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Viscoelastic Behavior of Concentrated Oil Solutions of Sulfo Polymers. 4. Magnesium Sulfo-EPDMs in Mixed Solvents

Pawan K. Agarwal,* Richard T. Garner, and Robert D. Lundberg

Exxon Research and Engineering Company, Corporate Research Science Laboratories, Annandale, New Jersey 08801. *Received June 29, 1983*

ABSTRACT: Concentrated solutions of magnesium sulfonated EPDMs in mixed solvents composed of paraffinic oils and alcohols have been characterized with respect to their viscoelastic behavior. It has been observed that the in-phase modulus is a strong function of time, especially in the low-frequency regime. The in-phase modulus increases substantially with time (at 23 °C), suggesting the formation of a progressively stronger network structure. Typically these systems require more than 10^4 s for an equilibrated system to form from which reproducible viscoelastic data can be obtained. Similar viscoelastic measurements were made at elevated temperatures, up to 75 °C. Aging behavior analogous to that at 23 °C was observed. In addition, it was observed that the in-phase modulus at low frequencies increased by a factor of 5 for a temperature change from 23 °C to 75 °C. This unusual increase in G' with increasing temperature is interpreted as an increase in the effective cross-link density at higher temperature due to changes in an equilibrium between the metal sulfonate groups and the alcohol cosolvent. These results demonstrate that, due to the exceptionally long relaxation times of these ionomer solutions, attempts to characterize such systems may be fruitless unless the systems are equilibrated either at high temperatures or after long periods of aging. The results at high temperatures demonstrate that the in-phase modulus of such systems can increase with temperature, in analogy with the viscosity behavior of such ionomer solutions. These results are all consistent with a more effective (stronger) ionic network occurring at high temperature or after longer aging times.

Introduction

In previous papers in this series[1-3] we have reported various aspects of the viscoelastic behavior of bulk EPDM and concentrated solutions of sulfonated EPDMs in a hydrocarbon solvent. When relevant, comparisons were made with the corresponding unfunctionalized base EPDM and with other high molecular weight polymers. These studies have shown that the viscoelastic behavior of the functionalized EPDM (ethylene–propylene–diene terpolymer) is a strong function of various variables: concentration, time, temperature, counterion, etc.

Among these variables the most remarkable effect is that of the counterion. We have observed that certain cations, e.g., magnesium and barium, have much stronger associating natures than others, e.g., zinc and ammonium. The outstanding associating nature of magnesium and barium is reflected in their sulfo-EPDM salts when dissolved in suitable nonpolar hydrocarbon solvents. These solutions, instead of forming a fluid having Newtonian characteristics (in certain limiting conditions), tend to form strong gels. Various measurements on as low a concentration as about 5 wt % sulfo-EPDM Mg salt (10 mequiv) in 100N[16] oil, up to greater than 250 °C above its glass transition, failed to exhibit any signs of viscous deformations. Some of these systems appear to form gels even at concentrations of about 1 wt %.

Theoretical studies of the process of gel formation of such ionomers have recently been attempted by Joanny[11] and Gonzalez.[12,13] Gonzalez,[13] following de Gennes'[14] ideas of the reptation of a chain in a permanently cross-linked gel and computations of the stress relaxation tensor of Doi and Edwards,[15] has derived viscoelastic functions of such ionomer gels which are qualitatively in agreement with the experiments.[2,3]

Among the strongly associative systems of the sulfonated polymer family, we have studied the magnesium salt of sulfo-EPDM in some detail and have observed various intriguing aspects of this material. Its high-temperature viscoelastic behavior appears to be unprecedented, having, to our knowledge, never been reported in the literature.[3] The gelation of sulfonated polymers generally appears to be a function of solvent, time, and temperature, and some aspects of these materials as a function of these variables are the subject of this paper.

Recently, Lundberg[4,5] characterized the dilute solution behavior of various kinds of metal sulfonated polymers. He observed that in mixed solvents the physical behavior of metal-neutralized sulfonated polymers is different from that of typical nonpolar polymers. His studies indicate that even strong physically associating systems, e.g., Mg salt of sulfo-EPDM in mixed-solvent systems, (apparently) form homogeneous solutions of low viscosities instead of forming gels of infinite viscosity. The viscosities of these solutions in mixed solvents, most often a hydrocarbon and an alcohol, are a strong function of concentration and the composition of the solvent mixture. It is interesting to observe the profound effects of small amounts of alcohols on the associations in these systems. The temperature–viscosity relationship of these systems is unusual[4] in that viscosities can increase substantially as temperature increases.

In this paper we report the viscoelastic behavior of sulfo-EPDM Mg salt (20 mequiv) in a mixed-solvent system.

Experimental Section

Solutions of magnesium sulfo-EPDM (20 mequiv)[10] at two concentration levels, 2.0 and 2.5 wt %, in 100N oil/hexanol[16] (98.5/1.5 by volume) were prepared. The magnesium sulfo-EPDM

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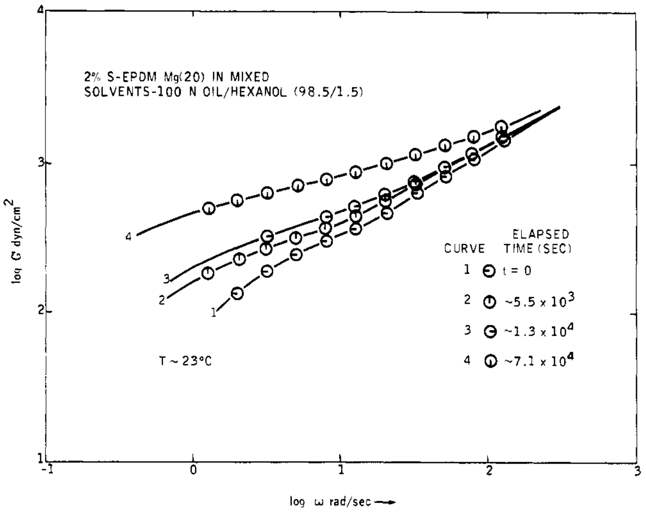

Figure 1. Plot of in-phase modulus G' (dyn/cm^2) vs. frequency (rad/s) as a function of time for 2 wt % sulfo-EPDM Mg salt solution in mixed solvents at 23 °C.

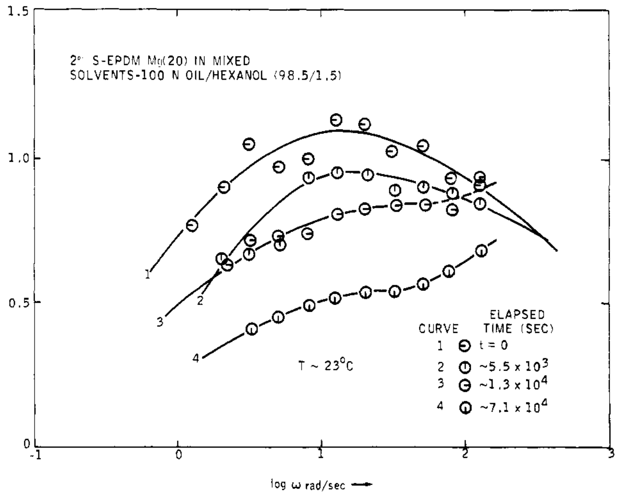

Figure 2. Plot of tan δ vs. frequency (rad/s) as a function of time for 2 wt % sulfo-EPDM Mg salt solution in mixed solvents at 23 °C.

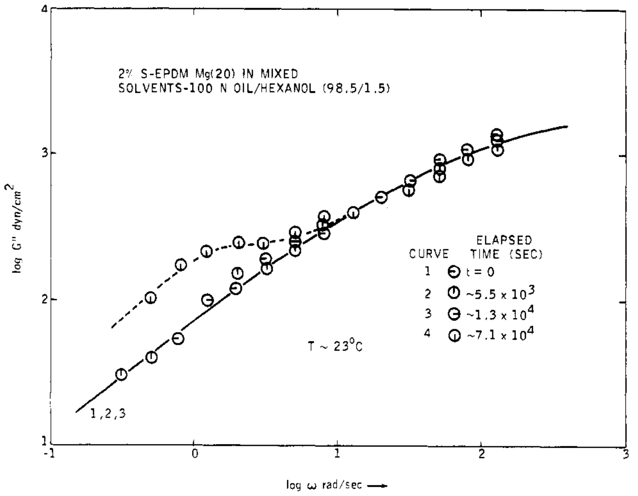

Figure 3. Plot of out-of-phase modulus G'' (dyn/cm^2) vs. frequency (rad/s) as a function of time for 2 wt % sulfo-EPDM Mg salt solution in mixed solvents at 23 °C.

polymer was the same used previously.[1-3] The amount of the alcohol in the solvent composition was deliberately kept low. The details of sample preparation and other characterization data have been reported previously.[3] In brief, weighed amounts of polymer crumbs were dissolved in a premixed solvent system in covered glass beakers with a magnetic stirrer. The solution was left stirring at room temperature over number of days, typically about 15–30 days to ensure complete dissolution. After visual inspection of the homogeneity of the solutions, preliminary viscosity measurements were made on the samples to check the reproducibility.

The dynamic viscoelastic measurements were made in the frequency range of about 2×10^{-3} to 20 Hz on a Rheometrics mechanical spectrometer and were confined to the linear range of viscoelasticity. The linearity was checked following the Boltzmann superposition principle. Most often, the maximum strain level imposed on the sample was less than 1% in order to minimize the possibility of irreversible structural changes. The reasons taken for such a precaution should be clear by the end of this report. A series of runs that were functions of time and temperature were made. Initially, most of the measurements were made only at room temperature; however, at later stages high-temperature measurements were also attempted. The maximum temperature covered was about 75 °C. Higher temperatures were not attempted, not only because of the difficulty in obtaining reliable data but also to avoid the possibility of any loss of solvent. At 75 °C, the loss of hexanol should be minimal, since the boiling point of hexanol is around 150 °C. The data were analyzed as discussed in detail previously.[2]

Results and Discussion

At the start of the measurements on all of the above-mentioned samples, we found the data highly irreproducible. Upon reviewing the data having various thermal and time histories, we discovered that a sample's structure is highly dependent on time and appears to be changing continuously, albeit in a systematic fashion.[18] We attempted to follow changes in the sample's response as a function of time, and this is the thrust of this report.

In Figure 1 various logarithmic in-phase modulus (G') data, as a function of logarithmic frequency, for the 2 wt % solution are shown. All the data were taken at room temperature. Curve 1 represents the response of the sample soon after placement in the instrument. Data below about 1 rad/s frequency could not be obtained because the responsive forces of the sample upon excitation were too small to be measured reliably with the instrumentation.

As is usual with nonpolar polymers and their solutions, the modulus is a monotonically increasing function of frequency. A careful look at the shape of curve 3 (Figure 1), however, reveals an interesting feature: in the vicinity of 10 rad/s the curve hints at a shallow plateau that indicates some slow relaxations in the sample.

The relaxations are seen more clearly in curve 1 in Figure 2, in which the corresponding data for the loss tangent are plotted against frequency. In the literature, because of ease in interpretation, the relaxation phenomena are most often identified or discerned based on the response of $G''(\omega)$ curves. In the present situation, however, no relaxation could be detected solely on the basis of G'' curves as can be seen from curve 1 of Figure 3.

As mentioned earlier, when we attempted to reproduce data such as curve 1 of Figures 1–3 (after a short period of initial measurements, which in practice typically ranged from a few hours to a few days), we were unsuccessful. Coincidentally we discovered that if the measurements were done on the sample after a period of more than a week or so the response of the material becomes stable and data represented by the curve could be reproduced.

Having learned of this strong dependency of sample structure on time, we followed these changes as a function of time. Curves 1–4 of Figures 1–3 represent data at the indicated time frames. Time at the start of the first run, that is, curve 1, has been arbitrarily set at zero. Thus, for example, the data for curve 3 would represent measurements approximately 3.5 h after the start of the first run.

Several interesting points can be noticed from the set of curves 1–4 of Figures 1–3. Sample response is a strong function of the time when it was first excited. This is evident from the position and shapes of various curves, especially in the low-frequency regimes. The high-frequency response of the in-phase modulus appears to be less sensitive to structural changes. At this stage perhaps it is worth pointing out that the shift of the curves with time is not just on the frequency scale; any attempt to reduce the data following the time–temperature superposition principle will fail. The "fanning out" trend of various curves of Figure 1 in the low-frequency region is somewhat analogous to a typical nonlinear response of viscoelastic fluids.[6] All the present data, however, were confined well within the linear range. The various curves thus strongly suggest that the structure of the material is a function of time, and they represent the structural responses of the material at the time of measurements. It is clear that as time progresses significant conformational changes take place in the sample. The in-phase modulus of the low-frequency region increases with time, suggesting the formation of a progressively stronger network-like structure. Also, note d log $G'(\omega)$/d log ω decreases rapidly at low frequencies. At $\omega \sim 1$ rad/s, over a period of about 20 h, a change of over a factor of 6 in the modulus occurs.

The configurational changes occurring with respect to time are also clearly seen in various loss tan δ $(=G''/G')$ curves in Figure 2. With aging the material's loss tangent decreases, pointing again, although indirectly, to the formation of a more elastic, three-dimensional, network-like structure. The most interesting feature of sample response is perhaps reflected in the G'' curves of Figure 3: all the data merge into a single curve.

Comparing Figure 3 with Figure 1 reveals that at first the interpretation of the data could be somewhat confusing. However, the in-phase modulus G' measures only the storage energy of the solution, which for dilute solutions of high polymers is a function primarily of the solute. The out-of-phase modulus G'', on the other hand, reflects the energy dissipation of the solution and is thus due to both solute and solvent. The concentration of the Mg sulfo-EPDM(20) in the solution is only 2 wt %, and in view of such a highly diluted state the contributions to G'' from the solute molecules are dominated by the overwhelming majority of the solvent.

Any structural changes in solute molecules are not clearly experimentally discernible in G'' response. However, it might be worth pointing out here that significant changes in the low shear viscosity values of dilute solutions of sulfonated EPDM polymers have been observed previously.[7] From the present studies, however, it appears that if a sufficient time has been allowed to pass, relaxations attributable to the structure could be observed. This can be seen by the low-frequency (dotted) portion of the curve of Figure 3. Nevertheless, since all the curves essentially reflect contributions from solvent molecules, they all tend to merge into each other.

Upon aging significant changes in the long relaxation times of the sample take place and are more clearly seen in various G' curves. Merging of various data from Figure 3 into a single line is somewhat reassuring in the sense that it indirectly validates that the behavior seen in Figure 1 is not due to the nonlinear response of the sample but reflects continuous changes in the relaxation spectra of the sample. Had the behavior been nonlinear, various G'' curves would have reflected in analogous fashion as G' curves of Figure 1. Qualitatively, similar observations of G' and G'' behavior were noted by Birnboim[8] sometime ago during his dynamic mechanical studies on poly(vinyl chloride) gels. In this case changes in network relaxations were suspected to be related to the changes in the number and size of crystallites.

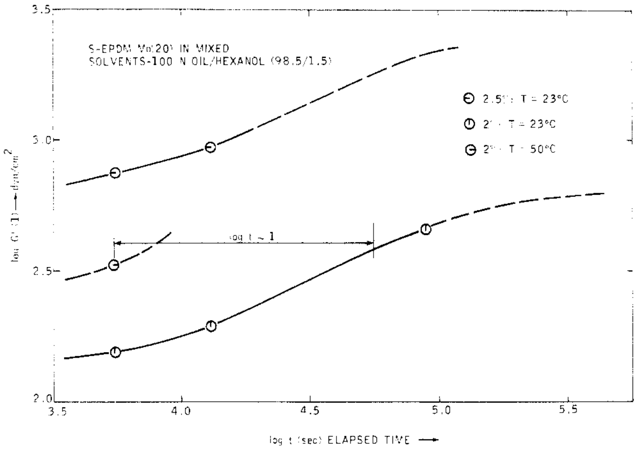

Figure 4. Plot of in-phase modulus G' (dyn/cm^2) at time zero (see text for time zero definition) vs. elapsed time (s) for 2 wt % and 2.5 wt % sulfo-EPDM Mg salt solutions in mixed solvents at 23 and 50 °C.

To summarize the behavior of this 2 wt % solution of the Mg sulfo-EPDM(20) system, its response is a strong function of time. Once this system is disturbed, it takes an excessively long period of time before it achieves equilibrium. Stated otherwise, the longest relaxation times, which are associated with changes involving the movement of magnesium sulfonate associations, change continuously, albeit slowly, and attempt to approach equilibrium. At any instant the sample is not only in a thermodynamically unstable state but due to high activation energy kinetically unable to rearrange. It is due to this latter reason that these time-dependent mechanical measurements were feasible to obtain.

At first we thought it exceedingly difficult, if not impossible, to achieve true equilibrium. However, we were able to reproduce the same set of data (within the experimental error of ±5%) for Figures 1–3 if measurements were repeated after about 5 days. Thus as a crude estimate it appears that the random distribution of metal sulfonate groups occurs over a period of about 4.3×10^5 s. Relaxation times of this order of magnitude for such dilute solutions (~2 wt %) and low viscosities (the Brookfield viscosity of this sample at room temperature is 14 P) are somewhat surprising.

In Figure 4 the $G'(1)$ data are plotted as a function of time. There are only a limited number of points, but nevertheless their trend tends to indicate that the equilibrium G' values could perhaps be attained only after a few hundred thousand seconds. From these measurements it is clear that, since at the 2 wt % concentration level it takes more than 10^4 s for the ionic groups to diffuse to some "equilibrium" state of aggregation, in the bulk, excessively long times may be required, making the attempt for such measurements fruitless.

Various measurements similar to those presented in Figures 1–3 were also made on a 2.5 wt % solution of Mg sulfo-EPDM(20) in the same mixed-solvent system (100N oil/hexanol = 98.5/1.5). The data are presented in Figures 5–7. Qualitatively, the same behavior is observed as with the 2 wt % solution. A much wider range of frequency data could be achieved for this sample because of its higher concentration; the measuring forces were higher than for the previous sample and could be easily monitored.

In the low-frequency region various curves are separated from each other (Figure 5), whereas in the high-frequency

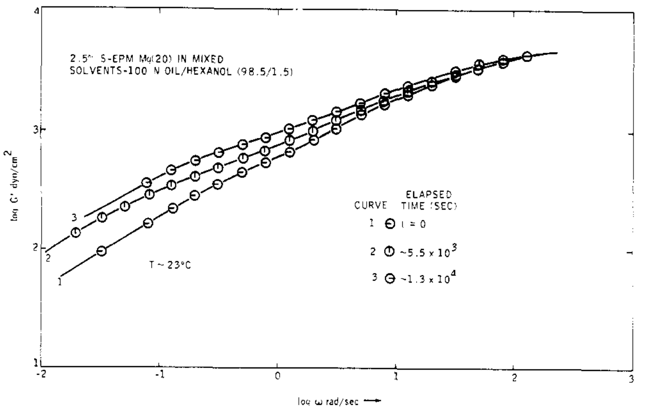

Figure 5. Plot of in-phase modulus G' (dyn/cm^2) vs. frequency (rad/s) as a function of time for 2.5 wt % sulfo-EPDM Mg salt solution in mixed solvents at 23 °C.

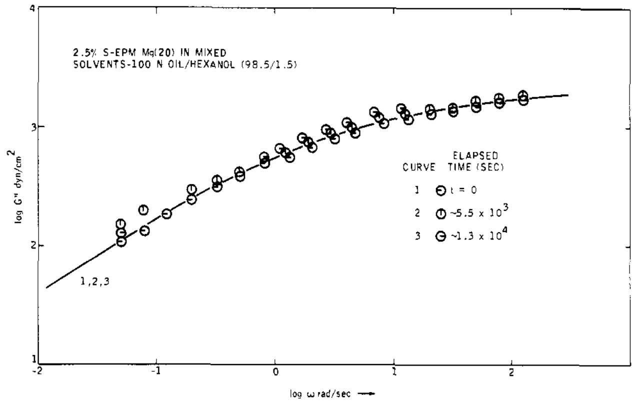

Figure 6. Plot of out-of-phase modulus G'' (dyn/cm^2) vs. frequency (rad/s) as a function of time for 2.5 wt % sulfo-EPDM Mg salt solution in mixed solvents at 23 °C.

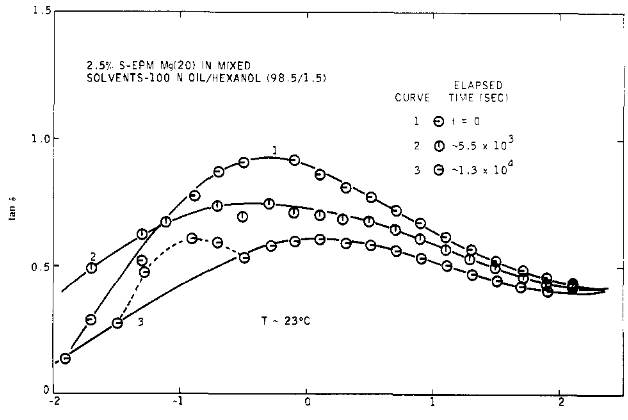

Figure 7. Plot of tan δ vs. frequency (rad/s) as a function of time for 2.5 wt % sulfo-EPDM Mg salt solution in mixed solvents at 23 °C.

region, all the curves merge into each other. Analogous to the previous case, as time progresses the contributions associated with the longest relaxation times increase. A progressively stronger network evolves as time passes. Complicated molecular rearrangements take place during this period. The merging of the curves at high frequency is perhaps either due to the viscoelastic transition from viscous fluid-like consistency at low frequencies to glass-like consistency at high frequencies or it might well reflect the response of a local structure other than that reflected in the aging phenomenon. All G'' data, Figure 6, merge into a single curve as seen before in the case of the 2 wt % solution; cf. Figure 3.

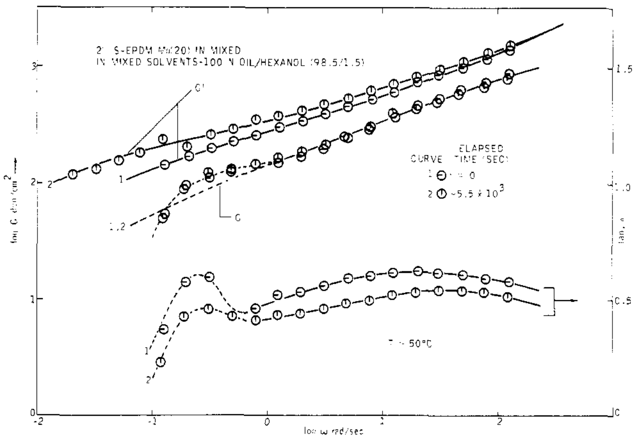

Figure 8. Plots of dynamic moduli G' and G'' (dyn/cm^2) and tan δ vs. frequency (rad/s) as a function of time for 2.5 wt % sulfo-EPDM Mg salt solution in mixed solvents at 50 °C.

With reference to the behaviors of both solutions studied, in the first couple of runs, we frequently observed a shallow shoulder in the low-frequency region of G'' and tan δ curves (see the data for curve 4 of Figures 2 and 3 and the data for curve 3 of Figures 6 and 7). It is not quite clear whether this short peak or shoulder is real or some sort of experimental artifact. These shoulders or peaks are shown by short dashed curves in these and subsequent figures. At the moment we are inclined to think they are real; if so, they might be reflecting some additional group of relaxation mechanisms that are generated in the system only after a certain period of time.

All the measurements reported in Figures 1–3 and 5–7 were made at room temperature. Additional time-dependent measurements were made on the 2 wt % solution at 50 °C. For the sake of space all the three viscoelastic functions are shown on a single graph (Figure 8).

Here again one observes the strong effects of aging on these functions. Qualitatively the behavior of the sample is the same as that seen at room temperature. An interesting point can be noted if one compares the values of $G'(\omega)$ and $G''(\omega)$ at 50 °C with those of Figures 1 and 3, which show room-temperature data. At any frequency both $G'(\omega)$ and $G''(\omega)$ are higher at higher temperature. The difference in values at these two temperatures is significantly higher than the rubber-like vertical correction, i.e., $\rho_0 T_0/\rho T$ factor, would account for.

After observing this unusual phenomenon we attempted to study in somewhat more detail and more carefully the temperature dependence of this solution. Dynamic moduli data taken at three temperatures, 25, 50, and 75 °C, for the 2 wt % solution are shown in Figures 9–11. At each temperature the samples were equilibrated to achieve the steady-state response. At low frequencies an increase in temperature from 25 to 75 °C increases $G'(1)$ by about a factor of 5 (Figure 9). Such changes in the modulus behavior of these solutions could be understood by the view that the density of effective associations in these systems increases with temperature.

Increase in temperature qualitatively has the same effect as that of time. But there does not seem to be a simple one-to-one relationship between the two variables such as embodied in WLF-type relations. Attempts to superimpose these curves by vertical or horizontal shifts even after taking into account the subtraction of the extrapolated equilibrium modulus, G_e, corresponding to this concentration[3] failed. Figure 10 contains $G''(\omega)$ data that are different from G'' data of other graphs (cf Figures 3 and 6). Apparently large changes in the temperature change

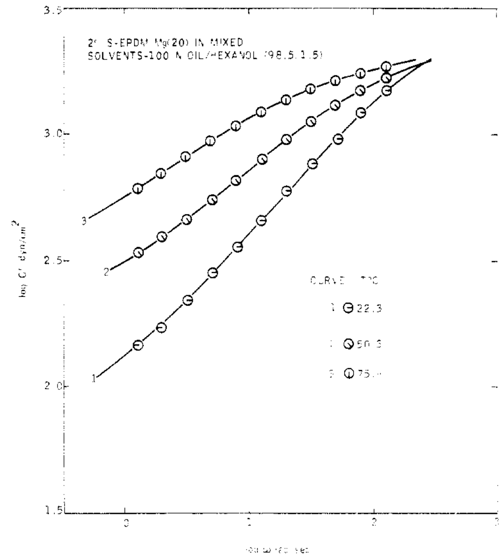

Figure 9. Plot of in-phase modulus G' (dyn/cm^2) vs. frequency (rad/s) as a function of temperature for 2 wt % sulfo-EPDM Mg salt solution in mixed solvents.

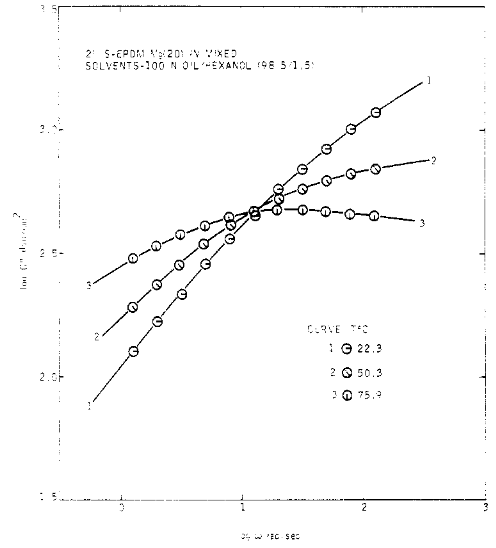

Figure 10. Plot of out-of-phase modulus G'' (dyn/cm^2) vs. frequency (rad/s) as a function of temperature for 2 wt % sulfo-EPDM Mg salt solution in mixed solvents.

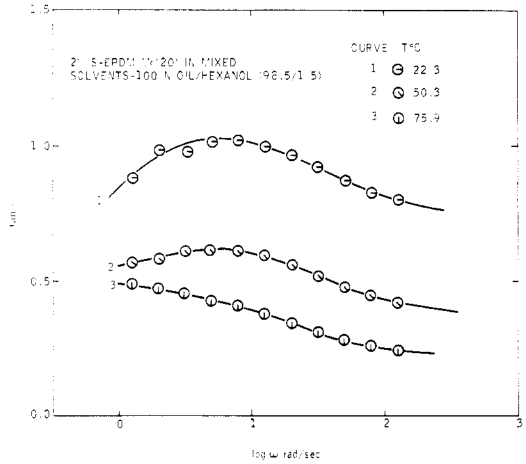

Figure 11. Plot of tan δ vs. frequency (rad/s) as a function of temperature for 2 wt % sulfo-EPDM Mg salt solution in mixed solvents.

the structure of the material to a significantly much greater extent than the first few hours of time do. These structural changes are reflected in their relaxation behaviors, i.e., in $G''(\omega)$ curves, as can be seen in Figure 10. At room temperature at low frequencies (curve 1) Newtonian flow seems to be approaching. However, at 75 °C, as seen in curve 3, d log $G''(\omega)$/d log (ω) has decreased significantly from 0.62 to 0.26. The sample behavior does not appear to be anywhere near the viscous flow region. These observations suggest than an increase in temperature builds up a network-like structure.

The increase in modulus of these solutions can also be rationalized on the basis of equilibria previously postulated to explain an increase in viscosity with temperature.[4,5]

$$\underset{\text{high temperature}}{(\mathrm{P{-}SO_3^-M^+})_n} \rightleftarrows \underset{\text{low temperature}}{n(\mathrm{P{-}SO_3^-M^+\cdot HOR})} \qquad (1)$$

The presence of low levels of alcohols results in a partial solvation of the sulfonate groups, decreasing their degree of association at a given temperature. However, an increase in temperature would be expected to favor the aggregated species (by desolvating the alcohol), thereby increasing the density of effective associations. It can be pointed out here that for the 2% polymer solution the mole ratio of alcohol to sulfonate groups is about 37 while for the 2.5% solution this ratio is about 30. Thus, in both the systems at any given instance roughly a similar excess amount of alcohol is present. Hence, over a range of alcohol contents and polymer levels, an increase in G' with temperature would be expected exactly analogous with similar observations on the change in viscosity with temperature.[7,17]

Similar considerations apply for G'' as shown in Figure 10. At room temperature the G'' relationship approaches that of a Newtonian solution. However, at 75 °C, G'' behavior as a function of frequency has changed so that it is not representative of viscous flow. Again, increasing the temperature provides G'' data consistent with a greater degree of association.

This interpretation is consistent with the equilibrium shown in eq 1. In the past, both in the bulk state and in concentrated solutions of sulfonated EPDM polymers, aging phenomena were not clearly discernible via such viscoelastic studies. In the presence of a cosolvent, especially in strongly associative systems such as the barium or magnesium salts, the solvated species equilibrate slowly. Hence it can be concluded that the equilibrium presented in eq 1 is strongly temperature dependent.

The data presented thus far with strongly associating ionomers, such as Mg sulfo-EPDM(20) in the presence of cosolvents, show that G' and G'' are dependent on the strain and aging histories. In addition, unusual temperature dependencies of G' and G'' are observed. However, our data do not demonstrate that they revert to their original structure upon aging or after a large strain disrupts the network structure of these systems.

In order to delineate the effect of strain and time, the following measurement was attempted. From the above experiments it became clear that at higher temperatures the rate of ionic interactions increases, that is, the fraction of metal sulfonate groups which actively contribute to a network increases, and finally a sort of pseudoequilibrium of network state exists in the system. A fresh sample (2.5 wt % solution) was installed in the instrument, and it was heated to 75 °C for about 30 min in order to allow it to reach equilibrium. Without disturbing the sample in any fashion the temperature was lowered to room temperature, and a series of low-amplitude dynamic measurements as a function of time were made. The resulting data are shown in Figure 12. No significant aging phenomena were

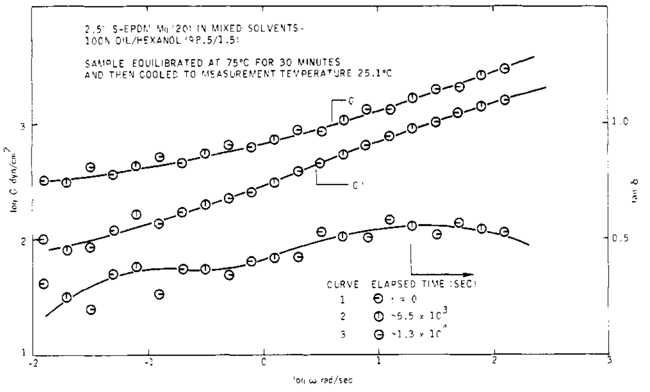

Figure 12. Plots of dynamic moduli G' and G'' (dyn/cm^2) and tan δ vs. frequency (rad/s) as a function of temperature for the 2.5 wt % sulfo-EPDM Mg salt solution in mixed solvents. The sample was equilibrated at 70 °C before measurements. See text for details.

observed. Within experimental error, G' values at various aging times are consistent.

It is interesting to observe that the absolute modulus values are different from those observed in Figures 5–7. Specifically, at low frequencies, G' determined by the approach described for Figure 12 is significantly higher; at high frequencies the values are lower. At low frequencies it appears to have an equilibrium modulus $G_e \sim 2.5 \times 10^2$ dyn/cm^2, a value in reasonable agreement with the previous result.[2,3] In the intermediate-frequency regime, in the annealed sample the emergence of a rubbery plateau is clearly observed as opposed to the case of unannealed sample (see top curve of Figure 5) which shows a monotonous increase of G' with frequency. Similarly, the loss tangents observed in Figure 12 are lower than those described in Figure 7. We conclude from this comparison that the exposure of the sample to elevated temperatures followed by cooling provided a more equilibrated sample than that obtained by simple aging at ambient temperatures.

In conclusion, these observations demonstrate that strongly associating ionomers dissolved in the presence of low levels of polar cosolvents provide solutions whose viscoelastic properties are very time dependent. This time dependence is related to the very long relaxation times observed in such systems. In this respect the presence of the cosolvent provides the ionic associations with a mobility not inherent either in the bulk polymer or in simple paraffinic solutions of these materials. Similarly, the presence of cosolvent in such solutions can give rise to a modulus dependence on temperature quite different from conventional polymer solutions.[9]

Acknowledgment. We thank Dr. W. W. Graessley for suggesting the experiment shown in Figure 12.

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