Infra-red investigation of sulphonated EPDM polymers

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Infra-red investigations have been conducted on a sulphonated ethylene propylene diene monomer system (sulpho EPDM) wherein the sulphonate is neutralized with various monovalent and divalent cations. Analysis of these systems was conducted on thin polymer films which were also analysed in spectra from which the unfunctionalized EPDM contribution was subtracted. These studies have revealed that the interaction of cation and sulphonated polymer differs for each cation, and some conclusions have been drawn regarding the symmetry of the cation–sulphonate complex. Surprisingly, the functionalization process induces ordering of the methylene groups in a *trans* fashion in the solid ionomer. The degree of ordering depends on the specific cation suggesting, for the first time with these polymers, that the ionic aggregation induces an ordered rearrangement of the polymer chains. The ordering in these systems disappears after prolonged heating, suggesting that thermal relaxation of the ionic aggregate destroys the order in the polymer chains.

(Keywords: sulphonated ionomers; infra-red spectroscopy; viscoelasticity; cation–sulphonate complexes; ordered polymer chains)

INTRODUCTION

The physical properties of ion-containing polymers are strongly influenced by the association of these ionic groups to form effective crosslinks. The ionomers that have attracted considerable attention are the carboxylate-containing polymers, which have been studied extensively[1]. Their unusual viscoelastic properties have been explained as being due to cluster-like morphology of the ionic groups[2]. However, less information has been published[3–8] on a newly emerging class of ionomers based on metal–sulphonate associations. In this family of ionomers, the physical associations are much stronger than those of carboxylate ionomers[4]. For this reason, in the bulk state the relaxations of polymer molecules are extremely sluggish and the effects of counterions on the rate of relaxation are difficult to evaluate by conventional polymer characterization techniques[5]. In order to evaluate the effect of various counterions on the rheological characteristics of such ionomers, solution viscoelastic studies have been attempted[6–8]. These results demonstrate that the nature of the metal counterion plays an important role in determining the relaxation mechanisms operative in these systems. For example, in the case of zinc-neutralized sulphonated EPDM polymers, their gross relaxation behaviour was found to be analogous to that of very high molecular weight conventional polymers, whereas in the case of more strongly associative systems, such as the barium and magnesium salts of sulphonated EPDMs, the behaviour approached that of covalently crosslinked networks. In the former, the motion of polymer molecules is coupled with relatively weak ion–ion dipole interactions. In a broad sense these interactions could be viewed as being similar to conventional polymer entanglements, but much stronger in magnitude, the existence of a sort of super-entanglement state has been suggested[3,6]. In the latter case, the relaxation is believed to be primarily due to ionic bond formation and dissociation mechanism. In these systems, at any given instant a constant number of ionic junction points exist which give rise to their unique viscoelastic characteristics[7,8].

This paper describes an infra-red spectroscopic investigation of a series of metal sulphonated EPDM-based ionomers. As mentioned above, it was known from previous work that the dynamic mechanical properties of metal sulphonated EPDM polymers are dependent on the nature of the cation[3,6,7]. This study focuses on the vibrational structure of these EPDM salts and the types of influence that the various cations have on the sulphonated EPDM polymers. In the past, infra-red spectroscopy (i.r.) has provided considerable information on the structure and association of other ionomers, such as polystyrene sulphonic acid and its salts and Nafion, a polyfluorosulphuric acid[9,10]. Various other ionomers, most notably the ethylene ionomer structure, have been studied in detail using i.r. spectroscopy by various groups, such as Rees and Vaughan[11], Otocka and Kwei[12] and MacKnight *et al.*[13]. Lowry and Mauritz[14] used *FT*i.r. to study the effect of water on various salts of perfluorosulphate ionomers and have shown that $-SO_3^-$ symmetric stretching mode is a function of both the nature of the cation and the degree of hydration. Risen and coworkers[15] have examined the far-i.r. work to elucidate the structure of domain formation in various ionomers. Such literature has been of considerable help in the assignment of the bands of sulphonated EPDMs. Our investigation was restricted to mid-i.r. studies and concentrated on the vibrations of the polymer backbone,

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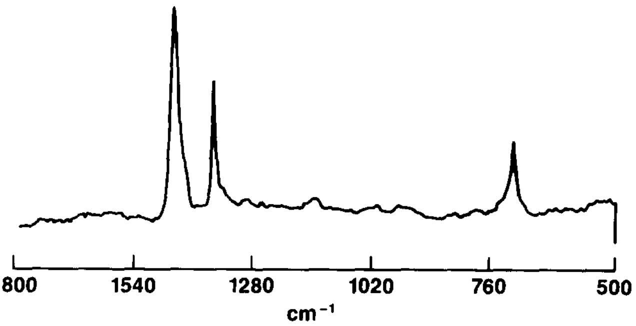

Figure 1 I.r. spectrum (1800–600 cm^{-1}) of the precursor EPDM polymer

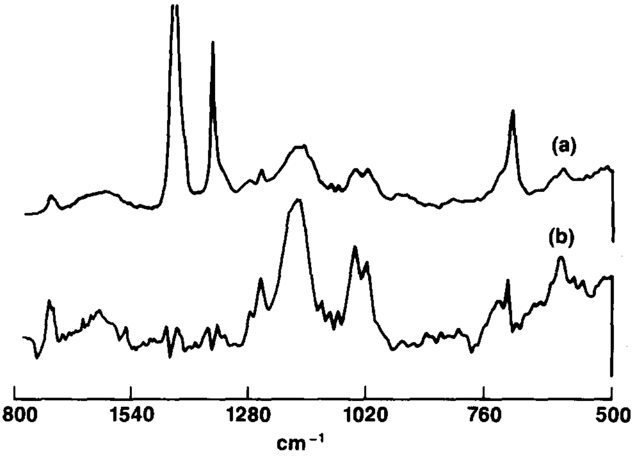

Figure 2 (a) I.r. spectrum of sulphonated EPDM-Li$^+$ salt. (b) Spectrum (a) minus the EPDM backbone spectrum

sulphonated groups and the water of hydration. The correlation of the structural information obtained from the spectroscopic study with the known viscoelastic behaviour of these sulphonated EPDMs is also discussed[3,6,7].

EXPERIMENTAL

Sulphonated EPDM was prepared and its neutralization with metal acetates done according to methods reported previously[3,16]. The ethylene and 5-ethylidene-2-norbornene (ENB) contents of these materials were 55 and 4.4% by weight, respectively. The sulphur content of these polymers was around 0.6–0.7 wt%; all of the sulphur introduced was present as sulphonic acids (as determined by titration).

The infra-red spectra of these materials were obtained on thin ($\simeq$20/1000 in), moulded films using attenuated total reflection (a.t.r.) spectroscopy. The a.t.r. prism used was made of KRS-5 (thallous bromide iodide) and typically about 500 scans at a resolution of 4 cm^{-1} were obtained for each sample. The a.t.r. accessory was mounted in a Digilab FTS-20 *FT*i.r. system.

The samples used to study the thermal relaxations were prepared by heating the metal EPDM salts at 110°C overnight ($\sim$15 h). The NH_4^+ salt turned black on heating, indicating some decomposition.

RESULTS

Figures 1. 2a, 3a, 4a, 5a, 6a and *7a* show the infra-red spectra (1800–600 cm^{-1}) of EPDM and the sulphonated lithium, barium, magnesium, zinc, lead and ammonium EPDM salts, respectively. *Figures 2b, 3b, 4b, 5b, 6b* and *7b* are the spectra of the sulphonated EPDM salts from which the contribution due to EPDM has been subtracted. These spectra should reflect any changes in the polymer backbone, the sulphonate groups and the

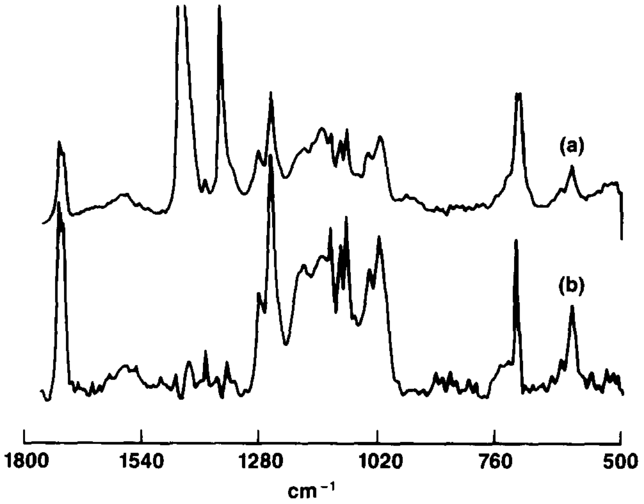

Figure 3 (a) I.r. spectrum of sulphonated EPDM-Ba^{2+} salt. (b) Spectrum (a) minus the EPDM backbone spectrum

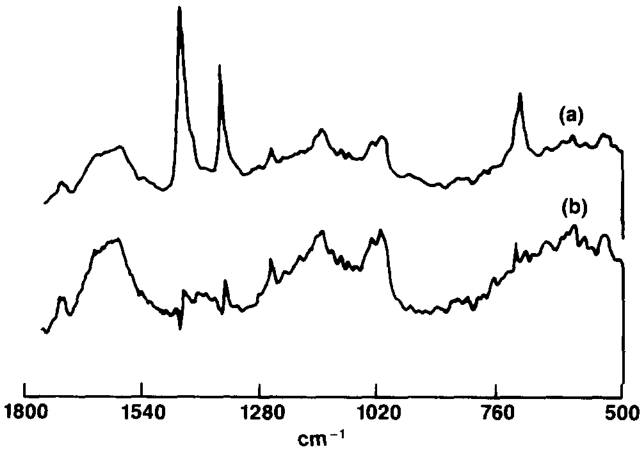

Figure 4 (a) I.r. spectrum of sulphonated EPDM-Mg^{2+} salt. (b) Spectrum (a) minus the EPDM backbone spectrum

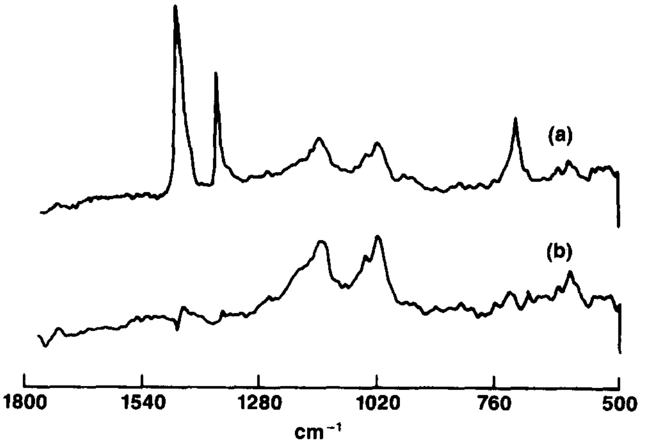

Figure 5 (a) I.r. spectrum of sulphonated EPDM-Zn^{2+} salt. (b) Spectrum (a) minus the EPDM backbone spectrum

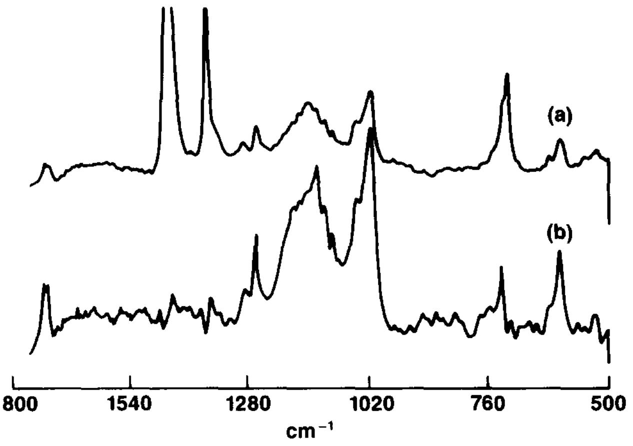

Figure 6 (a) I.r. spectrum of sulphonated EPDM Pb^{2+} salt. (b) Spectrum (a) minus the EPDM backbone spectrum

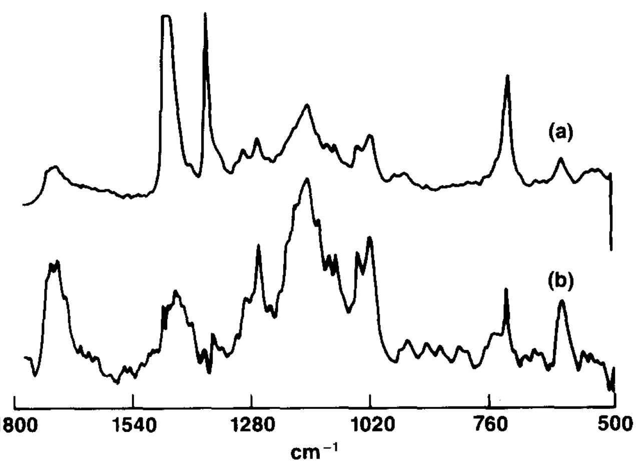

Figure 7 (a) I.r. spectrum of sulphonated EPDM-NH_4^+ salt. (b) Spectrum (a) minus the EPDM backbone spectrum

water of hydration. *Table 1* lists the vibrational bands observed in these spectra. The base EPDM polymer shows bands due to atactic polypropylene units and amorphous ethylene units.

The different regions of the vibrational spectra can be assigned to different vibrations as follows.

1750–1700 cm^{-1}

Two bands are observed in this region, at ~1725 cm^{-1} and ~1715 cm^{-1} in Li^+, Ba^{2+}, Mg^{2+}, Zn^{2+} and Pb^{2+}, and at ~1720 cm^{-1} and ~1700 cm^{-1} in the NH_4^+ salt. We assign these bands to the acetic acid that is liberated upon reaction of the metal acetate with the sulphonic acid and is retained by the polymer. Free acetic acid in the vapour phase shows bands at 1785 and 1800 cm^{-1}, whereas in solution these bands shift to 1710 cm^{-1} due to association. The intermediate frequencies of these bands in the EPDM salts reflect a different state of hydrogen bonding.

1650–1550 cm^{-1}

Both free and bound water molecules exhibit the ν_2 (scissor) vibration in this region. The free water molecules absorb below 1600 cm^{-1} and show an increase in frequency as a function of tighter binding. The Zn^{2+}, Pb^{2+} and NH_4^+ salts do not show much evidence of water adsorption, whereas the Li^+, Ba^{2+} and Mg^{2+} films show the presence of water. For Li^+ and Mg^{2+}, the water band appears at 1620 cm^{-1} due to cation-bound water of hydration, whereas the 1580 cm^{-1} band in the Ba salt is due to free water.

1255, 1135–1100, 730 cm^{-1}

Vibrational bands at these frequencies arise from an increase in ordering in the ethylene–propylene polymer background. Long-chain paraffinic fatty acids and other paraffinic molecules with polar end groups show a band at ~1250 cm^{-1} due to a $-CH_2$ wagging motion[17]. The intensity of this band is dependent on the polar end group and the conformation of the $-CH_2$ chains. The bands at ~1100 cm^{-1} are due to long-chain fatty acids. The band at 731 cm^{-1} is characteristic of crystalline polyethylene segments containing *trans* sequences of methylene groups[18].

1200 cm^{-1}

The asymmetric stretch of the sulphonate group occurs at this frequency. If the local symmetry of the $-SO_3^-$ group is C_{3v}, this is a degenerate vibration. Any asymmetry in this bonding arrangement will lift the degeneracy and this band will split into two. In case of Li^+, Mg^{2+} and NH_4^+ EPDM salts, this band appears at 1190, 1155 and 1162 cm^{-1}, indicating a symmetrical attachment to the $-SO_3^-$ anion. In the case of Ba^{2+}, the interaction with the sulphonate ion appears to be asymmetric, since well defined bands are observed at 1192 and 1155 cm^{-1}. For the Zn^{2+} and Pb^{2+} salts, there is also some splitting, indicating an asymmetrical bonding. However, the higher frequency component is only observed as a shoulder.

1050 cm^{-1}

The bands at this frequency are due to the symmetric stretch of the $-SO_3^-$ group. The origin of the splitting of this band is at present unclear.

600 cm^{-1}

The band at 610–615 cm^{-1} for the salts is due to C–S stretching of the polymer $-SO_3^-$ band.

DISCUSSION

It is clear from the results that the nature of the interaction between the cation and the sulphonated polymer differ with each cation and also that the resulting

Table 1 Vibrational bands (cm^{-1}) of sulphonated EPDM salts

Li	Ba	Mg	Zn	Pb	NH_4
1730	1728	1728	1725	1725	1720
1720	1718	1718		1718	1700
1620	1580	1620			
				1450	
1255	1255	1255	1255	1255	1255
1190	1192	1155	1200(sh)	1175(sh)	1162
	1155		1150	1150(sh)	
1135	1135	1135		1135	1135
1118	1115	1115	1115	1115	1115
1100	1100	1100	1100	1100	1100
1065	1052	1050	1055	1045(sh)	1052
1038	1030	1030	1030	1020	1025
731	731	731	731(sh)	731	731
615	610	608	608	605	610

conformational changes in the polymer microstructure are different.

Conformational changes

One of the most surprising changes that take place on forming the EPDM salts is the introduction of ordered domains in the solid ionomer, as evidenced by the presence of the 731 cm^{-1} band. Such ordering is most marked in the Ba^{2+} salt and is only present in small amounts in the Zn^{2+} salt, with various degrees of ordering in the other salts. This suggests that ionic aggregation due to the sulphonate cation interaction brings about an ordered rearrangement of the polymer chains, forming extended regions in which the methylene groups are in a *trans* configuration. The ionic interaction, as we shall see later, is dependent on the cation size and charge and it seems that these parameters are at an optimum in the Ba^{2+} salt for forming ordered domains. The presence of these regions[19] will influence the mechanical properties of these polymers. However, on heating the samples at 110°C for 15 h, the band at 731 cm^{-1} shifts to 720 cm^{-1} due to the conversion from *trans* to *gauche* forms. This indicates that the thermal relaxation disrupts the anion–cation association in such a way as to destroy the ordering of the polyethylenic units.

Sulphonate–cation interactions

The local symmetry of the cation–sulphonate complex determines the asymmetric stretch of the sulphonate group. If the symmetry is lowered from C_{3v}, the degeneracy of the vibration is lifted and the band splits into two. In the case of Li$^+$, Mg^{2+} and NH$_4^+$ salts, with ν_{asym} at 1190, 1155 and 1162 cm^{-1}, it appears that these cations are binding symmetrically to the anion. In case of polystyrene sulphonated salts, and Nafion salts, this band is usually split for all cations at low hydration levels[9]. However, for polyethylene sulphonic acid salts (Redcat membrane), this band is not split for a series of cations, indicating a symmetric binding to the sulphonate group[10]. The positions of these bands are influenced by the cation–anion Coulombic interaction as well as the cation's interaction with the induced dipole in the anion. It is expected that the stronger these interactions are, the more polarized the sulphonate group will be and this will increase the vibrational frequency. This suggests that the interaction in the lithium salt (ν_{asym} 1190 cm^{-1}, ν_{sym} 1065 cm^{-1}) is stronger than the ammonium salt (ν_{asym} 1162 cm^{-1}, ν_{sym} 1052 cm^{-1}).

For the case of divalent ions, the anions will be crosslinked and therefore the field of the one anion will weaken the cation field at the other ion. From the ν_{asym} band, it appears that the Mg^{2+} ion is symmetrically bound to the sulphonate, whereas the Ba^{2+}, Pb^{2+} and Zn^{2+} salts are not. *Figure 4* also shows that the Mg^{2+} ion is considerably hydrated, which is not surprising in view of the fact that its effective Coulombic field (charge/radius) was the highest amongst the ions examined. The bound water molecules act as a dielectric between the cation and anion, and therefore weaken the cation–anion interaction. Hydrated polystyrene sulphonates also exhibit symmetric bonding to the sulphonate ion. Barium salt shows the most pronounced splitting of the asymmetric mode, indicating a strong interaction with the sulphonate ion. The lead and zinc salts only show the high frequency band as a shoulder, indicating a weaker interaction with the anion. The pronounced interaction of the barium sulphonate ion pair could be responsible for the higher degree of ordering of the polymeric ethylene chains.

On heating these samples at 110°C for 18 h, the cation–anion interaction in all of the salts is weakened, the effect being predominant with the Ba^{2+} salt. Along with the loss of ordering, this indicates that the ionic association and the resulting tertiary structure of the polymer chains are altered on heating.

The dynamic mechanical properties of these polymers suggest that the ionic associations are stronger for the Ba^{2+}, Li$^+$ and Mg^{2+} salts, compared to the Pb^{2+} and Zn^{2+} salts. The melt viscosities, melt fracture properties, melt index data, tensile strength and elongation properties show that the Pb and Zn systems appear to be less strongly associated than the other cations[3,16]. The spectroscopic data are in agreement with the observed mechanical properties, since the Ba^{2+} salt is shown to have the strongest cation–anion interaction as well as the highest degree of *trans* character of the methylene groups in the polymer chains. The magnesium salt, however, is predicted to have weak cation–anion interaction due to the water of hydration. The mechanical properties of this ionomer will therefore be sensitive to temperature, since the amount of water of hydration is expected to decrease at higher temperatures[7,8]. The NH$_4^+$ salt shows evidence of decomposition at elevated temperatures; therefore, a correlation of its viscoelastic and spectroscopic behaviour is precluded.

CONCLUSIONS

This study on the infra-red spectroscopy of sulphonated EPDM polymers shows that there are various vibrational modes of the polymer system that are sensitive to cation–anion interactions. It appears that ordering of the polymeric backbone chains is dependent on the cation–anion interaction, which is governed by the size of the cation and its charge. The water of hydration present to a larger degree in smaller cations will also influence the ion–ion bonding. Ordering and ion–ion interactions are also sensitive to thermal changes.

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19 The level of ordering (crystallinity) in these materials was not studied in detail by i.r. or by X-ray techniques; however, it is suspected that the crystallinity level was low, being less than 20%