

# Viscoelastic Behavior of Concentrated Oil Solutions of Sulfonated Polymers. V. Effect of Metal Stearate Plasticizers

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## Synopsis

Linear viscoelastic studies of concentrated blend solutions of metal neutralized sulfonated elastomers and low molecular weight metal stearate plasticizers are presented. The data of the magnesium and zinc salts of sulfonated EPDM polymer solutions in 100 N oil solvent as a function of magnesium and zinc stearate polar plasticizers show that addition of the latter species into the ionomeric elastomer solutions enhances their low temperature relaxation spectrum. The changes in properties are directly related to the enhancement of ionic interactions and filler effects of the plasticizers. At high temperatures, the zinc stearate molecules behave more as a conventional plasticizer. For ionomeric associating polymers, the phenomenon appears to be quite general in nature. The enhancement in properties is found to be a function of the counterion structure on the ionomer and stearate. In the case of these solution blends, the studies confirm that an ion-exchange process can occur, especially at high temperatures, resulting in the counterion on the stearate moieties "exchanging" ionic sites on the ionomer. Apparently, this process proceeds quite slowly at low temperatures. However, it is clear from these measurements that the incorporation of metal stearates into the ionomeric solution changes the network structure at both low and high temperatures.

## INTRODUCTION

The incorporation of small amounts of ionic groups ( $< 1.0$  mol %) in poly(ethylene-propylene ethylidene norbornene) (EPDM) has a profound effect on bulk and solution properties.<sup>1,2</sup> Depending upon the level of ionic functionality and type of counterion, the ionic moieties aggregate to various extents which result in the formation of a rather strong network structure in the system. As a result, these materials have unusually high melt strength and viscosities particularly in the metal neutralized sulfonated EPDM products. Even with the use of typical processing additives, these materials are difficult to melt process via conventional processing techniques such as injection molding or extrusion. It was discovered in our laboratory that it is possible to add agents to metal neutralized sulfo-EPDMs which preferentially interact with the ionic groups, and thereby reduce their strength of association and, therefore, their melt viscosities. A large number of compounds which possess some polar functionalities were found to be effective.<sup>3</sup> In the bulk state the only requirement

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for such compounds is that they be nonfugitive under normal processing and use conditions. The saturated fatty acids such as palmitic and stearate acids and their neutralized derivatives were found to be well suited for sulfonated EPDM polymers. These compounds contain polar groups and a number of them are nonvolatile up to 200°C, a temperature suitable for processing. Various metal stearates were evaluated in depth to assess their effect on the processing and mechanical properties of sulfonated polymers. It was found that zinc stearate was the most effective ionic plasticizer. This plasticizer not only improved the processability of the polymer, but it enhances mechanical properties substantially.<sup>3,4</sup> The exact mechanism by which zinc stearate,  $Zn(St)_2$ , functions is still to be fully understood from a molecular point of view. However, qualitative models have been presented earlier on the basis of bulk viscoelastic and X-ray scattering studies<sup>1,3</sup> in order to rationalize these results.

Other metal stearates, such as magnesium, barium, and ammonium, etc., showed modest effects, if at all, on the flow properties of sulfo-EPDM polymers. The zinc stearate has been found to be effective for all the metal neutralized EPDMs irrespective of the type of counterion. However, its most remarkable effect was observed with zinc sulfo-EPDM polymer. Initially it was contemplated that zinc stearate perhaps associates with zinc sulfonate groups. At higher temperatures the zinc stearate melts and breaks the ionic associates and thus promotes flow of the polymer. If this simple hypothesis were true, one might expect that other metal stearates such as magnesium and barium stearate should also be effective plasticizers for the magnesium and barium neutralized sulfo polymers, respectively. However, contrary to expectations, it was found that these stearates had only mildly beneficial effects on the flow properties. Such entirely differing plasticization effects of various metal stearates on sulfonated polymers have been puzzling so far, especially in view of the properties of these stearates. Obviously, conventional free volume and simple polar plasticizer concepts cannot be applied to these ionomers system unilaterally. One explanation for this behavior could be the different melting points for the various metal stearates. For example, the melting temperatures of magnesium stearate is about 60°C higher than zinc stearate which melts at about 128°C. Typically, the carboxylate salts of Mg and Ba are higher melting than is the case for zinc. For example, the melting points for zinc laurate and stearate are reported to be 128 and 130°C, respectively, while the magnesium salts are 150 and 186–188°C, respectively. Nevertheless, it might be expected that other metal carboxylates should also be effective plasticizers, albeit at somewhat higher processing temperatures than those expected for the zinc salts.

In this paper, we attempt to rationalize the behavior of zinc and magnesium stearate on two sulfo ionomers, specifically the zinc and magnesium salts of sulfo-EPDM via viscoelastic studies. In the past, distinctions among these two ionomers in their dilute state had proven to be more beneficial and revealing over the bulk property measurements. Here, we report various isothermal linear viscoelastic measurements of solutions of magnesium and zinc sulfo-EPDMs in a nonpolar, nonvolatile solvent as a function of concentration of these two plasticizers. Clear distinctions in the terminal spectra of these systems were found, demonstrating significant differences in the behavior of magnesium and zinc stearate-ionomer blends. Based on these studies, it is concluded that zinc stearate preferentially interacts with metal-sulfonate groups and counterion

exchange occurs if other than zinc is present in the ionomer. It is primarily due to this exchange reaction mechanism occurring at higher temperatures that significant flow modification is promoted in the various metal neutralized sulfonated elastomeric polymers.

### EXPERIMENTAL

The sulfonation chemistry of the EPDM polymer has been discussed in previous publications.<sup>1</sup> Zinc and magnesium salts were prepared from the same precursor EPDM and its acid form having a sulfonation level of about 20 meq. Excess neutralizing agents (zinc and magnesium acetate) were used in order to assure the complete neutralization of the product. The number average molecular weight of the EPDM was about 40,000 and  $M_w/M_n \sim 2.1$ . The ethylene and ENB content of this elastomeric polymers were 55 and 5% by weight, respectively. On a molar basis, 20 meq sulfonation level corresponds to about 0.7 mol %, i.e., each sulfonate group is approximately 140 monomer units apart.

The zinc and magnesium stearate were of technical grades obtained from Aldrich Chemicals. All the solutions were made in 100 *N* oil solvent. The 100 *N* oil is a paraffinic petroleum hydrocarbon fraction of molecular weight of about 200 g mol<sup>-1</sup>. Its glass temperature is below -85°C and room temperature viscosity is about 40 cP. The composition of blends of zinc and magnesium sulfo-EPDM and stearate plasticizers are shown in Table I. The solutions were made with desired amounts of materials in covered glass beakers using a conventional magnetic stirrer. The dissolution of the polymer was facilitated at times by mild heating ( $\sim 50^\circ\text{C}$ ), and it took several weeks before satisfactory

TABLE I  
Composition of Blends of S-EPDM and Plasticizer in 100 *N* Oil

S-EPDM (20 meq) counterion	S-EPDM (20 meq) weight (g)	Plasticizer		Oil (g)
		Zn(St) <sub>2</sub>	Mg(St) <sub>2</sub>	
Zn	5.0			100
Zn	5.0	0.5		100
Zn	5.0	1.0		100
Zn	5.0	2.0		100
Zn	5.0	5.0		100
Zn	2.5	7.5		50
Mg	2.5			50
Mg	5.0		0.5	100
Mg	5.0		1.0	100
Mg	5.0		2.0	100
Mg	5.0		5.0	100
Mg	2.5		7.5	50
Mg	0.5	0.5		50
Mg	5.0	0.5		100
Mg	5.0	2.0		100
Mg	5.0	5.0		100
Mg	2.5	7.5		50

homogeneous solutions were obtained. At the end of this procedure all the samples had a gel-like consistency.

Linear viscoelastic measurements were made on a Rheometrics mechanical spectrometer. Various isothermal dynamic moduli data  $G'$  and  $G''$ , from 25 to 75°C, were collected as a function of frequency in the range of  $2 \times 10^{-3}$  to 20 Hz. As previously observed with such ionomers, these blend samples were found to be sensitive to strain and time histories. Hence, once the range of linearity of a given sample was established, each sample was allowed to equilibrate for a sufficient period of time before the start of the run. Data at different temperatures were taken on fresh samples.

## RESULTS AND DISCUSSION

Typical dynamic moduli obtained on these solutions are shown in Figures 1 and 2. Here, the in-phase modulus  $G'$  and out-of-phase modulus  $G''$  data at two temperatures, 25 and 75°C, for the 5 wt % solutions of sulfonated EPDM zinc salt having a sulfonation level of 20 meq ( $\sim 0.7$  mol %) in 100 *N* oil solvent and its solutions with various levels of zinc stearate are presented.

Various interesting features of the mechanical response of these solutions are readily apparent from the shape and position of the curves in Figures 1 and 2. Previous extensive viscoelastic measurements on the unblended metal neutralized EPDMs clearly showed that these polymers are highly physically associated and possess significantly different properties than the nonionic parent material.<sup>1,5,6</sup> It was observed that in the bulk state such polymers did not exhibit any experimentally discernible viscoelastic relaxations other than corresponding to configurational rearrangements associated with a glass-to-rubber transition. However, various viscoelastic relaxations were clearly observed in their diluted state.<sup>5,6</sup> Broadly speaking, grossly similar observations are noted in some of the present blend solutions. At low temperatures,  $G'$  measurements of both

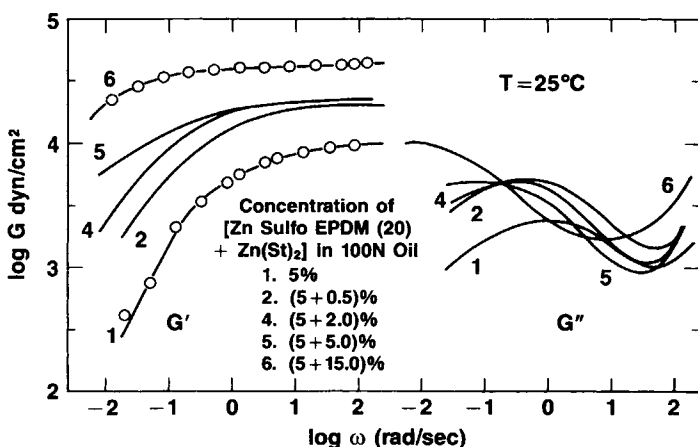


Fig. 1. Plots of moduli  $G'$  (in-phase) and  $G''$  (out-of-phase) vs. frequency as a function of wt % zinc stearate for the 5% zinc sulfo-EPDM solution in 100 *N* oil. Measurement temperature is 25°C and sulfonation level is 20 meq.

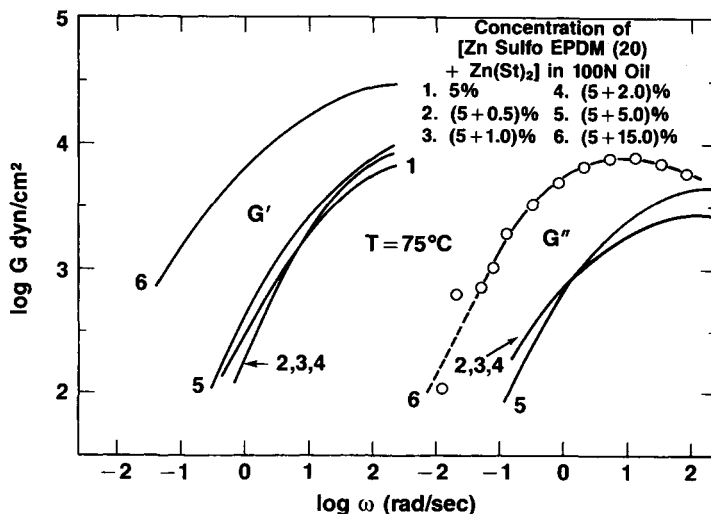


Fig. 2. Logarithmic plots of in-phase ( $G'$ ) and out-of-phase ( $G''$ ) moduli (at 75°C) vs. frequency of various blends of zinc sulfo-EPDM (20 meq) and zinc stearate in 100 N oil.

zinc and magnesium salts of sulfo-EPDMs and their blends with zinc stearate exhibit rubbery plateau (see Figs. 3 and 4 also).

At similar concentrations of the zinc stearate plasticizer, zinc and magnesium solutions differ in a noteworthy manner. In the case of the zinc-sulfo-EPDM system, an increase in the zinc level stearate increases the in-phase modulus and shifts the flow regime to lower frequencies. It has been known to us<sup>1</sup> for some time that zinc stearate not only preferentially interacts with zinc sulfonate groups but acts as a reinforcing filler if present in excess. The enhancement in the plateau modulus reflects the filler action of the plasticizer while the shift on the time scale reflects the strengthening of the associating groups. (All of these blend systems are on a stoichiometric basis containing excess zinc stearate plasticizer.) For a sulfonation level of about 0.7 mol %, only about 0.3 g of the

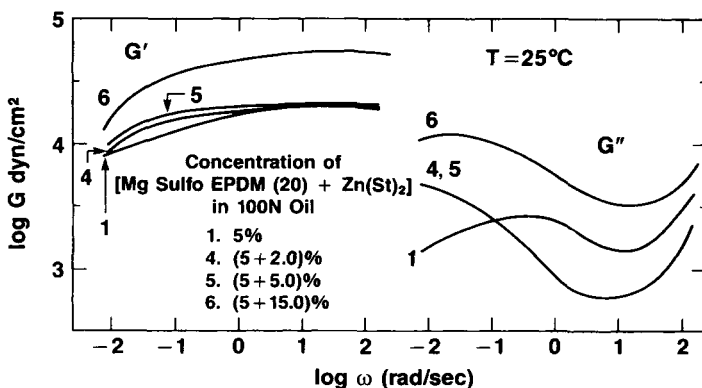


Fig. 3. Logarithmic plots of in-phase ( $G'$ ) and out-of-phase ( $G''$ ) moduli (at 25°C) vs. frequency of magnesium sulfo-EPDM (20 meq) solutions in 100 N oil containing various levels of zinc stearate.

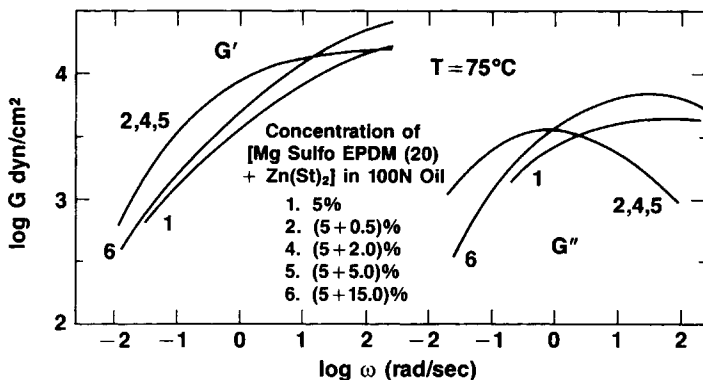


Fig. 4. Plots of moduli  $G'$  (in-phase) and  $G''$  (out-of-phase) vs. frequency as a function of wt % zinc stearate for the 5% magnesium sulfo-EPDM (20 meq) solution in 100 *N* oil. Measurement temperature is 75°C.

plasticizer is required to fully associate with zinc sulfonate groups of EPDM chains diluted to 5 wt % concentration.) An interesting point to note is that there is a nonlinear increase in the rubbery plateau with increasing levels of zinc stearate. In fact, the data do not permit any further analysis. Attempts to fit the rubbery modulus data (appearing in Table II) of all the blend solutions by conventional Guth–Gold and Kerner type relations<sup>7</sup> failed. The nonlinear enhancement is obviously in part due to the strong interaction between components—polymer and stearate plasticizers. Curve 6 of Figure 1 and curves 4–6 of Figure 3, reflect the formation of polymer metal salt–stearate complex in the system. The nature of the relaxation process with respect to polymer struc-

TABLE II  
Composition and Characterization Parameters of Blends of 5% Sulfonated EPDM Polymers (Sulfonation Level 20 meq) Solutions<sup>a</sup> and Metal Stearate Plasticizers

Counterion	Plasticizer type	Plasticizer amt <sup>a</sup>	Polymer wt. fraction, $W_p$	Plasticizer wt. fraction, $W_f$	Polymer vol. fraction, $V_p$	Plasticizer vol. fraction, $V_f$	Log $G'$ (dyn/cm <sup>2</sup> ) at $\omega = 10$ rad/s		Log $G''$ (dyn/cm <sup>2</sup> ) (°C)
							25°C	75°C	
Zinc	$Zn(St)_2$	0.0	0.048	0.000	0.059	0.000	3.99	3.79	3.40 (75)
		0.5	0.047	0.005	0.059	0.004	4.30	3.92	3.70 (25)
		1.0	0.047	0.009	0.059	0.008	4.25	3.89	3.67 (25)
		2.0	0.047	0.019	0.058	0.012	4.33	3.88	3.75 (25)
		5.0	0.045	0.045	0.056	0.042	4.44	3.92	3.77 (25)
		15.0	0.042	0.125	0.052	0.115	4.62	4.45	4.00 (25)
Magnesium	$Zn(St)_2$	0.5	0.047	0.005	0.059	0.004	4.20	4.14	3.70 (25)
		1.0	0.047	0.009	0.059	0.009	4.20	3.98	3.62 (25)
		2.0	0.047	0.019	0.058	0.017	4.27	4.19	3.72 (25)
		5.0	0.045	0.045	0.056	0.042	4.31	4.20	3.67 (25)
		15.0	0.042	0.125	0.052	0.115	4.71	4.36	4.08 (25)
		$Mg(St)_2$	15.0	0.042	0.125	0.052	0.121	4.61	4.51

<sup>a</sup> Amount in grams in 100 g of 100 *N* oil solvent.

ture are not clear, however, due to the crystalline nature of the stearates at and near room temperature in these dilute solutions.

Our previous semidilute and concentrated solution studies had demonstrated significant differences in the zinc and magnesium salts of sulfonated EPDM systems.<sup>5</sup> Comparing the data of Figures 1 and 3, it is interesting to note the effect of zinc stearate on these two systems. At low concentrations of zinc stearate, the effects on the viscoelastic spectrum of magnesium ionomer system are modest as compared to the zinc system. During preparation of these solutions, precaution was taken not to expose them above 50°C, well below the melting temperature of zinc stearate, in order to avoid any substantial interaction. However, it appears that zinc stearate has an affinity for magnesium sulfonate groups even at ambient conditions. Careful observation of the various curves of Figure 3 indicate that the addition of small amounts of zinc stearate in the magnesium system makes for a relatively more stable network system and promotes a faster onset of viscous flow regime—note the flatness of curves 4 and 5 and their low frequency dip versus that of curve 1, Figure 3. In the case of the zinc system, Figure 1, curves 2–5, shifts in the curves are noted both on the frequency and modulus scale. Just from these low temperature curves, in a general sense, it could be concluded that the rate of molecular relaxations is significantly decreased. At higher loading of the zinc stearate, curve 6 of Figures 1 and 3, the plateau modulus of both systems increases significantly, clearly acting as a reinforcing filler.

Another important feature to note is the influence of zinc stearate on the two systems at higher temperatures. Dynamic viscoelastic data were obtained at various temperatures, representative data taken at 75°C for the zinc and magnesium sulfo-EPDM solutions are shown in Figures 2 and 4, respectively. It can be readily observed that at all zinc stearate concentrations for both systems, the modulus drops precipitously and, in fact, very rapidly approaches the flow region. Either the plasticizer has virtually eliminated the metal sulfonate associations or simply the ionic domains are more liquidlike and an ion exchange type mechanism is enhanced, permitting a more facile flow of the polymer molecules. The evidence for flow is exhibited by the near Newtonian viscous flow response in the low frequency region of  $G''$  curves. It should also be noted that this low to high temperature is reversible behavior in a qualitative sense.

These observations in some aspects parallel other studies on the addition of zinc stearate to bulk sulfonated elastomers.<sup>5,6</sup> These ion containing polymers, as noted previously, strongly associate through multiplet or clustering of the ionic moieties. It was found that a crystalline nonfugitive additive, such as zinc stearate, can strongly affect the material properties in addition to being a highly compatible ionic plasticizer. These type of plasticizers selectively interact with the ionic domains as opposed to the more conventional plasticizers, which lower  $T_g$  and viscosity by increasing the free volume of the polymer. This occurs since these plasticizers effectively and selectively solvate the chain backbone. The selective interaction of stearate with the ionic domains permits the complete destruction or significant weakening of the network at melt processing temperatures, i.e., temperatures such as observed at 75°C or higher. However, zinc stearate is highly crystalline and as such can reinforce the ionomer through both reestablishment of the network structure and microphase separation into

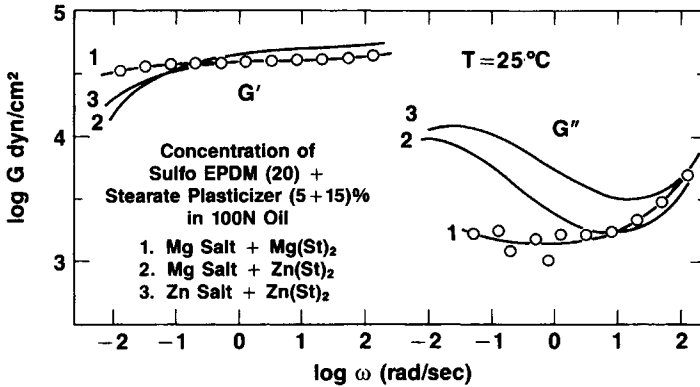


Fig. 5. Logarithmic plots of in-phase ( $G'$ ) and out-of-phase ( $G''$ ) moduli (at  $25^\circ\text{C}$ ) vs. frequency of various blends of 5 wt % magnesium and zinc neutralized sulfo-EPDM (20 meq) with 15 wt % magnesium and zinc stearate in 100 N oil.

a reinforcing filler even at  $75^\circ\text{C}$ , as can be observed in the case of zinc system—curve 6, Figure 2. The effects, however, become pronounced with modification of the counterion on either the ionomer and/or stearate. The results presented in Figures 4, 5, and 6 for the magnesium system demonstrates this clearly.

First, as can be noted from Figure 4, only modest increase in the modulus levels occur with relatively large increases in the stearate level as opposed to the zinc system mentioned above. In fact, to a good approximation, the modulus remains invariant. The  $G''$  curves indicate rapid molecular relaxation processes that are changing in accordance with  $G'$  curves. With regard to these observations, it appears that due to the very stable network structure, the filler effect has only a modest influence on mechanical properties and the rate of the relaxation process is nearly independent of zinc stearate level.

Second and perhaps the most important feature to note from the curves of Figure 4 is that at low frequencies they all clearly indicate viscous flow regime.

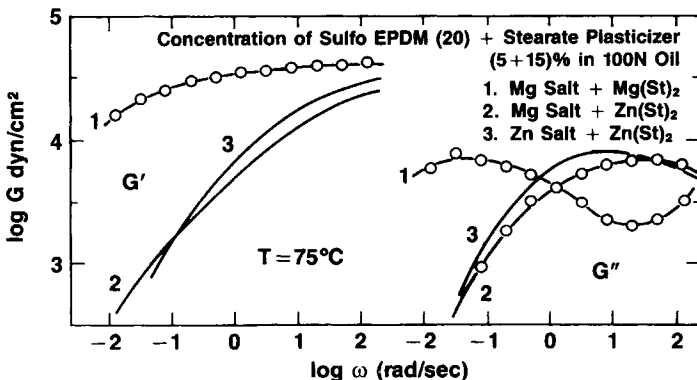


Fig. 6. Logarithmic plots of in-phase ( $G'$ ) and out-of-phase ( $G''$ ) moduli (at  $75^\circ\text{C}$ ) vs. frequency of various blends of 5 wt % magnesium and zinc neutralized sulfo-EPDM (20 meq) with 15 wt % magnesium and zinc stearate in 100 N oil.



This is in complete contrast with the previous measurements<sup>5</sup> on the magnesium neutralized EPDM solution behavior. These measurements demonstrated no viscous flow in these systems and, in fact, the structure of the magnesium system was found invariant up to 160°C acting grossly similar to covalently swollen crosslinked systems. The zinc solution behaves more like that of an excessively high molecular weight amorphous polymer. The data of Figure 4 indicate that magnesium salt when plasticized with zinc stearate either: (a) is no longer a magnesium salt because of conversion to a zinc ionomer, or (b) although less likely, all the magnesium-sulfonate crosslinks have been totally dissociated by the zinc stearate plasticizer. If the former is true the deformation in the magnesium system is due to the exchange of ionic linkages which are continuously forming and dissociating at lower rates.

In order to determine whether ion exchange has taken place, the polymer from the zinc stearate plasticized magnesium solution was recovered for analysis. Although the recovery of typical polymers from their solutions is a straightforward easy route and routinely done in polymer laboratories, however, it turned out that the recovery of these associating polymers was tedious and time consuming. The (strongly gelled) oil solutions were slowly dissolved with incremental increase in the solvent level (toluene/methanol, 95/5 by vol) over weeks with constant stirring. Occasionally during this period, stirring was stopped for the excess zinc and (*in situ* formed) magnesium stearates particles to settle down. They were removed by decanting the supernatant fluid. The oily portion of the solution was removed as well, by a simple blotting technique at this stage. This procedure was continued until a clear polymer solution was obtained. The final product was obtained by precipitating the polymer with excess methanol and drying it. The overall process took about 5 months. Subsequently, elemental analysis for the zinc and magnesium concentrations on the recovered sample was done to compare with the original magnesium sulfo-EPDM sample. The data are shown in Table III. The concentration of the zinc in the recovered polymer is 200 times than that of magnesium, confirming that ion exchange of the counterions occurred between the zinc stearate plasticizer and magnesium sulfonate moieties of the magnesium salt of sulfonated EPDM. Since the concentration of zinc counterions in these instances were clearly in larger numbers, the presence of relatively small number of Mg counterions in

TABLE III  
Quantitative Elemental Analysis of Various Sulfonated EPDM Polymers

Polymer	Amount of the material used for analysis	Relative amounts of elements	
		Zinc	Magnesium
Base EPDM	3.91 g	1.45	10.20
Zinc stearate	0.02 g	11.10	< 0.01
Sulfo-EPDM Mg salt	2.78 g	40.80	4000.00
Sulfo-EPDM Mg salt [Recovered sample— after solution blended with Zn(St) <sub>2</sub> ]	0.11 g	10.40	0.06

the zinc stearate plasticized magnesium system did not noticeably influence the ionomer properties.

Figure 5 shows a typical series of dynamic moduli at 25°C of the blending of both zinc and magnesium stearates with zinc and magnesium sulfo-EPDM. It is apparent that the modulus of all blends are fairly similar to each other. Curves 2 and 3 clearly indicate this behavior. This leads to the conclusion that very little, if any, ion exchange of the counterions take place at low temperatures (25°C). In a broad sense, these data confirm the trends noted previously. As perhaps could have been expected from magnesium sulfo polymer behavior, the addition of magnesium stearate plasticizer results in a much tighter network, see curve 1. The  $G''$  behavior demonstrates this more clearly. The relaxation spectrum of the magnesium stearate plasticized magnesium sulfo polymer is broad and sluggish, indicating rather long relaxations of the system.

The behavior, however, of each blend can be easily distinguished at high temperatures as shown in Figure 6. In the Figure,  $G'$ , curves 2 and 3, are approximately superimposable due to the addition of the large amount of zinc stearate. The initial Mg sulfo-EPDM now behaves as a zinc salt and these properties do not revert back to its initial behavior even at 25°C. The  $G''$  values also confirm that the molecular relaxations of these two blends are approximately the same. Small differences in the two samples, as observed from the position of curves 2 and 3, are believed to be due to various impurities such as the presence of the released magnesium ions/stearate in blend number 2 and inherent impurities during the neutralization and recovery process of original zinc and magnesium sulfo EPDM polymers. Finally, to keep in perspective the effects of polar plasticizers, it is worth noting the effect of magnesium stearate plasticizer on the magnesium solution, curve 1 of Figure 6. The magnesium stearate even at 75°C acts more like a filler. Although  $G''$  curve indicates relaxations, flow is not observed in the system. Obviously the solubility of the magnesium stearate in the magnesium salt of sulfo-EPDM is significantly less than that of zinc stearate in the latter.

## CONCLUSION

The viscoelastic properties of solution blends of metal neutralized sulfonated elastomer with varying levels of metal stearates were examined. It was found that an enhancement in properties occurs with an increasing level of stearate at low temperatures. This is primarily due to a marked "filler" effect since these stearates are highly crystalline in nature and can interact with the microphase separated ionomeric rich regions within the polymer structure. In general, the ionomer chains have reduced mobility as the stearate level is increased and, in addition, substantial changes in the relaxation behavior are observed. An increase in the associative effects as reflected in an enhanced rubbery plateau is found. However, at high temperatures, the viscoelastic properties are decreased due to the plasticizer effect of the metal stearates particularly that of zinc stearate. Superimposed on this behavior is the discovery of the ability of the counterion on both species of these solution blends to rapidly exchange at elevated temperatures and promote flow in sulfonated EPDM polymers if the counterion other than zinc is present. That the metal stearates

“control” behavior in these blends is simply due to their large percentage in the blend compositions. As a result, the viscoelastic properties of these solution blends can be controlled over a broad range of conditions with only modest changes in temperature, mixture composition, and the nature of the counterions on both components of the blend.

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