM	5	~30	Zn
1-2 sulfo-EPDM	2	~20	Zn
1-5 sulfo-EPDM	2	~20	Mg
1-3 sulfo-EPDM	5	~20	Zn
1-5 sulfo-EPDM	5	~20	Mg

[a] 30 mequiv ≈ 1 mol %.

Viscoelastic measurements on the solutions were carried out on a Rheometrics mechanical spectrometer. In most of the cases both steady-state shear viscosity and dynamic moduli data were obtained, using either a parallel-plate or a cone-and-plate geometry. Dynamic measurements were confined to the linear range of viscoelasticity. For each solution a series of isothermal measurements, typically in the frequency range 2×10^{-3} to 20 Hz, were made. The lowest temperature of measurement was limited to −5 °C; below about −15 °C the paraffinic wax in the 100N oil crystallizes. This problem precluded measurements near or below the primary transition region, and hence most of the data on the solutions were collected in the terminal and plateau regions only. The high-temperature limit varied from solution to solution depending upon the sample response and instrument sensitivity. In the case of concentrated solutions of EPDM and in most of the sulfonated EPDM solutions the highest temperature of measurement was 160 °C. For the two lowest concentration solutions of EPDM the viscosity data were obtained with a calibrated Brookfield viscometer. The room-temperature viscosity values obtained from the Brookfield were checked with a Contraves rheometer and agreed within ±3%. In-phase modulus, G' and out-of-phase modulus G'' measurements on the bulk polyisobutylene were measured from −50 to +50 °C. A rectangular-bar geometry was used for measurements below and near the primary transition region, and above it a parallel-plate geometry was used. Repetitive measurements were made in the overlapping region to ensure reproducibility. Satisfactory agreement of the data was found from the two sets of measurements.

All the solution data were analyzed with the established constitutive equations of linear viscoelasticity.[1] The equations most

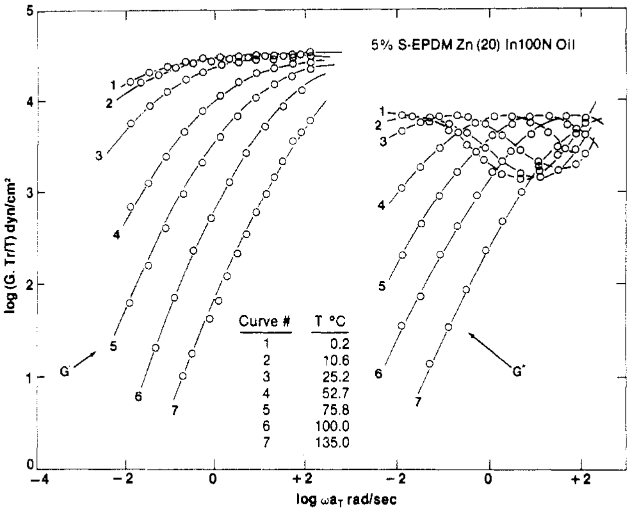

Figure 1. Isothermal plots of dynamic moduli $G'(T_r/T)$ and $G''(T_r/T)$ (in dyn/cm^2) vs. frequency (in rad/s) at the indicated temperatures for 5% Zn sulfo-EPDM salt solution in 100N oil.

often used were the following. In simple steady-state flows the viscosity and normal stress functions are related to the flow field through shear rate as follows:

$$\eta(\dot{\gamma}) = \sigma_{12}/\dot{\gamma} \tag{1}$$

$$\sigma_{11} - \sigma_{22} = \psi(\dot{\gamma})\dot{\gamma}^2 \tag{2}$$

where $\eta(\dot{\gamma})$ is the shear-rate-dependent viscosity, σ_{12} is the shear stress, $\dot{\gamma}$ is the shear rate, σ_{11} and σ_{22} are the normal stresses, and $\psi(\dot{\gamma})$ is the first normal stress function. In the limit of vanishing shear rates, $\eta(\dot{\gamma})$ and $\psi(\dot{\gamma})$ take the form

$$\eta_0 = \lim_{\dot{\gamma}\to 0} \eta(\dot{\gamma}) \tag{3}$$

$$J_e^0 = \frac{1}{2\eta_0^2} \lim_{\dot{\gamma}\to 0} \psi(\dot{\gamma}) \tag{4}$$

Alternatively

$$J_e^0 = \frac{1}{2} \lim_{\dot{\gamma}\to 0} \frac{\sigma_{11} - \sigma_{22}}{\sigma_{12}^2} \tag{4a}$$

where η_0 and J_e^0 are the zero-shear viscosity and recoverable compliance, respectively. Under steady-state conditions, η_0 is related to the portion of the deformation of the material that is nonrecoverable, while J_e^0 is related to the recoverable portion of the total deformation. From second-order viscoelasticity theory, under limiting conditions, both η_0 and J_e^0 are related to the dynamic viscoelastic functions $G'(\omega)$ and $G''(\omega)$ as follows:

$$\eta_0 = \lim_{\omega\to 0} \frac{G''(\omega)}{\omega} \tag{5}$$

$$J_e^0 = \lim_{\omega\to 0} \frac{G'(\omega)}{\omega^2\eta_0^2} \tag{6}$$

where $G'(\omega)$ and $G''(\omega)$ are the in-phase and out-of-phase moduli, respectively, and ω is the angular frequency.

Since η_0 and J_e^0 are the steady-state parameters that are determined by the terminal zone of the viscoelastic spectrum of a polymer, another parameter, called the terminal relaxation time, τ_m, can be defined as

$$\tau_m = \eta_0 J_e^0 \tag{7}$$

Physically, τ_m is the time that governs the rate of response of the material in the "slow" deformation region.

In the case of fairly high molecular weight polymers another property of interest that is reflected in their viscoelastic spectra is G_N^0, the plateau modulus. G_N^0 can be obtained from $G'(\omega)$, if the function has a reasonable constant region, or, more accurately, from the terminal loss modulus peak using the following equation.

$$G_N^0 = \frac{2}{\pi}\int_{-\infty}^{+\infty} G''(\omega)\, \mathrm{d}\ln\omega \tag{8}$$

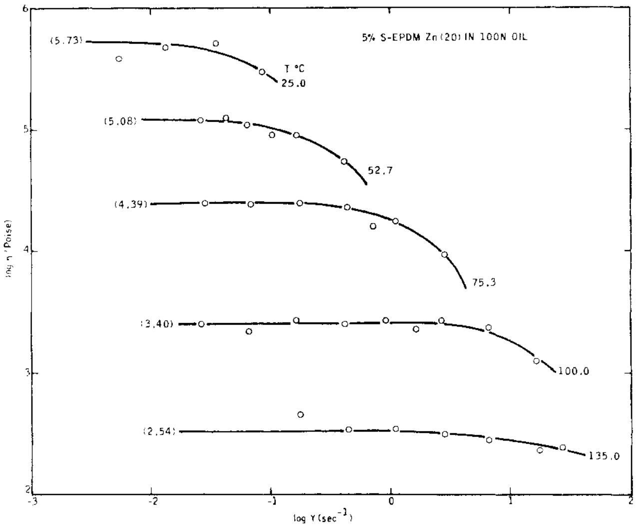

Figure 2. Viscosity (in P) vs. shear rate (in s^{-1}) as a function of temperature for 5% Zn sulfo-EPDM salt solution in 100N oil.

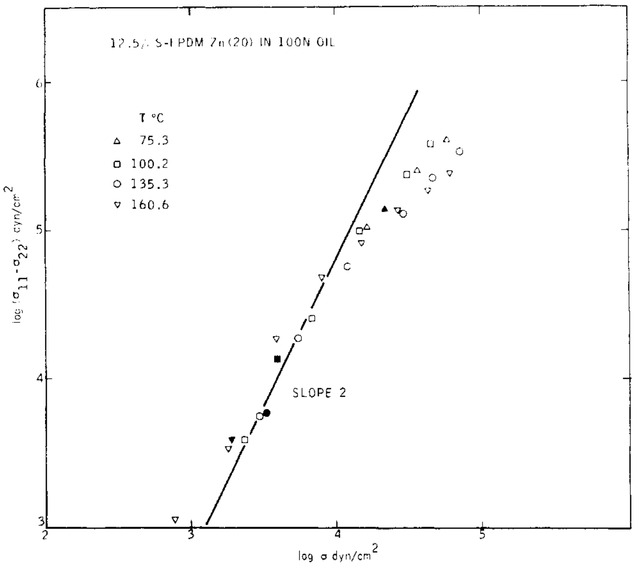

Figure 3. First normal stress difference $(\sigma_{11} - \sigma_{22})$ (in dyn/cm^2) vs. shear stress (in dyn/cm^2) as a function of temperature for 12.5% sulfo-EPDM Zn salt solution in 100N oil.

Results and Discussion

Comparison of G' and G'' Behavior of 5 wt % Solutions of Sulfo-EPDM Zinc Salt and EPDM. Typical dynamic moduli and steady-state viscosity and normal stress data taken on these solutions are shown in Figures 1–3. Figure 1 is a plot of the in-phase and out-of-phase moduli G' and G'', vs. frequency as a function of temperature for the 5 wt % solution of sulfonated EPDM zinc salt having a sulfonation level of about 20 mequiv (~0.7 mol %) in 100N oil solvent. Figure 2 is the a plot of shear viscosity vs. shear rate for the same solution. Figure 3 shows the normal stress data plotted against shear stress for a 12.5 wt % solution of the polymer. As mentioned earlier all the solution data were obtained over a wide enough temperature and shear-rate range to achieve the terminal viscoelastic regions as judged from the limiting slopes of G' and G'' in dynamic measurements and the limiting zero-shear viscosities in steady-shear measurements, respectively. It was always more difficult to attain the desired limiting slope in the G' curves. We believed this to result from the polydispersity of the sample which may be further exacerbated by ionic association. In cases for which satisfactory lines could not be drawn through

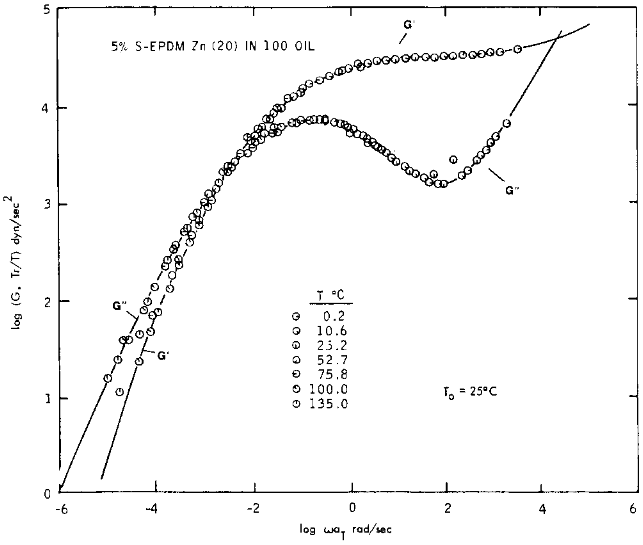

Figure 4. Reduced moduli $G'(T_r/T)$ and $G''(T_r/T)$ (in dyn/cm^2) vs. frequency (in rad/s) at 25 °C for 5% sulfo-EPDM Zn salt solution in 100N oil.

the terminal data points, the curves were matched by horizontal and vertical shifting with those solutions for which the terminal region was satisfactorily obtained. The viscoelastic functions were then calculated from such final curves.

While making viscosity measuremets in the Rheometrics mechanical spectrometer, we could simultaneously gather normal stress data. In most cases under low limiting conditions of shear the normal stress coefficient reached its limiting behavior quite well. However, quite often we noted a small positive or a negative value of $\sigma_{11} - \sigma_{22}$ where $\sigma = 0$ on a linear plot of $\sigma_{11} - \sigma_{22}$ vs. σ^2. Somewhat more scatter was observed with these data, especially at low shear rates, than is typically observed in the viscosity and dynamic measurements. Attaining a slope of 2 was somewhat difficult in such cases, and there is some room for doubt about these measurements. Judgment was used in drawing the lines through the normal stress data. However, the recoverable compliance values calculated from these measurements provided a check of the values obtained through the dynamic measurements. This will be discussed later.

Various interesting features of behavior, not previously observed, are readily apparent from the shape and position of curves in Figure 1. The viscoelastic behavior of bulk sulfonated polymer has been reported.[3] As mentioned in this reference these polymers are highly physically associated, and in their bulk state no viscoelastic relaxations other than those corrsponding to configurational rearrangements associated with a glass-to-rubber transition could be practically observed. Various isothermal G'' curves demonstrate the relaxations of the zinc sulfonated EPDM(20)[22] in a highly diluted state. The dominant viscous flow contribution in the terminal region is clear at high temperatures. For example, curves 6 and 7 (Figure 1) represent data taken at 100 and 135 °C, respectively; at low frequencies a slope of 1 is attained. The low-temperature measurements (see curves 1–3) of G' clearly demonstrate the existence of a rather strong and wide rubbery plateau. At room temperature the plateau extends more than 3 decades. These observations suggest the existence of a fairly strong, three-dimensional, network-like structure in the system.

In order to evaluate the temperature dependence of these viscoelastic relaxation processes in a more refined fashion, the usual method of reduced variables was adopted. Various curves of Figure 1 could be successfully reduced to a single curve by translating them along the time axis. An excellent superposition of the data was achieved and the resulting reduced curve is shown in Figure 4. The data shown in Figure 1 as well as the data for all other solutions were reduced to a common reference temperature of 25 °C. All comparisons of behavior were made at this temperature. Glass-temperature (T_g) effects should not affect the analysis made at this corresponding temperature because this reference temperature is perhaps about 100 °C above the glass temperature of each solution. Also any small changes or differences in T_g of various solutions, except those of concentrated EPDM polymer solutions, will have little if any affect on the position of the reduced curve on the time scale.

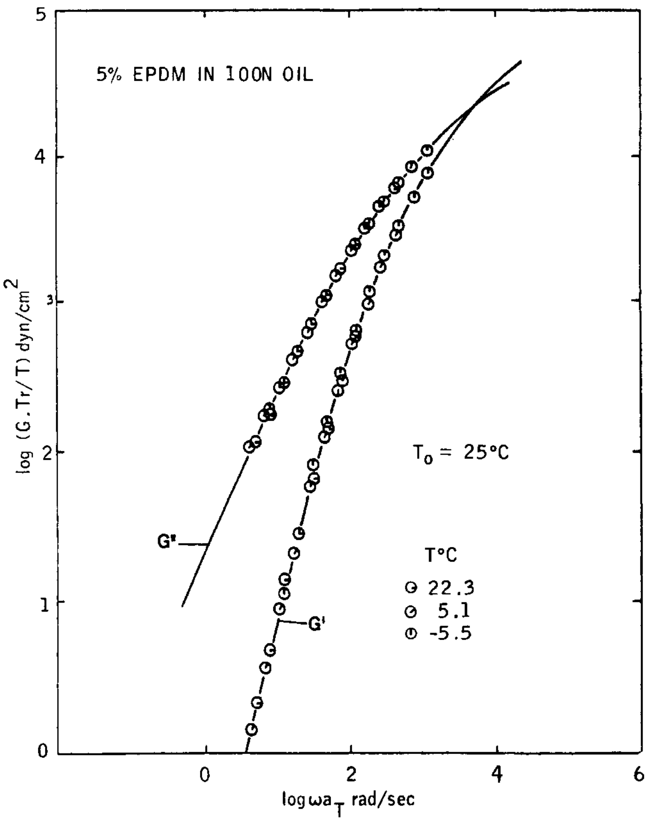

Figure 5. Reduced moduli $G'(T_r/T)$ and $G''(T_r/T)$ (in dyn/cm^2) vs. reduced frequency (in rad/s) for the 5% unsulfonated EPDM solution in 100N oil. Reference temperature 25 °C.

From Figure 4 the comments made earlier with reference to the behavior of zinc sulfo-EPDM(20) become more evident. The equilibrium modulus G_e of this sample is $\sim 7 \times 10^4$ dyn/cm^2. The behavior of this sample at high frequencies resembles very closely that of a lightly covalently cross-linked elastomer, while at low frequencies the behavior is that of a typical Newtonian fluid. To our knowledge such behavior by any polymer of comparable molecular weight (M_w of the EPDM $\sim$84 000) at such dilution 5 wt %) has not been observed before. Such extensive plateaus are typically observed in viscoelastic behavior of amorphous, monodisperse polymers in their bulk state, provided that their molecular weight is very high.[8] The behavior exhibited by this sample result from the strong ionic interactions of metal sulfonate groups. What is surprising is that only about 1 metal sulfonate group per 300 backbone carbon atoms increase the relaxation times to such a dramatic extent.

Comparing Figure 4 with listed 5 (the reduced curve of base EPDM solution) gives a better perspective of the strong influence of such small amounts of ionic interactions on the viscoelastic behavior of EPDM polymers. For this sample only a very limited temperature range could be covered. The lowest temperature at which the measurements could be carried out were limited because of the nature of the solvent (as explained in the Experimental Section). Nevertheless, it is very clear from the shape of the curve that there is no hint of the plateau zone. Low-temperature and/or somewhat higher frequency measurements would have shown that the "nonplateau" behavior of this solution would have persisted directly from the terminal-flow region to the glassy region.

In such a highly diluted state the EPDM polymers exhibit only meager signs of entanglement coupling, if any at all. Our subsequent measurements on various other concentrated solutions of EPDM indicate that only above 35 wt % one is able to see clearly relaxations, as reflected in G'' curves of this polymer that could be attributed to entanglements; cf., Figure 7. A clear and distinct rubbery or entanglement plateau (in G' curve) develops only in the bulk state; see the top curve of Figure 10. In view of its low molecular weight, the behavior of this polymer is not surprising and is typical of a variety of high polymers.[1,2]

Various points have been highlighted to demonstrate the effect on viscoelastic behavior of the addition of zinc sulfonate groups in EPDM. In the past most of the studies on sulfonated polymers in our laboratories were conducted mainly in the bulk state or in dilute solution. At times this has led to the viewpoint that these ionic linkages can be sufficiently strong and stable to truly behave like covalently cross-linked rubbers.

In the bulk state the zinc and various other metal-neutralized sulfonated polymers to not exhibit truly viscous flow. From Figure 4 it is now very clear that the zinc sulfonate linkages are not permanent. On the basis of such information, the structure of the zinc sulfonated EPDM only appears to be stable and intact in certain frequency or time domains, which at room temperature are excessive, perhaps more than 10 decades. In a broad sense such ionic linkages can be viewed as conventional polymer entanglements, the differences being that these linkages are more localized and much stronger in nature, a sort of "superentanglement". The ionic charge regions of the zinc sulfo-EPDM polymer create severe local constraints that inhibit the configurational deformations of the polymer chains and increase their slow relaxations tremendously. The distinct peak seen in G'' curve of Figure 4 at low frequencies substantiates the latter statement. The ionic linkages so increase the long relaxation times that they are distinctly separate from the fast relaxation associated with rubber–glass transition.

Viscoelastic Behavior of EPDM Solutions and PIB. Figures 6 and 7 show G' and G'' curves for various solutions of the base EPDM in 100N oil. The dotted curve in both of the figures represents the response of pure PIB (polyisobutylene). In each case all the isothermal data were reduced to the common reference temperature 25° C.

It could be argued that a direct comparison between bulk PIB and EPDM on the time scale at this temperature is not fair because of their differing glass temperatures. The T_g of PIB is about −68 °C, and the T_g of EPDM is around −58 °C. If the difference of 10 °C in the T_g of the two samples is taken into account, the position of the PIB curve will be shifted to higher frequencies by only 0.45 log unit. Differences in the response behavior of the two samples thus just cannot be accounted for by T_g differences.

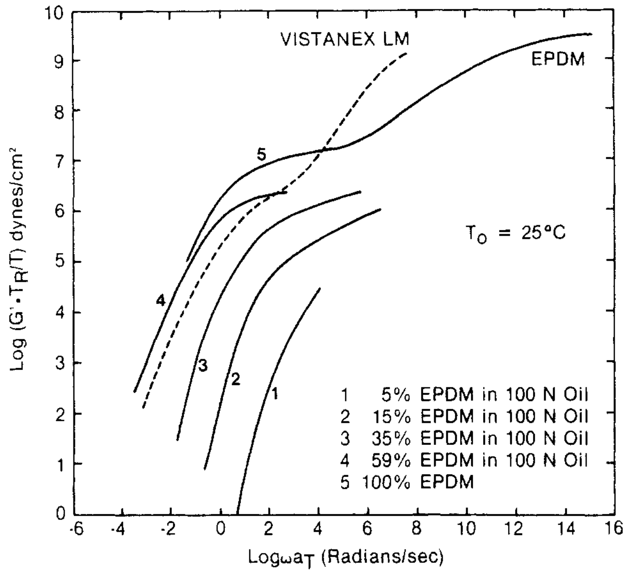

Figure 6. Reduced in-phase modulus $G'(T_r/T)$ (in dyn/cm^2) vs. frequency (in rad/s) of concentration for various EPDM solutions in 100N oil. The dashed line is the corresponding plot of polyisobutylene. Reference temperature 25 °C.

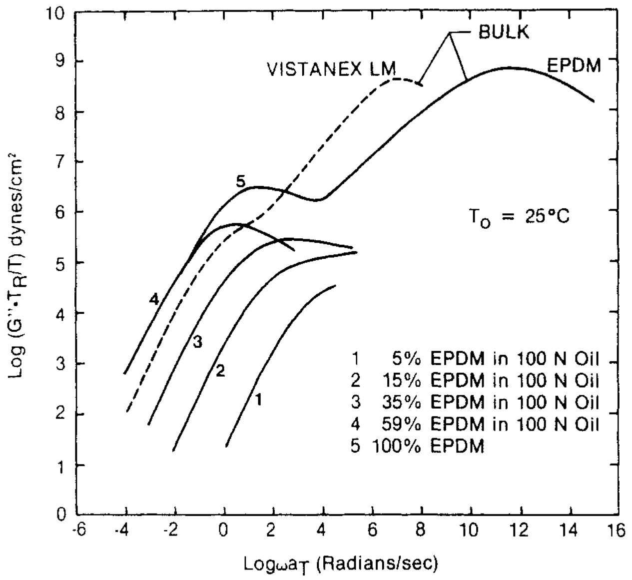

Figure 7. Reduced out-of-phase modulus $G''(T_r/T)$ (in dyn/cm^2) vs. frequency (in rad/s) of concentration for various EPDM solutions in 100N oil. The dashed line is the corresponding plot of polyisobutylene. Reference temperature 25 °C.

The following differences are clear from these figures. The position of the primary transition region of the PIB is shifted by more than 2 decades, reflecting differences in the structure of the two samples. The rate of relaxation in the PIB is faster than EPDM. This is more clearly seen in Figure 8, in which the logarithm of the relaxation distribution $H(\tau)$ is plotted against log time. The relaxation spectra were calculated with Ninomiya and Ferry's equation, using both G' and G'' data:

$$H(\tau)_{\tau=1/\omega} = \frac{G'(a\omega) - G'(\omega/a)}{2 \ln a} - \frac{a^2}{(a^2-1)^2}\,\frac{G'(a^2\omega) - G'(\omega/a^2) - 2G'(a\omega) + 2G'(\omega/a)}{2 \ln a} \tag{9}$$

$$H(\tau)_{\tau=1/\omega} = \frac{2}{\pi}\left[G''(\omega) - \frac{a}{(a^2-1)^2}\{G''(a\omega) + G''(\omega/a) - 2G''(\omega)\}\right] \tag{10}$$

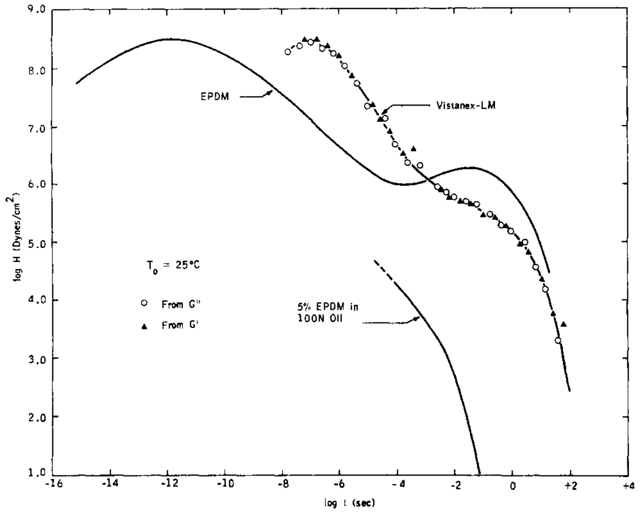

Figure 8. Relaxation modulus H (in dyn/cm^2) vs. time t (in s) for bulk EPDM, 5% EPDM solution, and polyisobutylene.

where a is a constant, equal to 1.58.

The spectra were also calculated with Tschoegl's second-order approximation method[9b] using the following equations.

$$H(\tau) = G'[\mathrm{d}\log G'/\mathrm{d}\log\omega - \tfrac{1}{2}(\mathrm{d}\log G'/\mathrm{d}\log\omega)^2 - (1/4.606)\,\mathrm{d}^2\log G'/\mathrm{d}(\log\omega)^2]|_{1/\omega=\tau/2^{1/2}} \quad (9a)$$

$$H(\tau) = (2/\pi) \times \left[G'' + \frac{4}{3}\,\mathrm{d}G''/\mathrm{d}\ln\omega + \frac{1}{3}\,\mathrm{d}^2G''/\mathrm{d}(\ln\omega)^2\right]\Bigg|_{1/\omega=\tau/5^{1/2}} \quad (10a)$$

A computer program was developed and used for the calculations. Generally satisfactory agreement of $H(\tau)$ between the two methods was found; however, the spectra calculated from the Tschoegl method were smoother than those obtained from the Ninomiya and Ferry method.

The structural differences, as revealed in the position and shape of the primary transition of these samples, were also reflected in their calculated monomeric friction coefficients, ζ, which was calculated by the following modified Rouse theory as discussed by Ferry[1] and coworkers, who have extensively used such analysis in their work:

$$\log \zeta_0 = 2\log H + \log\tau + \log(G/k\tau) + 2\log(\pi M_0/a\rho N_0) \quad (11)$$

where M_0 is the "average" monomer molecular weight, and a is the root-mean-square end-to-end distance per square root number of monomer units. The rest of the terms have their usual meanings.

The ζ_0 values are listed in Table III. At 25 °C, for PIB ζ is $10^{-4.24}$, and for EPDM, ζ is $10^{-6.31}$, a difference of 2 orders of magnitude. The higher value of ζ for PIB has been attributed to the methyl groups steric hindrance of the motion of the polymer chain. Both of these values are in good agreement with those reported by Ferry.[9a] ζ_0 values for other EPDM and zinc sulfo-EPDM solutions are also listed in Table III. In most of the solutions, since the data did not extend near the end of the transition region, reliable values of monomeric function coefficient could not be calculated. (See Figure 9, which shows relaxation spectra for various sulfo-EPDM solutions. The numbers are roughly calculated values and hence are presented in the parentheses. They are presented here for readers who may want to compare these values with those obtained on various other types of gels.[10])

Table III
Monomeric Friction Coefficient of Various Solutions at 25 °C

sample	log ζ_0,[a] (dyn s)/cm
Vistanex LM (PIB)	-4.24
EPDM (bulk)	-6.31
EPDM (15% solution)	(-8.94)
EPDM (35% solution)	(-7.76)
Zn sulfo-EPDM(20) (1% solution)	(-13.30)
Zn sulfo-EPDM(20) (2% solution)	(-12.08)
Zn sulfo-EPDM(20) (5% solution)	(-10.90)
Zn sulfo-EPDM(20) (12.5% solution)	(-8.06)
Zn sulfo-EPDM(10) (5% solution)	(-10.62)
Zn sulfo-EPDM(30) (5% solution)	(-10.20)
Mg sulfo-EPDM(20) (5% solution)	(-10.88)

[a] Using M_0 = 38.0 and a = 5.5 × 10^{-8} cm for EPDMs. Using M_0 = 56 and a = 5.9 × 10^{-8} cm for Vistanex LM (PIB). (See ref 1.)

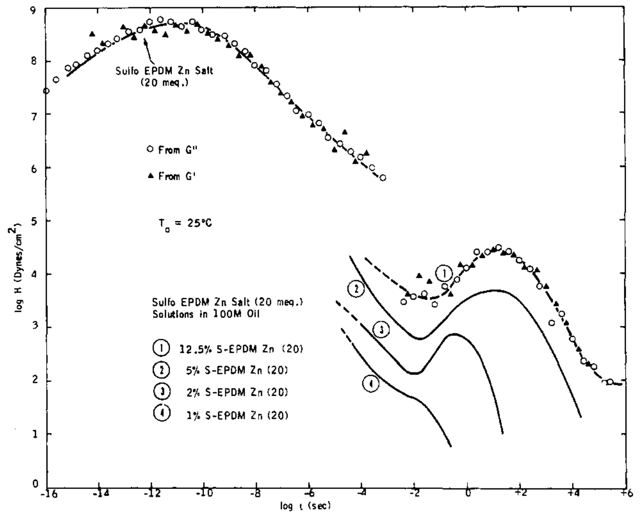

Figure 9. Relaxation modulus H (in dyn/cm^2) vs. time t (in s) as a function of concentration for sulfo-EPDM Zn salt solutions in 100N oil.

In addition to friction coefficient, there are several other differences between PIB and EPDM. One difference between the two samples observed from Figures 6 and 7 is in their rubbery plateau region. In the case of EPDM, a reasonably well-developed rubbery plateau is observed, while in PIB only a shoulder is seen. This is not surprising in view of the fact that the molecular weight between entanglements M_e for PIB[18] is about 8900, while for EP copolymers it is much lower, being about 2000. Another difference is that at low frequencies the G'' curve for EPDM shows a clear peak. Since the M_w of the two polymers is nearly the same, the entanglement network formation in EPDM starts taking place at much lower molecular weights than in PIB. A third difference, seen in Figure 7, is the onset of the viscous-flow region. In PIB it starts at much shorter times than EPDM.

Comparing the behavior of various solutions of EPDMs, an expected strong dependence of G' and G'' on concentration is observed. With increase in concentration the curves shift to lower frequencies, i.e., to longer times, and signs of entanglement formation begin to appear. At concentrations above ~40 wt %, peaks in G'' curves begin to emerge.

Effect of Concentration on G' and G'' of Sulfo-EPDM Zinc Salts. In Figures 10 and 11 the reduced

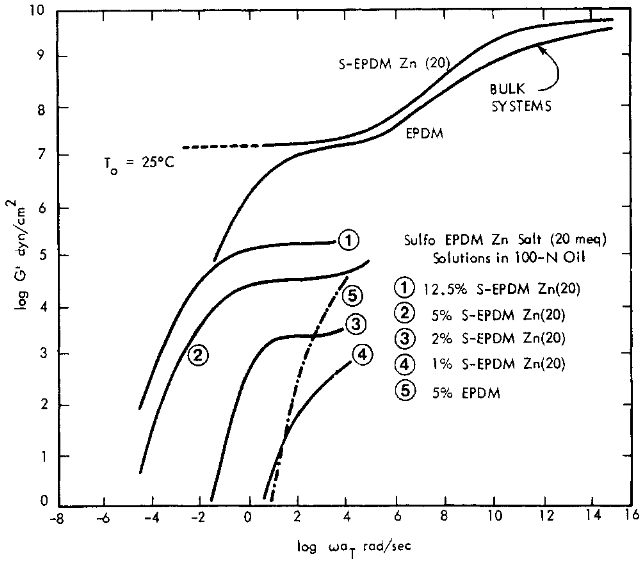

Figure 10. Reduced in-phase modulus G' (in dyn/cm^2) vs. reduced frequency (in rad/s) as a function of concentration for various sulfo-EPDM Zn salt solutions and bulk EPDM. Reference temperature 25 °C.

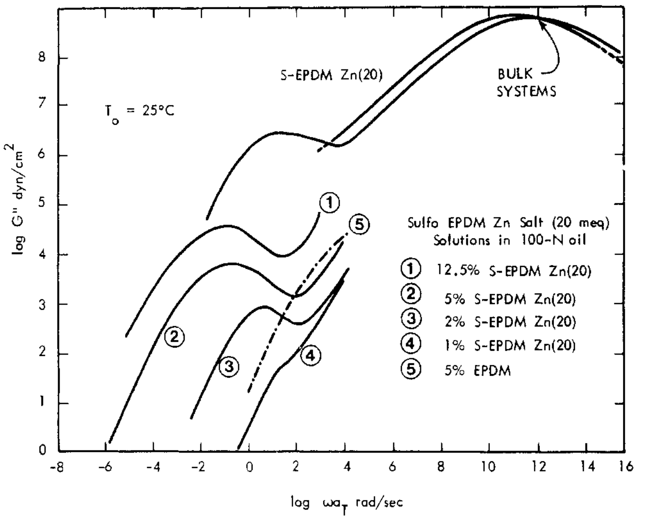

Figure 11. Reduced out-of-phase modulus G'' (in dyn/cm^2) vs. reduced frequency (in rad/s) as a function of concentration for various sulfo-EPDM Zn salt solutions and bulk EPDM. Reference temperature 25 °C.

curves of G' and G'' for various solutions of the zinc sulfonated EPDM(20) are compared to each other and with the reduced curves for the 5 wt % solution of EPDM and bulk EPDM. The reduced curve for the bulk sulfo-EPDM zinc salt sample is also shown in the graphs. The reduction temperature in all the cases is 25 °C. Within the experimental uncertainty in the superposition of such data the temperature dependence of shift factors for G' and G'' were nearly the same. Because of the limited temperature range covered for most of the solutions, a critical test of the temperature dependence of shift factors was not possible. However, as can be seen in Figure 12, both the EPDM and zinc sulfo-EPDM solutions, the shift factors appear to follow a WLF-type behavior, contrary to the expected Arrhenius type.

Several conclusions can be reached from Figures 10 and 11. As expected, an increase in concentration decreases the frequency region for the onset of the terminal zone of response. Above 1 wt % of zinc salt solution, the frequency dependence of both G' and G'' changes significantly. The onset of the entanglement plateau begins to distinctly appear in G'. The width of the rubbery plateau of the 2 wt % solution is roughly equal to the width of that of bulk EPDM. The onset of such well-developed plateaus at 2 wt % polymer, which obviously are reflecting the presence of some sort of entanglement couplings, is unique in our experience. Recent studies made by Riande et al.[11] on a narrowly molecular distributed polystyrene of M_w = 860 000 in tricresyl phosphate indicate that, even in such a high molecular weight polymer, clear rubbery plateaus attributable to entanglements are seen only above ~40 wt % polymer concentration. Because of the extreme dilution, the modulus value of the plateau of the 2 wt % solution is very low, being only ~2.30 × 10^3 dyn/cm^2 as compared with ~1.20 × 10^7 dyn/cm^2 for bulk EPDM. An increase in concentration increases the level of the rubbery plateau.

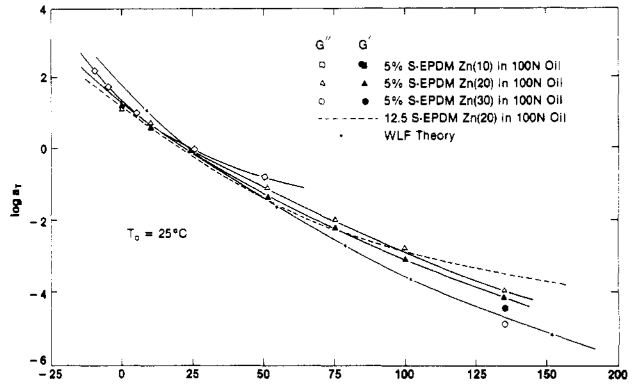

Figure 12. Shift factors vs. temperature (in °C) as a function of G' and G'' for various sulfo-EPDM Zn salt solutions in 100N oil.

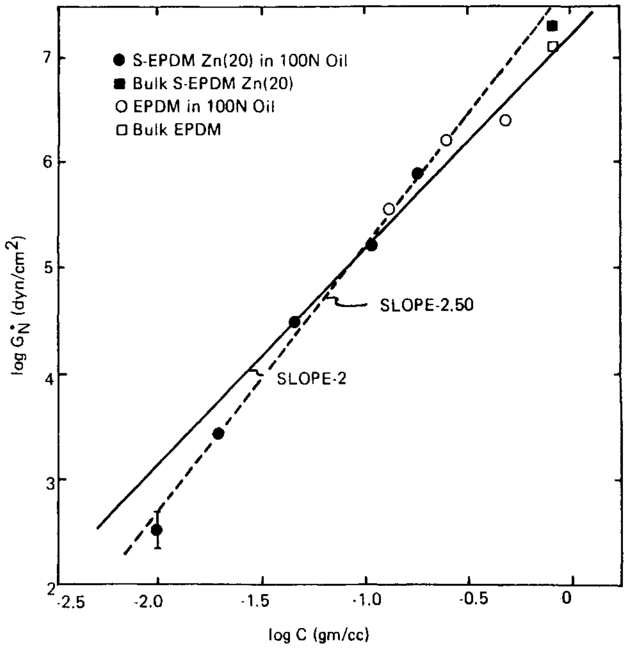

Figure 13. G_N (in dyn/cm^2) vs. concentration (in g/cm^3) for various sulfo-EPDM Zn salt and EPDM solutions.

Effect of Concentration on $G_N{}^0$. The concentration dependence of $G_N{}^0$ for a variety of polymers have been evaluated.[12] In concentrated solutions the plateaus are observed when the molecular weight exceeds some critical molecular weight, $(M_e)_{\text{soln}}$, a characteristic of the polymer.[2] Above this molecular weight the chains are long enough to entangle. Studies on concentrated solutions suggest that $G_N{}^0$ is proportional to C^2. However, de Gennes'[13] recent

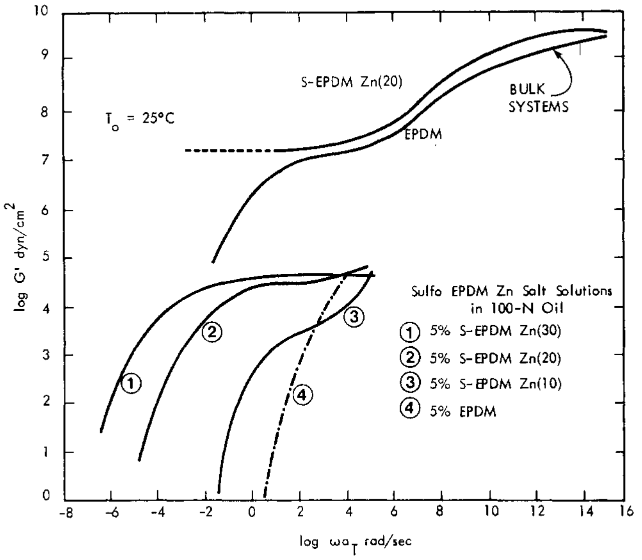

Figure 14. Reduced in-phase modulus G' (in dyn/cm^2) vs. reduced frequency (in rad/s) as a function of sulfonation level for 5% sulfo-EPDM Zn salt solutions in 100N oil and bulk sulfo-EPDM Zn salt and EPDM. Reference temperature 25 °C.

scaling arguments for concentrated systems suggest a somewhat stronger dependence of $G_N{}^0$ on concentration: $G_N{}^0 \propto C^{2.25}$.

In Figure 13 the $G_N{}^0$ data of various 20-mequiv sulfo-EPDM zinc salt on a logarithmic graph are plotted. All the sulfo-EPDM data appear to fall on a line having a slope of 2.45. The points for EPDM solutions follow a line having a slope of ~2.0.

Careful observation will reveal small deviations for some points, especially those for EPDM solutions. In part, this could be due to the errors involved in the calculation of $G_N{}^0$. Solutions of less than about 50 wt % EPDM do not really exhibit entanglement plateaus sufficiently well developed to determine $G_N{}^0$ unambiguously, and the terminal G'' peak is not well enough resolved on the high-frequency side to complete the integration, indicated by eq 8.

In the case of sulfonated-polymer solutions, as seen earlier, excellent peaks and well-developed flat plateaus were observed. In all such cases the value of $G_N{}^0$ was evaluated from both the plateau level of G' and from the integration of the G'' peak, eq 8. Generally the values were found to be in very good agreement with each other. Values of $G_N{}^0$ from both sets are listed in Table IV.

Virtually all the viscoelastic studies of which we are aware concerning concentrated solutions of high molecular weight polymers in which coil overlap occurs, the region where $G_N{}^0 \propto C^b$ is typically limited to ~10 wt % solutions. Thus, on a logarithmic plot only a narrow scale is typically available, which limits the critical testing of the exact dependence of $G_N{}^0$ on concentration.

The interesting point to note from Figure 14 is that in the case of sulfo-EPDM solutions, the b power concentration dependence region of $G_N{}^0$ has been extended to lower concentration by about a decade more than what is observed for any other amorphous polymer system. This suggests that in sulfo-EPDM zinc salt systems extensive coil overlap begins to occur at significantly lower concentrations (~0.5 wt %). Various earlier dilute-soluton studies[19,20] on these systems suggest a similar result. The strong influence of the addition of only about 0.5 mol % zinc sulfonate groups in EPDM, on increasing its effective molecular weight and consequently relaxation times is also very clear. Such systems thus could prove to be useful in testing various theories dealing with the concentration dependence of $G_N{}^0$ and other viscoelastic parameters.

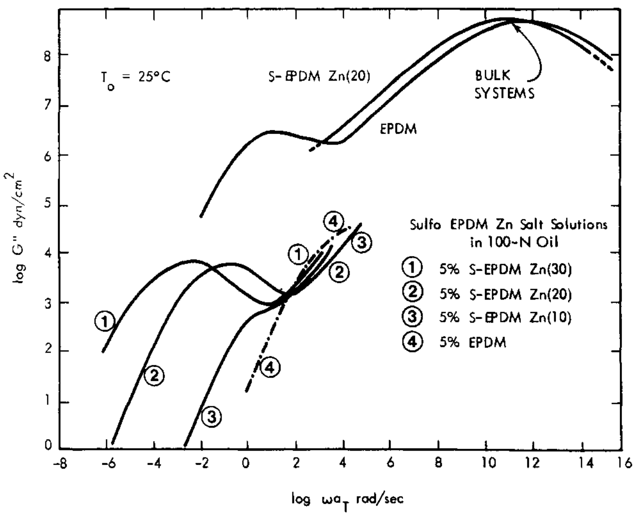

Figure 15. Reduced out-of-phase modulus G'' (in dyn/cm^2) vs. reduced frequency (in rad/s) as a function of sulfonation level for 5% sulfo-EPDM Zn salt solutions in 100N oil and bulk sulfo-EPDM Zn salt and EPDM. Reference temperature 25 °C.

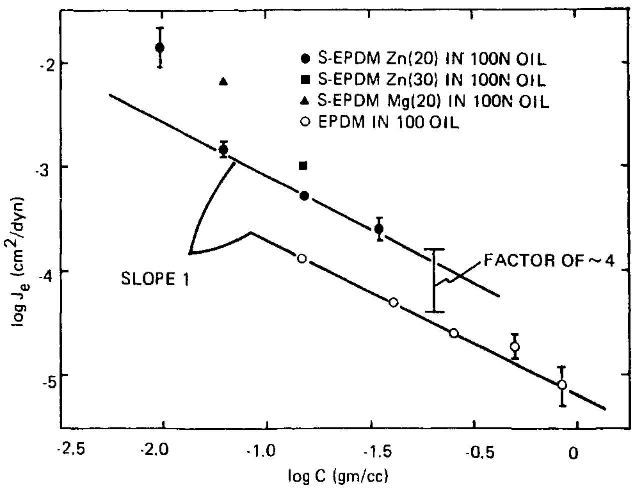

Figure 16. Steady-state compliance J_e (in dyn/cm^2) vs. concentration (in g/cm^3) for various sulfo-EPDM Zn salt and EPDM solutions.

Effect of Sulfonation. The effect of the level of sulfonation on the viscoelastic properties of zinc sulfonated EPDM in dilute solutions is shown in Figures 14 and 15. The data are for 5 wt % EPDM solutions in 100N oil and 5 wt % solutions of various zinc sulfonated EPDMs which vary only in sulfonation level.

Qualitatively, all the effects mentioned in reference to the concentration dependence of the viscoelastic behavior of 20 mequiv zinc salt of sulfo-EPDM polymers apply here as well; cf. Figures 10 and 11 also. Typically at a given concentration, an increase in the sulfonation level (i) decreases the frequency at which the viscous-flow region starts dominating and (ii) increases the width and level of the entanglement plateau. It is interesting to note that at 5 wt % even the sample with the lowest sulfonation level (10 mequiv ~ 0.3 mol %) exhibits a significant degree of association as manifested by a shoulder in its G' curve at ω ~ 10 rad/s and by the associated loss peak seen in the G'' peak. This shoulder is clearly missing in the case of 5 wt % EPDM solution (see dash-and-dot curve of Figure 15).

Concentration Dependence of Steady-State Compliance. In Figure 16 the steady-state compliance $J_e{}^0$ data are plotted against concentration of both EPDM and zinc

Table IV
Characterizing Parameters of Various Solutions

sample no.	log C, (g/cm^3)	log G''(max), dyn/cm^2	log G_N^0, dyn/cm^2	log G_e, dyn/cm^2	log J_e,[b] cm^2/dyn	log J_e,[c] cm^2/dyn
1-0-1 (EPDM)	−2.01					−2.44
1-0-2 (EPDM)	−1.60					−2.74
1-0-3 (EPDM)	−1.33				−3.90	−3.12
1-0-4 (EPDM)	−0.89	5.02[a]	5.54		−4.30	−3.56
1-0-5 (EPDM)	−0.60	5.44	6.18	6.10[a]	−4.55	−3.85
1-0-6 (EPDM)	−0.30	5.71	6.36	6.35	−4.67/−4.80	−4.15
1-0 (EPDM)	−0.07	6.46	7.08	7.10	−4.92/−5.30	−4.38
1-1 Zn sulfo-EPDM(20)	−2.01	2.0[a]	2.36		−1.67/−2.05	−2.44
1-2 Zn sulfo-EPDM(20)	−1.71	2.93	3.44	3.36	−2.76/−2.90	−2.74
1-3 Zn sulfo-EPDM(20)	−1.33	3.82	4.47	4.48	−3.30	−3.12
1-4 Zn sulfo-EPDM(20)	−0.98	4.58	5.20	5.18	−3.50/−3.70	−3.47
1-9 Zn sulfo-EPDM(10)	−1.33	2.83[a]	3.34		−2.84	−3.12
1-3 Zn sulfo-EPDM(20)	−1.33	3.82	4.47	4.48	−3.30	−3.12
1-10 Zn sulfo-EPDM(20)	−1.33	3.89	4.45	4.60	−3.00	−3.12
1-2 Zn sulfo-EPDM(20)	−1.71	2.93	3.44	3.36	2.76/−2.90	−2.74
1-5 Mg sulfo-EPDM(20)	−1.71			3.1	−2.20(?)	−2.74
1-3 Zn sulfo-EPDM(20)	−1.33	3.82	4.47	4.48	−3.30	−3.12
1-5 Mg sulfo-EPDM(20)	−1.33	3.67	4.29	4.33	−3.76	−3.12

[a] Values taken at the inflection point. [b] Numbers from G' and N_1 data. Single value means either both are same or only from one measurement. [c] From Rouse model.

sulfo-EPDM(20) solutions. The J_e^0 values for a higher sulfonation level zinc salt and for the magnesium salt of 20 mequiv sulfonation level are also shown. Most of the J_e^0 data presented in this figure were obtained from both dynamic (G') and normal stress $\sigma_{11} - \sigma_{22}$ measurements, and in most cases the values agreed reasonably well with each other. Various numbers are tabulated in Table IV. The error bars on the figure represent the maximum difference in the value of J_e^0 from the two sets of measurements. Note that sometimes the limiting region of the viscoelastic spectrum of these samples, that is, a slope of 2 in the terminal region of the log G' vs. log ω curve and the slope of 2 in the logarithmic plot of log N_1 vs. log σ, was not quite achieved experimentally. The values in such cases were obtained through reasonable extrapolation of the curve, and there may be some uncertainty in their absolute accuracy. Nevertheless, the J_e^0 values obtained from the two independent sets and types of measurements does provide reasonable confidence.

There were several unexpected results. The J_e^0 data of the EPDM solutions of this figure suggest a much weaker concentration dependence, $J_e^0 \propto C^{-1}$. This is in contrast to most linear amorphous high-polymer systems,[2] which show an inverse square concentration dependence of J_e^0, as well as to studies wherein a higher inverse power of concentration dependence of J_e^0 has been observed.[14] Ignoring the slight scatter at very high concentrations all the samples of the present study appear to follow the J_e^0 concentration relationship as predicted by the normal mode theory of Rouse right up to the undiluted polymer.

All the experimental data and calculated values from the modified Rouse model are listed in Table IV. In a recent study by Raju et al.[12] such J_e^0 dependence on concentration has been reported on narrowly distributed star-branched polybutadiene solutions in a Flexon oil. This solvent is very similar to the 100N oil used in the present studies. Details regarding the degree of branching of the EPDM used by us are not available. Studies are currently under way to characterize systematically the effect of branching on the viscoelastic behavior of EP copolymer systems both in bulk and in solutions and will be published soon.[15] The EPDM used is not believed to be significantly branched; however, owing to the presence of the diene monomer, a slight random branching cannot be ruled out.

Past studies on the concentration dependence of recoverable compliance most often have been done on very narrowly distributed linear polymers. The EPDM used for the present studies has $M_w/M_n \sim 2.1$. It is now well established that in practically all cases an increase in molecular weight distribution increases the long-term retardation mechanism[17] and hence increases J_e substantially. The observed dependence of J_e on concentration in the cited studies thus could be primarily due to the molecular weight distribution of the EPDM used and to a lesser extent due to the branching.

For the zinc sulfo-EPDM solutions, a similar dependence of J_e^0 on concentration ($J_e^0 \propto C^{-1}$) is observed. The data for this system were obtained at lower concentrations for reasons mentioned earlier. Measurements for more concentrated solutions (which actually are strong gels at room temperature) are difficult to obtain. Measurements at very high temperatures at very low frequencies will be required and these are difficult to achieve without sample deterioration.

In the intermediate concentration region it is very clear that J_e^0 values for the sulfonated EPDM solutions are significantly higher than for the EPDM solutions. For the zinc sulfo-EPDM(20) solutions they are higher by approximately a factor of 4. For EPDM solutions below 5 wt % reliable J_e^0 data could not be achieved.

The low-concentration data (cf. Table IV also) of the sulfo-EPDM solutions indicate that, in very dilute solutions, J_e^0 rises steeply and may perhaps go through a maximum. Holms, Ninomiya, and Ferry[17] observed such J_e^0 behavior at very low concentrations during their studies on the solutions of polystyrene (M_w = 267 000) in chlorinated diphenyl solvent. This sort of behavior is analogous to that most often observed in binary blends of two polymers of significantly different molecular weight in which the concentration of the higher molecular weight component is very low. In solution the solvent is the lower molecular weight component. It is possible that we are observing a similar sort of behavior.

In view of various other polymer–solvent systems studied, and from Figure 16, it seems that the whole relationship of J_e^0 and concentration for the present system is somewhat complicated. Nevertheless, it is evident that the metal sulfonate groups do significantly influence the

Table V
Viscosities of Various EPDM and Sulfo-EPDM Zinc Salt Solutions in 100N Oil and at Various Temperatures

EPDM or sulfo-EPDM	T, °C	log η, P
Vistanex LM (PIB)	24.5	6.05
	50.6	5.15
	75.1	4.52
	100.8	3.88
	130.2	3.44
15% EPDM	-10.5	4.80
	10.2	(4.60)
	+0.3	4.27
	9.6	3.97
	25.0	3.23
	50.7	2.57
58.8% EPDM	28.2	(6.38)
	100.7	5.10
	150.1	4.60
5% Zn sulfo-EPDM(30)	135.6	3.44
	160.3	3.23
2% Zn sulfo-EPDM(20)	23.1	3.25
	50.1	2.42
12.5% Zn sulfo-EPDM(20)	75.3	5.74
	100.2	4.95
	135.3	4.12
	160.6	3.98
5% EPDM	-8.5	2.50
	+5.0	2.00
	24.5	1.35
35% EPDM	0.7	5.50
	10.7	5.13
	24.5	4.70
	49.6	4.05
	74.8	3.58
	100.7	3.24
1% EPDM	25.0	0.06
5% Zn sulfo-EPDM(10)	-9.7	5.03
	-5.0	4.64
	+5.0	3.96
	25.4	2.84
	50.8	1.93
1% Zn sulfo-EPDM(20)	-12.7	(3.25)
	-5.5	2.66
	+5.3	1.74
	+22.6	0.85
5% Zn sulfo-EPDM(20)	25.0	5.73
	52.7	5.08
	75.3	4.39
	100.0	3.40
	135.0	2.54
2% Zn sulfo-EPDM(10)	25.0	0.83

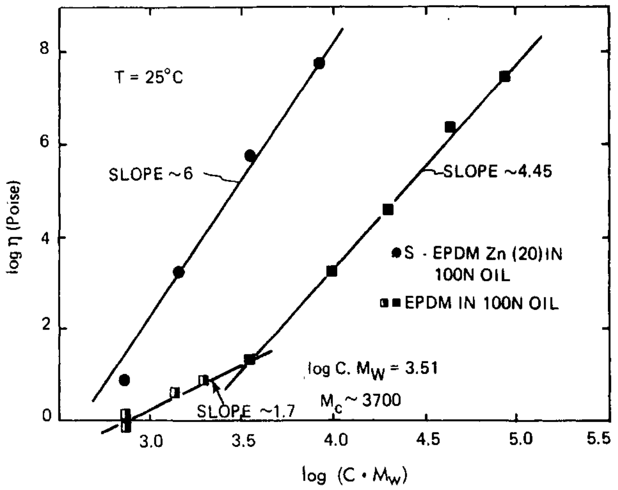

Figure 17. Zero shear viscosity η_0 (in P) vs. concentration for the sulfo-EPDM(20) Zn salt and EPDM system.

steady-state recoverable compliance J_e^0. It appears that these groups promote a highly elastic response and consequently contribute actively to J_e^0.

Concentration Dependence of Viscosity. Figure 17 shows the zero shear viscosity (η_0) data at 25 °C vs. CM_w for solutions of EPDM and zinc sulfo-EPDM(20). The data at various temperatures are listed in Table V. For the EPDM solutions, two regions of molecular weight dependence of η_0 are observed. Below log (CM_w) ~ 3.51, the data fit the line with a slope of 1.7, and above this a much stronger dependence of viscosity on concentration is observed. This dependence is much stronger than that of most of the previous studies of polymer solutions, which yield $\eta_0 \propto M$ below M_c (the critical molecular weight of polymer) and $\eta_0 \propto M^{3.4}$ above M_c.[19] The viscosity values reported in Figure 17 are the isothermal zero-shear-rate viscosities at 25 °C and are not corrected for any changes in their segmental friction factor as a function of concentration.[18] For solutions of this low concentration this did not seem necessary in view of their diluted states and their extremely low (and nearly equal) glass temperatures. Also, since the T_g of the solvent and of the polymer in this system are very similar to each other, all the solutions at 25 °C can be expected to be virtually at iso-free volume state. Thus, we suspected that the correction of the data to a constant friction factor will not significantly affect the slopes of the lines.

From the intersection of the two lines, the characteristic molecular weight, M_c, of EPDM was calculated to be ~3700 (using $c = \rho = 0.86$ and log (CM_w) = 3.51). Interestingly, this value of M_c is similar to that reported by Berry and Fox[18] in their review article for polyethylene. However, recent data of Pearson and Ver Strate[21] taken on various narrowly distributed polyethylene samples suggest this value to be about 5000.

A much stronger dependence of viscosity on concentration for the sulfonated solutions was observed, $\eta_0 \propto (CM)^{6.0}$. At a given concentration the viscosities of the sulfonated solutions were significantly higher than those of the EPDM solutions, and, at any intermediate concentrations from Figure 17, it is clear that the difference in viscosities could be several orders of magnitude. These viscosity data once again demonstrate the dominate role of ionic interactions.

Finally, in Figure 18, the data for the maximum relaxation time as defined by eq 7, are plotted against concentration. For the EPDM system, $\tau_m \propto C^{3.5}$, and for the sulfo-EPDM zinc salt system, $\tau_m \propto C^5$. The concentration regions in which these relationships are followed are different for the two systems. These data are in accord with all the previous observations of the viscoelastic behavior of these polymers. Incorporating the metal sulfonate linkages in EPDM dramatically hinders the slow relaxations associated with the terminal region of the viscoelastic spectrum of the system. In sulfonated EPDM polymers, the rate of increase of such relaxation times is a strong

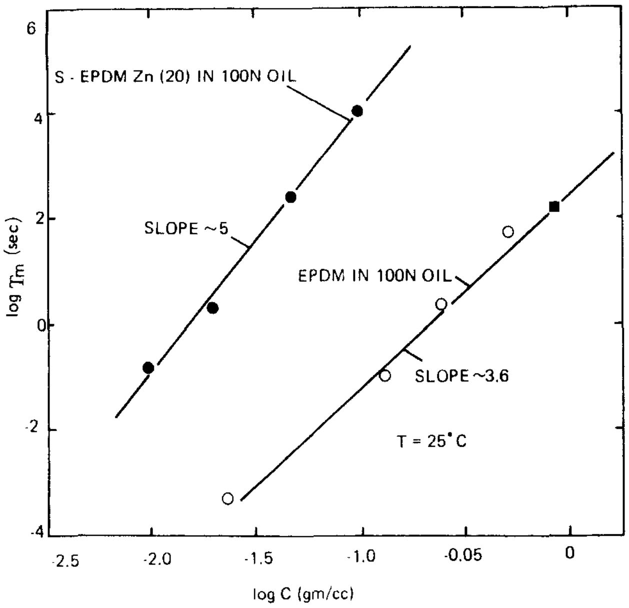

Figure 18. Maximum relaxation time τ_m (in s) vs. concentration (in g/cm^3) at 25 °C for sulfo-EPDM Zn salt and EPDM system.

function of the metal counterion, the concentration, and the degree of sulfonation.

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Viscoelastic Behavior of Concentrated Oil Solutions of Sulfo Polymers. 3. Magnesium and Barium Sulfo-EPDMs

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ABSTRACT: The viscoelastic behavior of concentrated solutions of barium and magnesium sulfo-EPDM has been studied. Unlike the more weakly associating zinc sulfo-EPDM, the barium and magnesium salts exhibit a pronounced rubbery plateau over a wide temperature range (75–160 °C) in which G' is independent of temperature. On the basis of these measurements, it appears that the rate of relaxation is independent of temperature. The usual time–temperature superposition relationships for these samples do not hold. Various interpretations of these unusual phenomena are discussed. It is concluded that for strongly associating ionomers in concentrated solutions a state of transient ion pair aggregate exists. Near ambient conditions at any instance there is a balance of ionic linkages which are continuously forming and dissociating. However, for systems which interact sufficiently strongly, it is feasible for the ionic aggregate to increase in strength or persistence to some degree as temperature increases.

Introduction

Previous papers[1,2] in this series have been concerned with the viscoelastic behavior of ethylene–propylene–ethylidenenorbornene terpolymer (EPDM) and zinc sulfonated EPDM in bulk and when dissolved in paraffinic oils. The viscoelastic behavior of EPDM in oil is unremarkable in that a suitable entanglement plateau is observed for the storage modulus in very concentrated (>50 wt %) solution and in the bulk polymer. However, when diluted to 5 wt % polymer, there is no evidence for an entanglement plateau in G' over the frequency range studied. Sulfonated EPDMs, on the other hand, can display marked evidence of such a plateau at low sulfonate contents (10–30 mequiv/100 g) and even at polymer concentrations as low as 1 or 2 wt % polymer. It is clear that the ion-pair association in these systems manifested at extremely low ionic levels.

The viscoelastic behavior for zinc sulfo-EPDM in oil has been studied in some detail.[2] We have observed a substantial difference in the viscoelastic behavior of bulk sulfo-EPDM that is dependent upon the type of cation used to neutralize the sulfonate.[1] For example, magnesium,