Behaviour of sulphonated EPDM in multicomponent/multiphase systems

D. G. Peiffer and R. D. Lundberg

Corporate Research Science Laboratories, Exxon Research and Engineering Company, PO Box 45, Linden, New Jersey 07036, USA

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The interactions of polymers containing low levels of ionic groups in selected environments has been a relatively unexplored area. For selected applications, it is important to understand how these polymers interact with a variety of cosolvents and/or solid substrates. The purpose of this study is aimed towards gaining an insight into these interactions. The solution behaviour of various inorganic salts (calcium, magnesium and zinc) of sulphonated ethylene–propylene diene monomers (EPDM) was investigated in order to determine the relative strength of interactions between sulphonate groups, cosolvents of varying structure and substrates possessing a specific chemistry. Viscosity–time–temperature relationships show that the properties of the polymer–cosolvent solutions are controlled to a large extent by ionic forces. The magnitude of these forces is dependent upon the nature of the cation and the specific molecular structure of the cosolvent. The weakest interaction was found to occur between the calcium neutralized polymer and cosolvent, while magnesium and zinc neutralized samples showed progressively stronger interactions. The extent to which these ionic forces can interact with their 'environment' depends upon the molecular structure of the cosolvent, in particular the structure of the polar 'head' is of paramount importance. These become even more apparent when the polymer and polymer–cosolvent complex is permitted to adsorb onto insoluble, solid substrates possessing a specific surface chemistry (in this instance, metal sulphate substrates). The results show that if the cation on the sulphonated polymer is identical to the cation contained in the metal sulphate, the adsorption of polymer is maximized (i.e., like prefers like). In addition, the nature of the cation is very important in determining the extent and, most probably, the mechanism of adsorption.

Keywords Sulphonated ionomer; counterion; cosolvent; substrate surface; viscosity; adsorption

INTRODUCTION

It is widely recognized that the introduction of ionic moieties onto the backbone chain of a polymer results in marked changes in its solid state physical properties[1–3]. These property changes are caused by ionic crosslinks which arise due to the mutual association of the ionic groups. The driving force for this microphase separation can be related to the low dielectric constant of the medium in which the ionic groups generally find themselves. The nature and extent of this association is also dependent on other factors including anion–cation structure and temperature[4], but the major factor affecting material properties is undoubtedly the strength of the cation–anion bond[5]. At high temperature the lifetime of the association is relatively short because sufficient energy is placed into the polymer structure as to allow the counterion to escape the coordination sphere of the ion attached to the chain backbone. A corresponding increase in lifetime is found with a decrease in temperature. This reversibility has been used for producing polymers that possess relatively good flow properties at elevated temperatures while still maintaining a crosslinked system at low temperatures.

The ionic groups are capable of associating, through secondary, noncovalent interactions, with other polar molecules such as alcohols and amines. This concept[6] has been fully utilized in the study of the dilute solution properties of sulphonated polymers and its metal neutralized counterparts. For example, incorporation of metal sulphonate groups into a hydrocarbon polymer system reduces the solubility of these polymers in hydrocarbon diluents. This reduced solubility is, of course, a direct manifestation of the strong ionic bonding in these materials. Addition of small amounts of alcohols will reduce these ionic attractions resulting in enhanced polymer solubility. This phenomena has been rationalized in terms of an alcohol–polymer equilibrium in which the alcohol and associated polymer is postulated to be in equilibrium with a strongly solvated species[6]. Adequate alcohol is required to dissociate the associated sulphonate groups, but if the alcohol–ionic association is strong, a 'stoichiometric amount' of alcohol may totally eliminate the ionic associations. In most instances it appears that the equilibria favours the associated ionic groups.

A wide range of phenomena[7–12] is observed to occur through the interactions of polymer molecules and low molecular weight compounds. The effect of the incorporation of ions on polymer properties is well known[1], but only recently has extensive experimentation proceeded on the modification of polymer properties by low molecular weight ionic salts. The elevation of the glass transition of polyethers by metal salts[8] and the suppression of the crystallization rate and melting point of nylons by inorganic salts[9] are examples of these specific

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interactions. A general mechanism of direct interaction between the salts and the polar groups of the noncrystalline phase seems to be involved. Similar interactions can also take place in solutions[7]. Methanol, normally a nonsolvent for poly(ethylene oxide) (PEO), becomes an excellent solvent for PEO with the addition of small quantities of certain metal halides. The reduced viscosity of the polymer is found to be inversely proportional to the salt concentration. This effect was attributed to the association of PEO with salt molecules through ion–dipole interactions which ultimately lead to a coulombic-type repulsion of the associated species.

In this present investigation we report upon the specific interactions of several neutralized sulphonate polymers with various alcohols and how these interactions influence solution properties. It is observed that the strength of interactions depends upon the nature of the cation and the molecular structure of the cosolvent. A general picture emerges from this study relating the extent to which sulphonated polymers (specifically ethylene–propylene terpolymers) interact with an alcohol cosolvent and how these molecular complexes influence solution behaviour. Also the adsorption behaviour from solution of the alcohol–metal neutralized sulphonated polymer complex in contact with insoluble metal sulphate substrate surfaces is studied. Again a very specific interaction is found related to both the molecular structure of the associated alcohol–metal salt complex and the chemistry of the substrate.

EXPERIMENTAL

Sample preparation

Sulphonation and neutralization of ethylene–propylene terpolymer containing a diene comonomer (EPDM) were prepared by methods reported previously[13]. The unconjugated diene monomer onto which the sulphonation reaction took place is 5-ethylidene-2-norbornene. The sulphonation reaction occurred on the substituted exocycle double bond with acetyl sulphate, obtained from the combination of sulphuric acid with acetic anhydride. The neutralization of the sulphonic acid was accomplished without prior isolation of any product.

All the sulphonated polymers were prepared from the same base EDPM. The number-average molecular weight of the polymer was 40 000 and its heterogeneity index M_w/M_n 2.10, as determined from gel permeation chromatography with trichlorobenzene solvent at 147°C. The propylene and ENB composition of this polymer was 45 per cent and 4.4 per cent by weight, respectively.

Two sets of sulphonated EDPM solutions were prepared. The first group, used in the high temperature dilute solution experiments, consisted of three samples containing an equivalent amount (10 meqiv.) of metal neutralized sulphonate moieties. Each of these polymers varied only in cation type (Zn, Mg and Ca). The second group, used in the adsorption experiments, included the first group plus two EDPM's containing 15 and 20 meqiv. calcium neutralized sulphonate groups.

Measurements

Solutions containing 3 per cent by weight (unless specified otherwise) of the 10 meqiv. metal neutralized EPDM with 3 per cent by weight of cosolvent were prepared. High boiling point for both the solvent and cosolvent is essential, so No. 2 diesel oil and tridecyl alcohol (b.p. 274°C) were the solvent and cosolvent, respectively. Normally the solutions were heated in the temperature regime from 25° to 200°C with heating times up to 16 h. The solution was subsequently cooled to room temperature and the viscosity measured. All viscosity measurements were performed on a Brookfield viscometer (Model LVT) utilizing a UL adapter for low viscosity solutions and various size spindles for the higher viscosity measurements. In several instances the viscosity was measured *in-situ* at high temperatures so as to avoid the additional complications in the interpretation of the data brought about by cooling to room temperature.

The adsorption of the metal neutralized sulphonated EPDM took place at 25°C in a 1 per cent solution of the polymer in *p*-xylene with 1 per cent by weight of cosolvent. Isopropanol, tridecyl alcohol and oleic acid were used as cosolvents. It should be noted that these three cosolvents were chosen in order to study the effect of molecular size and functionality on the adsorption process. Zinc, magnesium, and calcium sulphate were the insoluble substrate surfaces upon which adsorption occurred. In all cases 50 weight per cent of the metal sulphate was added to the polymer solution. After a predetermined amount of time (usually 24 h), an aliquot of solution was obtained and centrifuged until a clear liquid layer was visible. This clear liquid was then placed into a weighed, teflon coated aluminium pan and evaporated to dryness in a vacuum oven (60°C). The pan was again weighed and the weight per cent polymer adsorbed calculated.

Elemental analysis of the polymers recovered from these mixtures using standard filtration methods confirms that ion-exchange processes are inoperative in these highly nonpolar solutions.

Light microscopy observations indicate that the size distribution of the metal sulphate particulates are approximately equivalent.

RESULTS AND DISCUSSION

Viscosity temperature phenomena of ionomer solutions

Typical dilute solution viscosity data are shown in *Figure 1* where the viscosity is plotted against heating time at four different temperatures. The material used in this instance was the unmodified base polymer (EPDM). The response of the unmodified polymer is typical of dilute polymer solutions susceptible to oxidation at elevated temperatures. Essentially no viscosity change is observed at 50°C, while at 100°C the viscosity rises with time. This observation is somewhat surprising, but could be rationalized as being due to a small amount of reaction of residual double bonds, increasing the molecular weight, causing the viscosity to increase. It would be expected that the viscosity would continue to increase with longer heating times and ultimately lead to a gel phase.

It is apparent that a 'transition' in the performance of this solution occurs at 150°C. Over a major portion of this curve a marked deterioration in viscosity is evident which is a direct consequence of chain scission due to oxidation. Examination of the first data line in *Table 1* clearly shows that with the addition of a small amount of antioxidant, the viscosity does not drop but slightly increases as observed at 100°C. (No change in viscosity is noted whenever the solution is blanketed with nitrogen gas.) At

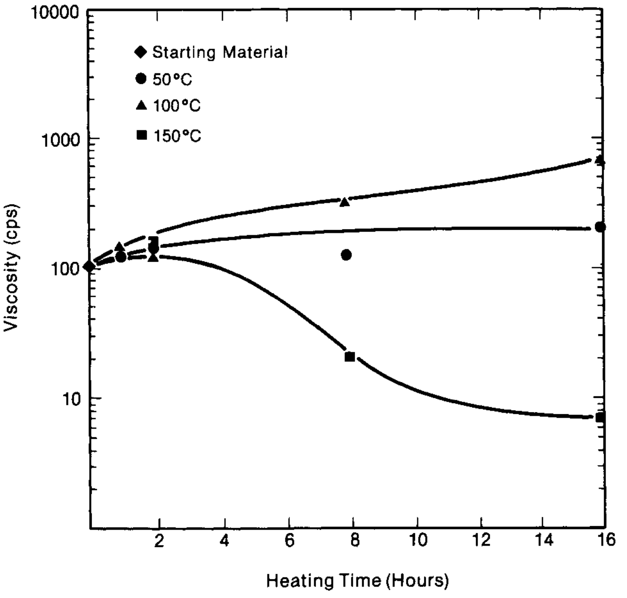

Figure 1 Effect of temperature and heating time on the viscosity of unsulphonated EPDM. The concentration of polymer in the diesel oil is 3 percent by weight

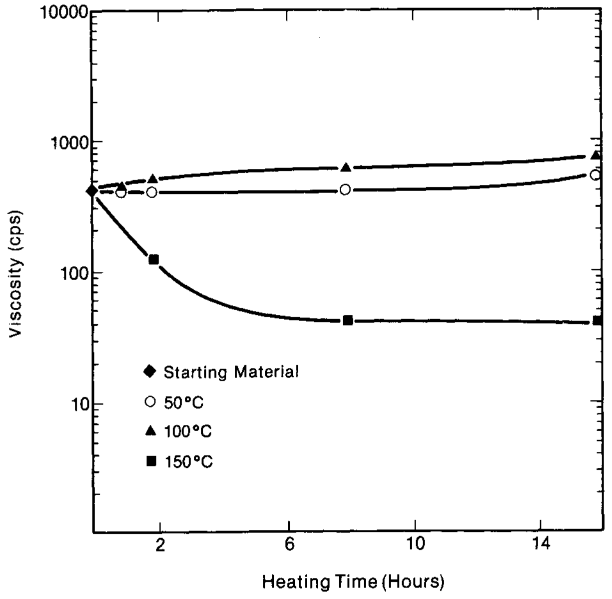

Figure 2 Effect of temperature and heating time on the viscosity of zinc neutralized sulphonated EPDM. The concentration of polymer in the diesel oil is 3 percent by weight

Table 1 Oxidative stabilization of solutions containing metal sulphonate EPDM

Solution	Initial viscosity (cps)	Viscosity[a] (cps)	Viscosity[b] (cps)
Socabu 55	80	20	100
Zn	400	40	600
Mg	500	60	*
Ca	28000	400	*

* Phase separation occurred

[a] Solution heated for 8 h at 200°C in air

[b] Solution containing 0.5 weight % antioxidant (hindered phenyl) was heated for 8 h at 200°C

heating times of less than three hours a slight rise in viscosity is found. The reason for this behaviour is that a competition exists between the association of polar functionalities and chain breakage with the former mechanism predominating.

The incorporation of zinc sulphonate groups onto EPDM does not significantly effect the time–temperature profiles (*Figure 2*) except for the fact that the viscosity is generally higher at these polymer levels. This is due primarily to the association of the ionic groups resulting in an apparent increase in molecular weight. However at 150°C chain scission is the major mechanism responsible for the dramatic viscosity drop.

In order to ascertain the effect of counterion structure on the time–temperature profile, viscosity measurements were made on various metal neutralized sulphonate-containing systems at 150°C. Due to the similarity of the backbone, sulphonation level, cosolvent structure and concentration, it was suspected that any viscosity change would be due solely to the counterion. Typical viscosity–heating time curves are presented in *Figure 3*. The one fact that is readily apparent is the five orders of magnitude viscosity change dependent upon the nature of the cation. With the exception of the calcium salt all of the curves show a viscosity decrease with time. It should be noted that the viscosity of the magnesium sample begins to

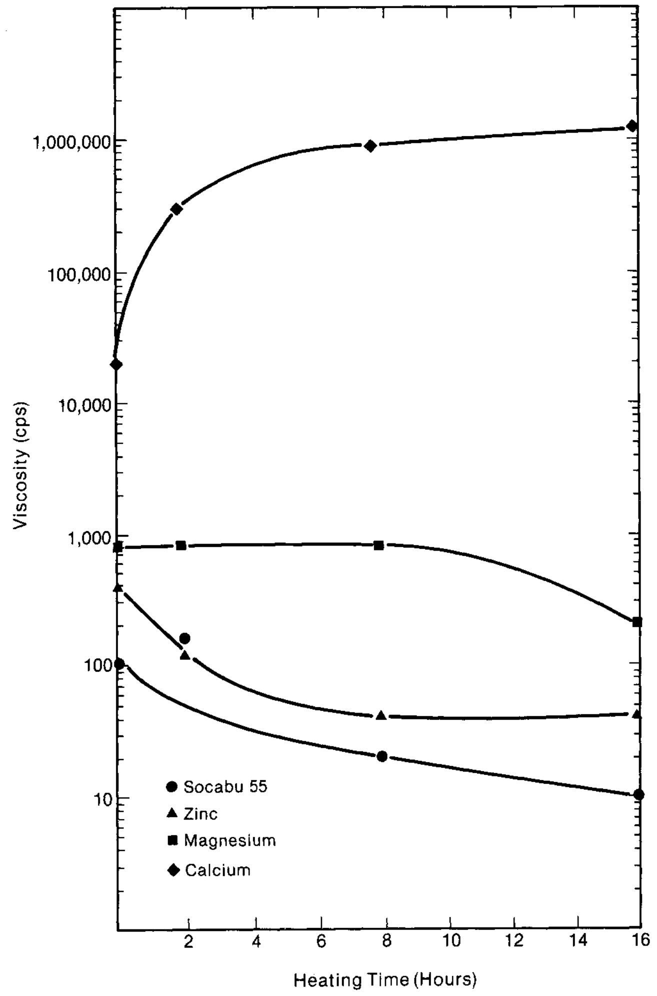

Figure 3 Viscosity of several metal neutralized sulphonated EPDM solutions (3 percent by weight of polymer in diesel oil) as a function of heating time at constant temperature (150°C)

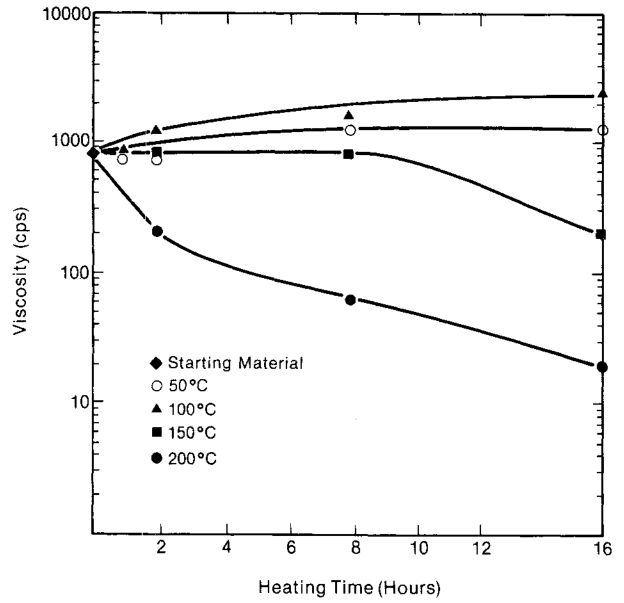

Figure 4 Effect of temperature and heating time on the viscosity of magnesium neutralized EPDM. The concentration of polymer in the diesel oil is 3 percent by weight

decrease only after 9 h. The magnitude of the viscosity or its change upon heat treatment does follow a specific hierarchy. As it will be seen throughout this study, this order (Ca > Mg > Zn) is maintained because the controlling factor is essentially the strength of the interaction between the cation and its 'environment'.

Increasing the temperature to 200°C produces a monotonic decrease in viscosity for all solutions, as shown in *Figures 4* and *5*. A comparison of the magnesium sulphonated sample (*Figure 4*) with the calcium salt (*Figure 5*), shows that the viscosity of the latter salt drops less precipitously at short times than the former. Again this effect is a result of the strength of interaction between the metal neutralized sulphonate groups. With equal amounts of dissolved polymer in solution, the calcium salt produces the greatest changes in viscosity, while progressively less viscosity enhancement is produced with the magnesium and zinc salts. In any event, the same trend (Ca > Mg > Zn) is generally observed within identical temperature regimes.

From the position of the polymer salt in each temperature regime (as in *Figure 3*) several important conclusions could be drawn. In purely qualitative terms, the shape and positions of the temperature–time profiles of both the unmodified and zinc neutralized polymers are similar. In view of this response it appears that the alcohol is tightly bounded to the zinc sulphonate group. This attraction is quite stable up to approximately 150°C. The alcohol prevents the metal sulphonate groups from associating because of its nonpolar, hydrocarbon tail. In essence, the sulphonate group acquires a significant degree of nonpolar character due to the complexed alcohol.

The influence of the magnesium and calcium ions in affecting the interaction strength varies quite differently from zinc. At high temperatures instead of observing a viscosity decrease, the opposite is found. This is explained by assuming that the strength of the calcium and magnesium salt–alcohol complex is less than that of zinc. Therefore, it takes relatively less energy to release the associated alcohol. With the alcohol unassociated, the metal neutralized sulphonate groups will associate producing a rise in the apparent molecular weight. The increase in viscosity of the calcium and magnesium solutions can be explained with this mechanism.

A model is proposed for the viscosity–temperature behaviour of these metal salt/cosolvent solution systems (*Figure 6*). As alluded to previously, the dissolution of the polymer salt into solution is aided by the presence of a cosolvent. This is due, in large part, to the association of the cosolvent to the metal sulphonate group forming a solvated species. Subsequent heating of this solution in the presence of oxygen can cause two competing effects to occur. The first effect is essentially oxidation of the EPDM backbone. If the force of attraction between the sulphonate groups and the alcohol is strong, the association will remain even at high temperatures. The solution containing the solvated species is of relatively low viscosity which allows oxygen from the atmosphere to 'penetrate' the solution interface causing chain oxidation and a corresponding viscosity deterioration. The unmodified EPDM and the zinc salt are two examples in which oxidation predominates. The second competing effect is the reassociation of the metal sulphonate group due to the detachment of the cosolvent. The rapid reassociation of the ionic groups causes an increase in viscosity, which, in turn, will not permit a significant quantity of oxygen from penetrating the solution–

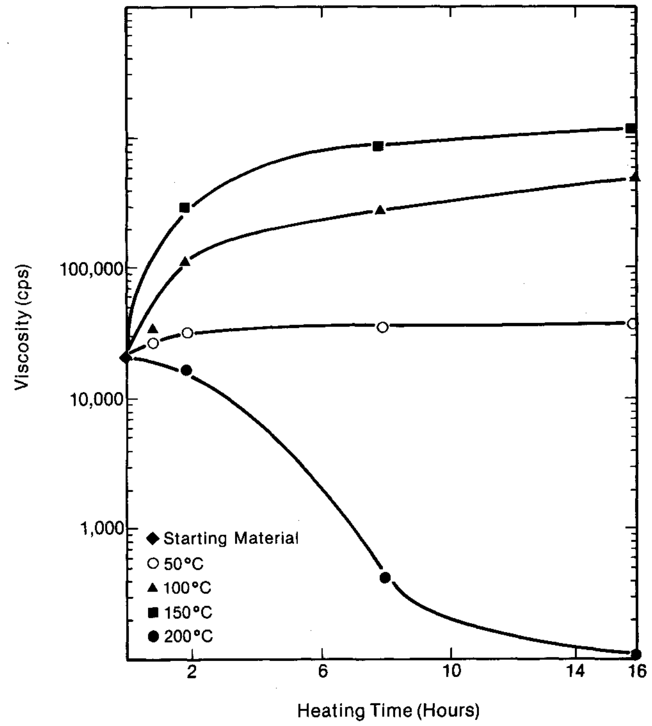

Figure 5 Effect of temperature and heating time on the viscosity of calcium neutralized EPDM. The concentration of polymer in the diesel oil is 3 percent by weight

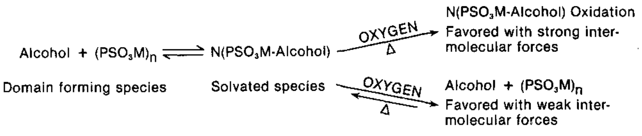

Figure 6 Model for sulphonate ionomer solution behaviour at elevated temperature

Table 2 Effect of oxygen on the stability of various metal sulphonate EPDM's

Solution	Initial Viscosity (cps)	Viscosity^a (cps)	Viscosity^b (cps)
Socabu 55	100	20	200
Zn	400	40	300*
Mg	800	60	120*
Ca	20 000	400	396 000*

* Phase separation occurred

^{a} Solution heated for 8 h at 200°C in air

^{b} Solution heated for 8 h at 200°C under a blanket of nitrogen gas

atmosphere interface resulting in oxidation of the polymer backbone. The calcium salt exemplifies this mechanism. Both of the above mentioned solution destabilizing mechanisms are essentially balanced in the magnesium salt system, at least up to about 9 h at 150°C. After 9 h sufficient oxidation has taken place to cause the viscosity to decrease. At 200°C, polymer oxidation predominates in all solutions indicating that at this temperature the kinetics of the oxidation process is much faster than the reassociation of the sulphonate groups.

Effects of ionic association

From the discussion presented above it becomes clear that oxidation of the polymer backbone and dissociation of the alcohol from the sulphonate group play important roles in the behaviour of sulphonated polymers in solution. These effects become more clearly evident when the solutions are heated to 200°C with and without an antioxidant. The antioxidant must be effective at low concentration ($\sim$0.5 weight per cent) and in addition, the molecule (or its oxidative products) must not interact to any great extent with the sulphonate group. In any event, the data presented in *Table 1* confirm the fact that the deterioration in the molecular weight of the polymer can be hindered with small amounts of antioxidant. The polymer has now become stabilized to such a degree that a large number of sulphonate groups can reassociate forming a separate phase. The amount of polymer remaining in solution is quite low ($\sim$1.0 weight per cent). (The separated material can be put back into solution with vigorous mechanical agitation at room temperature.)

An investigation of the properties of this very dilute polymer solution reveals that the viscosity differs from the original starting materials (*Table 2*). The zinc and magnesium materials show a lower viscosity while the calcium sample is markedly higher. This data suggest that again the zinc and magnesium salts are extensively solvated, whereas the calcium material is not. Since such a low concentration of polymer produces a very viscous solution, a point can be made that some type of structure has developed in the solution containing the calcium salt. As alluded to previously, the calcium salt has the greatest propensity for sulphonate group reassociation due to the relatively weak bond formed between the alcohol cosolvent and the metal sulphonate group. Thus we observe that even in cases where the concentration of metal sulphonate groups is very low, a sufficient number of these groups are capable of reassociation causing dramatic changes in solution properties. It is probable that an undefined crosslinked structure has developed with the metal sulphonate groups acting as labile crosslinks (i.e., a pseudo-network structure). This structure is undoubtedly a function of molecular weight, backbone chemistry, sulphonation level, etc. Experiments are being conducted in order to elucidate the nature of these tie points and overall structure.

Effect of cosolvent structure

In *Figure 7* the viscosity–time data for a 10 meqiv. calcium neutralized EPDM containing various cosolvents are plotted as a function of heating time (200°C). The three cosolvents (listed in *Figure 7*) were chosen because of their anticipated strong interaction with the metal sulphonate groups on the polymer. If the interaction is of sufficient strength, then heating this complex would not cause dissociation resulting in a viscosity rise. The solutions in this experiment were protected from oxidation with a nitrogen gas blanket. The measurements performed *in-situ* at 200°C show that insignificant changes in viscosity occurred. In addition cooling to room temperature (25°C) does not affect the ultimate viscosity value. Based on these measurements, it is concluded that highly polar moieties, such as some carboxylic acids, glycols, and disulphonates, can be strongly attached to the metal sulphonate and remain associated up to high temperatures. Comparison of *Figures 5* and *7* confirms this conclusion.

Interactions of sulphonated ionomers and solids

The nature of the interactions of the metal sulphonate–cosolvent complex can be studied in even greater detail by measuring its adsorption onto various insoluble metal sulphate substrates. This is in keeping with the observations that changes in the properties of a polymer do occur through the interactions with low molecular weight compounds$^{6-12}$. It is expected, however, that the extent of interaction with the substrate surface would be a direct function of the counterion structure, the detailed structure of the cosolvent, and the chemistry of the substrate.

Typical adsorption rate data are shown in *Figure 8* where the weight fraction adsorbed polymer is plotted against the time the substrate surface is in contact with the solution. The shape of the curves are typical for the adsorption of a polymer from dilute solution. At short times relatively rapid adsorption takes place, while at longer times an asymptotic approximation to the equilibrium adsorption occurs. Analogous results were obtained in experiments pertaining to the adsorption of fractionated polystyrene on aluminium and aluminium oxide^{14}. The adsorption equilibrium was established within a few hours on the smooth aluminium surface, and

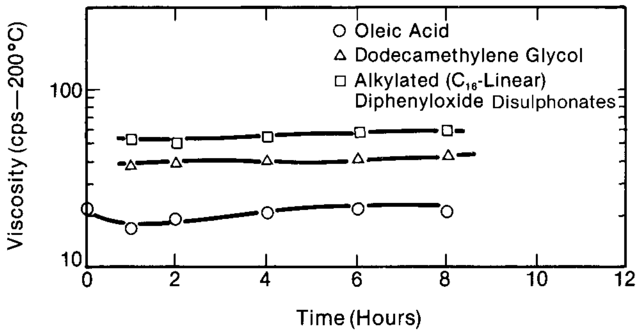

Figure 7 Time–temperature–viscosity profiles of calcium neutralized (10 mequiv.) EPDM containing various cosolvents. During the heating process, these solutions were blanketed with dry nitrogen gas

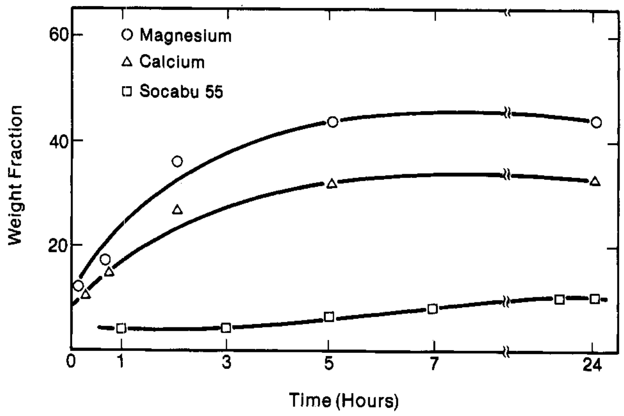

Figure 8 Adsorption rate of unsulphonated and several metal neutralized sulphonated EPDM (10 meqiv.) onto a $MgSO_4$ surface. The cosolvent in these solutions was isopropanol

Table 3 Adsorption of metal neutralized (10 meqiv.) EPDM's onto various sulphate substrate surfaces[a] (isopropanol is the cosolvent)

	$ZnSO_4$	$MgSO_4$	$CaSO_4$
Socabu 55	13	12	11
Zinc	95	44	43
Magnesium	13	74	16
Calcium	17	32	78

[a] Data correspond to weight percent adsorbed polymer

Table 4 Adsorption of metal neutralized (10 meqiv.) EPDM's onto various sulphate substrate surfaces[a] (tridecyl alcohol is the cosolvent)

	$ZnSO_4$	$MgSO_4$	$CaSO_4$
Socabu	10	12	10
Zinc	42	33	28
Magnesium	36	43	30
Calcium	21	32	38

[a] Data correspond to weight percent adsorbed polymer

within a few days on the porous aluminium oxide. For porous adsorbents, equilibrium is established more slowly, since diffusion of macromolecules into the pores takes a longer time. The porosity of the metal sulphate particulates is assumed to be low in all cases, since the establishment of the adsorption equilibrium occurs in a rather short period of time.

The adsorption asymptote is reached more rapidly for the ion-containing polymer as compared to the unmodified material. This indicates that there is a higher driving force for adsorption in the former polymers. Furthermore, the magnesium neutralized EPDM adsorbed to a greater extent than the calcium sulphonate sample on the magnesium sulphate surface. A more detailed study of this observation is given in *Tables 3* and *4*. Several important results can be noted. That is, if the cation on the sulphonated polymer is similar to the cation contained in the metal sulphate, the adsorption of polymer is maximized. Such behaviour is directly attributable to the ionic sulphonate groups on EPDM. In addition the driving force for adsorption is dependent on the nature of the counterion. There is a strong tendency for the zinc neutralized EPDM to absorb to a much greater extent than either the magnesium and calcium samples under identical experimental conditions indicating the ionic forces are greater in the former material. Similar behaviour was found in the viscosity–time–temperature profiles. The unmodified material does not show a tendency for preferential adsorption (i.e., like prefers like).

The differences between polymers become less clearly manifested with changes in the molecular structure of the cosolvent. The adsorption values are the largest utilizing isopropanol (*Table 3*), while the least adsorption is found with oleic acid (*Table 5*). On the basis of these results, it is clear that large increases in the length of the hydrocarbon 'tail' of the cosolvent reduces the extent of adsorption. The ionic sulphonate group has become less ionic in character. However, a significant amount of adsorption still occurs with tridecyl alcohol (*Table 4*). Only oleic acid reduces the level of the adsorption to that observed in the unmodified EPDM. Clearly, the overall structure of the cosolvent is very important in determining the extent and, most probably, the mechanism of adsorption, but the structure of the polar 'head' determines to a great extent the amount of adsorption. Clearly the acid functionality is more effective than the alcohol group in shielding the sulphonate group from possible interaction with the substrate surface.

The adsorption data of polymers in the absence of cosolvent is shown in *Table 6*. The extent of adsorption is comparable to systems containing tridecyl alcohol. It is quite likely that under these dilute solution conditions, the sulphonate groups interact through both intra- and intermolecular associations with other sulphonate groups, reducing the strong adsorption tendency of the polymer. In this instance, the ionic groups are 'shielded' from interacting with the substrate surface. Even though the exact structure produced by these interactions is not known, we can conclude that the polymer has become less ionic in character. Therefore, it may not be too surprising to find that this structure has a comparable adsorption level with systems containing tridecyl alcohol.

In *Figures 9–11* the adsorption of calcium neutralized sulphonated EPDM's is plotted against the calcium concentration. The curves in each figure correspond to a specific metal sulphate surface and cosolvent. A careful study of these curves shows that the incorporation of increasing levels of metal sulphonate groups primarily affects the amount of polymer adsorbed. Increasing the calcium concentration produces a corresponding rise in

Table 5 Adsorption of metal neutralized (10 meqiv.) EPDM's onto various sulphate substrate surfaces[a] (oleic acid is the cosolvent)

	$ZnSO_4$	$MgSO_4$	$CaSO_4$
Socabu 55	12	14	17
Zinc	17	18	13
Magnesium	14	13	16
Calcium	10	14	16

[a] Data correspond to weight percent adsorbed polymer

Table 6 Adsorption of metal neutralized (10 meqiv.) EPDM's onto various sulphate substrate surfaces[a] (no cosolvent present) *

	$ZnSO_4$	$MgSO_4$	$CaSO_4$
Socabu 55	8	11	8
Zinc	48	27	38
Magnesium	18	33	29
Calcium	10	21	29

[a] Data correspond to weight percent adsorbed polymer
* These results are applicable for both 1/4 and 1 weight percent polymer solutions

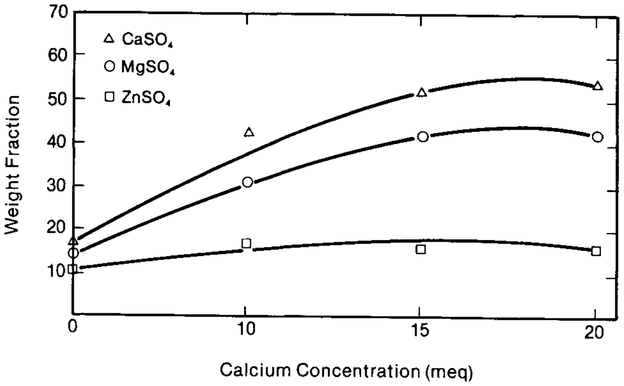

Figure 9 Adsorption of calcium neutralized sulphonated EPDM (cosolvent is isopropanol) onto various sulphate surfaces

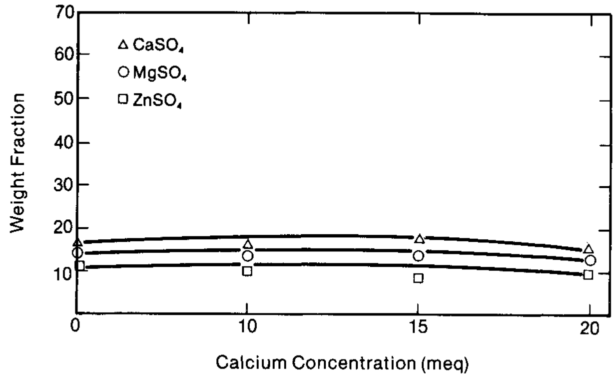

Figure 11 Adsorption of calcium neutralized sulphonated EPDM (cosolvent is oleic acid) onto various sulphate surfaces

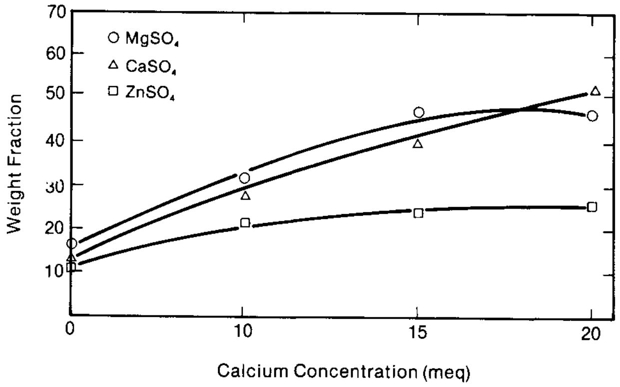

Figure 10 Adsorption of calcium neutralized sulphonated EPDM (cosolvent is tridecyl alcohol) onto various sulphate surfaces

the polymer absorbed. An asymptote is approached quite rapidly at the 15 meqiv. sulphonation level with little change in the level of adsorption with further increases in the sulphonate content.

The wide variation in the extent of absorption is shown clearly in a comparison between the different substrates (for example, *Figure 9*). As previously observed the polymer has the strongest preference for calcium sulphate, the weakest for zinc sulphate. This trend is again evident in the samples containing higher sulphonation levels. It is concluded that the driving force for adsorption correlates with the number of ionic groups, which most probably, exist as individual and, independent units.* As expected, the degree of polymer–substrate interaction is a function of the molecular structure of the colsolvent. In addition over a wide range of sulphonation the adsorption level utilizing oleic acid is again comparable to the adsorption of the unmodified EPDM.

CONCLUSIONS

Sulphonated ionomers have been shown to interact in very specific ways with its surrounding 'environment'. The magnitude of this interaction depends upon the strength of the ionic forces controlled to the first approximation by the nature of the counterion located at the neutralized sulphonate centres. In addition, it is shown that the extent to which these ionic centres could influence physical properties depend on the 'complexing' strength of various cosolvents. In more specific terms, the polar 'head' of the cosolvent controls, to a large extent, the behaviour of the ionomer (i.e., time–temperature–viscosity profiles). These interactions are shown to be of paramount importance in the adsorption of the metal neutralized sulphonated EPDM–cosolvent complex on to cosolvent various metal sulphate surfaces. An interesting feature of this study is that if the counterion of neutralized sulphonated group is identical to the metal cation contained in the sulphate salts, adsorption is at a maximum (i.e., like prefers like). Subtle changes in the molecular structure of the cosolvent does, however, significantly affect the extent of adsorption. Therefore, the extent to which the sulphonate groups are 'shielded' by the cosolvent from the sulphate surfaces determines the efficiency of the adsorption process.

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* At higher sulphonate concentrations (~15 mequiv.) an insufficient amount of cosolvent is present in solution to associate with all of the ionic groups causing the observed levelling in polymer adsorption.