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Plasticization of an ionic thermoplastic elastomer based on a zinc sulfonated ethylene–propylene–diene terpolymer of high ethylene content

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Zinc sulfonated ethylene–propylene–diene terpolymer (EPDM) behaves as an ionic thermoplastic elastomer. Both paraffin oil and dimethyl sulfoxide (DMSO) act as plasticizers for this polymer; while paraffin oil plasticizes the hydrocarbon backbone, DMSO plasticizes the ionic domains. Results obtained from dynamic mechanical analysis (d.m.a.) show that DMSO does not affect the glass–rubber transition temperature (T_g), occurring at around −26°C, but adversely affects the broad transition in the temperature range from +27 to +80°C, which is believed to be due to the hard phase resulting from the ionic aggregates in the polymer. Paraffin oil, however, causes a lowering of the T_g (from −26 to −34°C) without affecting the high-temperature transition. Results obtained from dielectric thermal analysis (d.e.t.a.) indicate the existence of two types of ionic aggregates, namely multiplets and clusters which are responsible for the occurrence of two types of dipolar relaxation in the ionic-transition zone. Processability studies using the Monsanto processability tester (MPT) show that DMSO causes a higher extent of plasticization than paraffin oil. Incorporation of DMSO also leads to greater loss in physical properties of the zinc sulfonated EPDM when compared to paraffin oil.

(Keywords: zinc sulfonated EPDM; plasticization; thermoplastic elastomer)

INTRODUCTION

Ionomers are ion-containing polymers, composed of a hydrocarbon backbone, containing pendant acid groups which are neutralized at least partially, with the concentration of salt groups in the ionomers being, in general, less than 10 mol%[1]. Ionomers are now emerging as important industrial polymers[2]. The ionic groups aggregate in the bulk and form physical crosslinks which cause a profound improvement in the physical properties of the ionomers[3–7].

Ionomers in general show unusually high melt viscosities due to strong intermolecular associations and the relatively high stability of the ionic clusters, thus making their melt processing difficult[8]. As in the case of conventional polymers, plasticizers may be incorporated into ionomers for lowering their melt viscosity and improving their processability. The two-phase morphology and the large difference in the polarity of the hydrocarbon and ionic phases offer two possibilities for the plasticization of ionomers, namely the plastization of the hydrocarbon phase, and the plasticization of the ionic clusters.

Bazuin and Eisenberg[9] have studied the effects of polar (glycerol) and non-polar (ethylbenzene) plasticizers on the dynamic mechanical properties of styrene/methacrylic acid ionomers. Recently Hara *et al.*[10] have reported the role of *N,N*-dimethylformamide (DMF) as a dual plasticizer for sulfonated polystyrene ionomers. DMF is a polar solvent which is known to disrupt ionic interactions[11]. Navaratil and Eisenberg[12] have reported the use of dimethyl sulfoxide (DMSO) as an ionic plasticizer for sodium-neutralized poly(styrene-*co*-methacrylic acid).

This present paper reports the results of studies on the paraffin oil and DMSO plasticization of the zinc salt of a sulfonated ethylene–propylene–diene terpolymer rubber containing 75 wt% ethylene.

EXPERIMENTAL

Materials

The materials used in this study are (i) a thermoplastic ethylene–propylene–diene terpolymer (EPDM) containing 75 wt% ethylene, 20 wt% propylene and 5 wt% 5-ethylidene-2-norbornene and (ii) the zinc salt of the sulfonated terpolymer, which is formed by sulfonation of the pendent unsaturated groups in the thermoplastic EPDM followed by neutralization of the resultant

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EPDM sulfonic acid, using the procedure described by Makowski *et al.*[13]. The level of sulfonation in the zinc sulfonated EPDM was 30 meq per 100 g of polymer. Both of the polymers were supplied by Exxon Research and Engineering Company, New Jersey, USA. The % crystallinity in both of the polymers was around 20%[14]. The paraffin oil used was rubber grade and had a density of 0.83 g cm^{-3}. Dimethyl sulfoxide (DMSO), with a density of 1.10 g cm^{-3}, was obtained from E. Merck (India) Ltd, Bombay.

Sample preparation

The rubber compounds were mixed in a Brabender Plasticorder (Model PLE-330) using cam-type rotors for 6 min at a rotor speed of 80 rev min^{-1} and at a temperature of 150°C. The test specimens were prepared by moulding in an electrically heated hydraulic press for 5 min at 160°C.

Dynamic mechanical analysis

Dynamic mechanical analysis was performed in a Rheovibron DDV-III-EP viscoelastometer at a frequency of 3.5 Hz and a strain amplitude of 0.0025 cm. The measurements were carried out over the temperature range from −150 to +200°C, at a heating rate of 1°C min^{-1}.

Dielectric thermal analysis

Dielectric thermal analysis was carried out in a Du Pont DEA 2970 Dielectric Analyser in a nitrogen environment. Square-shaped specimens (25 × 25 × 0.5 mm^3) were used, with the measurements being carried out over the frequency range from 1 to 10^5 Hz, and the temperature range from 20 to 200°C, at a heating rate of 5°C min^{-1}.

Processability studies

The flow properties of the materials were measured by a Monsanto Processability Tester (MPT) at shear rates of 36, 90, 181 and 289 s^{-1} and a temperature of 170°C. The capillary length (29.97 mm) to diameter (1.50 mm) ratio was 20 with an entrance angle of 45° and 60° (compound). The preheat time for each sample was 5 min.

Measurement of physical properties

The hysteresis behaviour was determined according to ASTM D412 (1980) by stretching dumb-bell-shaped specimens to a strain level of 400%. The stress–strain properties were determined at 25, 50 and 70°C according to ASTM D412 (1987) using dumb-bell-shaped specimens in a Zwick Universal testing machine (Model 1445), fitted with a temperature controlled cabinet, using a crosshead speed of 500 mm min^{-1}.

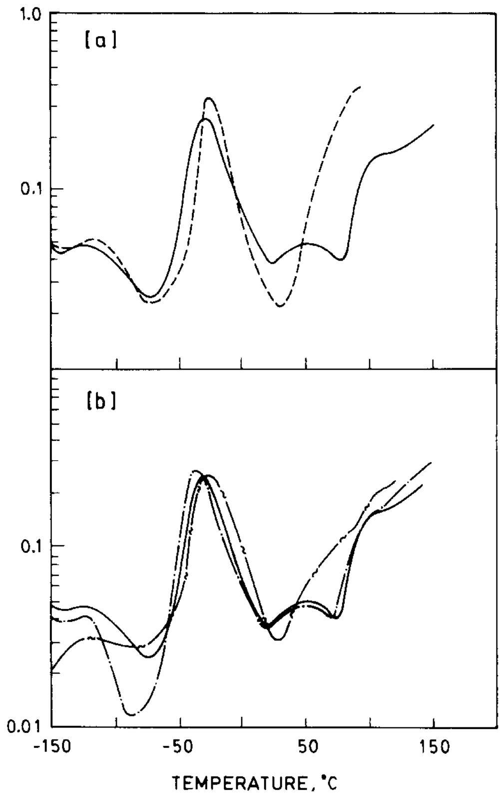

Figure 1 (a) Semilogarithmic plots of tan δ vs. temperature for: (- - - - -) EPDM; (———) zinc sulfonated EPDM. (b) Semilogarithmic plots of tan δ vs. temperature for: (————————) zinc sulfonated EPDM; (—•—•—) zinc sulfonated EPDM + 10 phr paraffin oil; (—~—~—) zinc sulfonated EPDM + 10 phr DMSO

RESULTS AND DISCUSSION

Dynamic mechanical properties

The variation of the dynamic mechanical properties with temperature gives information about the different transitions in the polymers. *Figure 1a* shows the plots of loss tangent (tan δ) *versus* temperature of EPDM and zinc sulfonated EPDM. The glass–rubber transition (T_g) occurs at around −26°C for both polymers. Apart from the T_g, the zinc sulfonated EPDM shows two other transitions, namely at +119°C, which is believed to be due to the melting of the crystalline zone of the polyethylene block, and another broad transition in the temperature range from +27 to +80°C, which is ascribed to the ionic aggregates. It has been reported earlier that in the case of crystalline ionomers transition due to ionic aggregates occurs at a lower temperature than the crystallite melting temperature[15,16]. In the case of rubbery ionomers, a transition due to ionic groups has been found to occur in the same temperature range[17]. In the case of EPDM, as expected the broad transition (27 to 80°C) due to the presence of ionic aggregates was not observed, while in addition the high-temperature transition due to the crystalline zones could not be detected as a result of softening of the sample above 100°C. In the case of the zinc sulfonated EPDM, the presence of ionic aggregates makes the matrix rigid enough for crystallite melting zones to be detected[15,16].

Figure 1b shows the effects of plasticization on the dynamic mechanical properties of the zinc sulfonated EPDM. Paraffin oil is known to be a plasticizer of EPDM[18]. This oil causes a reduction in the glass–rubber transition (T_g) due to the plasticization of the backbone chain, while the transition due to ionic aggregates is only marginally affected. However, DMSO causes no reduction in T_g, but the transition due to ionic aggregates is not detectable due to the disruption of the ionic domains. The results from the dynamic

Table 1 Results obtained from dynamic mechanical analysis[a]

Sample	T_g[b] (°C)	Transition due to ionic aggregates (T_i)[c] (°C)	Transition due to melting of crystallites[c] (°C)
EPDM	−26	–	Not detectable
Zinc sulfonated EPDM	−26	+27 to +80	+119
SE + paraffin oil (10 phr)	−34	+27 to +73	+99
SE + DMSO (10 phr)	−24	–	+89

[a] SE = zinc sulfonated EPDM
[b] From $(\tan\delta)_{max}$ in the plot of tan δ vs. temperature
[c] From the tan δ vs. temperature plot

mechanical analysis are summarized in *Table 1*. The melting of the crystallites occurs at a lower temperature in the presence of plasticizer, with this effect being more pronounced in the case of DMSO than oil.

Dielectric thermal properties

Figure 2 shows the tan δ *versus* temperature plots obtained from the dielectric thermal analysis study of EPDM and zinc sulfonated EPDM. In the case of EPDM the transition at 115°C is due to the melting of the crystalline zone of the polyethylene block. However, the zinc sulfonated EPDM shows two transitions, one at +122.7°C and another at a lower temperature of 57.4°C. The high-temperature transition is ascribed to the crystalline melting point, while the transition at the lower temperature is believed to be due to the ionic aggregates[15–17]. *Figure 3* shows the effects of plasticizers on the log (tan δ) *versus* temperature plots of zinc sulfonated EPDM. It is observed that the compound containing paraffin oil exhibits both transitions. However, the low-temperature transition due to the ionic aggregates is not detectable in the compound containing DMSO. Thus, paraffin oil plasticizes the material by affecting the hydrocarbon backbone, but does not break up the structure of the ionic associations. On the other hand, DMSO does not affect the non-ionic hydrocarbon backbone, but clearly plasticizes the ionic domains. probably through the solvation of ions. The results from dielectric thermal analyses confirm the observations made in the case of dynamic mechanical analysis study.

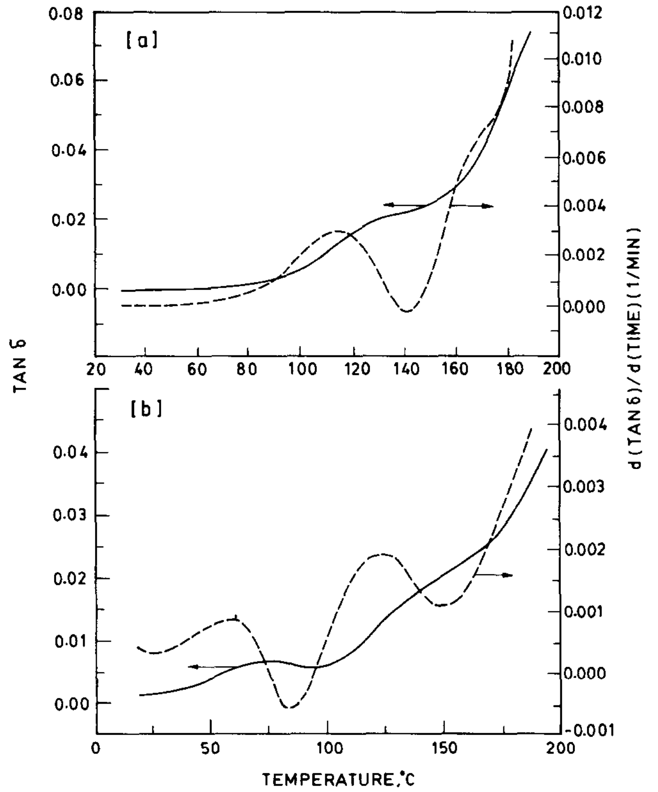

Figure 2 Temperature dependence of dielectric loss tangent (tan δ): (a) EPDM at 1 Hz; (b) zinc sulfonated EPDM at 100 Hz

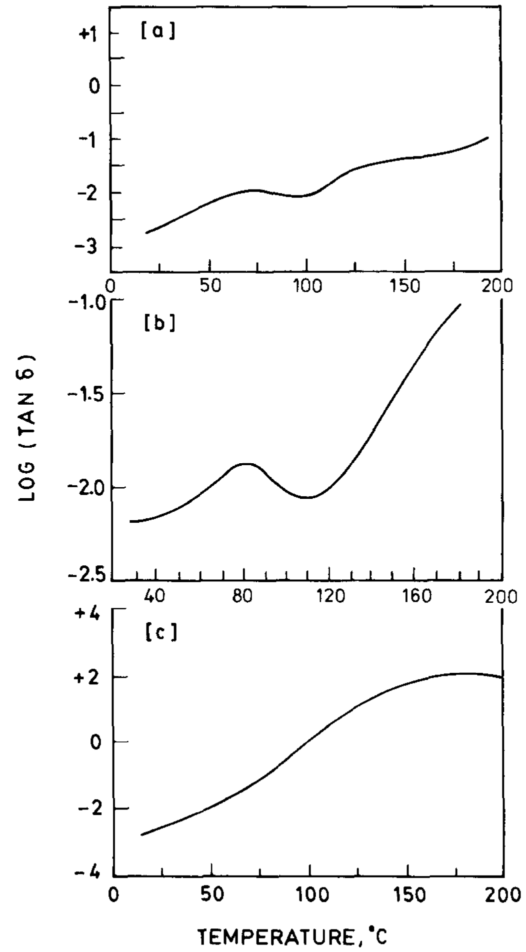

Figure 3 Semilogarithmic plots of dielectric loss tangent (tan δ) vs. temperature: (a) zinc sulfonated EPDM; (b) zinc sulfonated EPDM + 10 phr paraffin oil; (c) zinc sulfonated EPDM + 10 phr DMSO (all measurements made at 100 Hz)

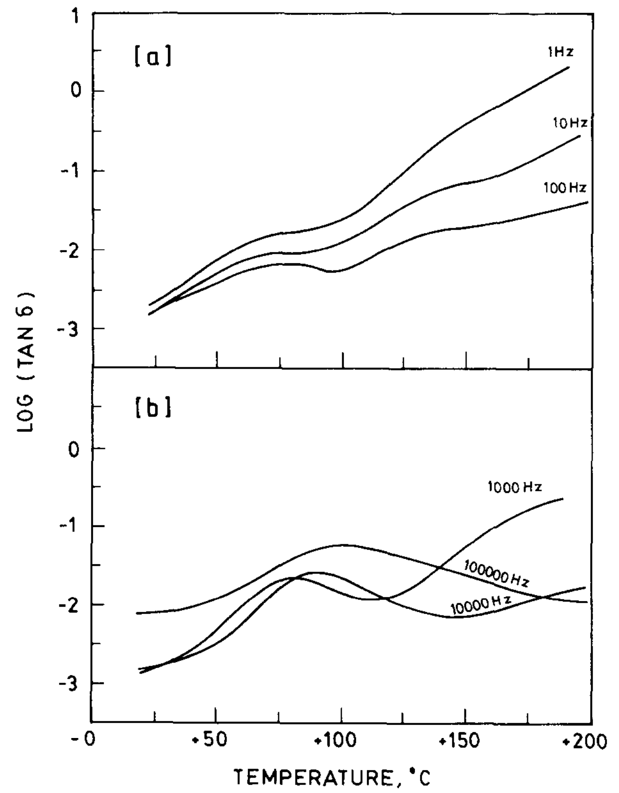

Figure 4 Frequency dependence of dielectric loss tangent (tan δ) for zinc sulfonated EPDM at: (a) 1–100 Hz; (b) 1–100 kHz

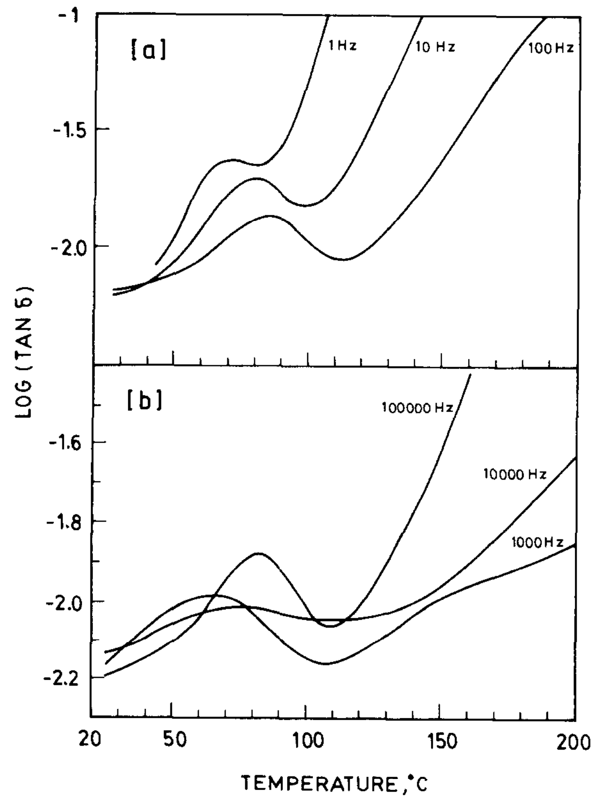

Figure 5 Frequency dependence of dielectric loss tangent (tan δ) for zinc sulfonated EPDM containing 10 phr paraffin oil at: (a) 1–100 Hz; (b) 1–100 kHz

Figures 4–6 show the log tan δ *versus* temperature plots obtained from dielectric thermal analysis of zinc sulfonated EPDM and the corresponding plasticized compounds at frequencies ranging from 1 to 100 Hz and from 1 to 100 kHz. The compound containing DMSO showed no ionic transitions even at very high frequencies. However, zinc sulfonated EPDM and the compound containing paraffin oil showed ionic transitions at all frequencies. It was also observed that the temperatures corresponding to these ionic transitions shifted to higher values with the increase in frequency.

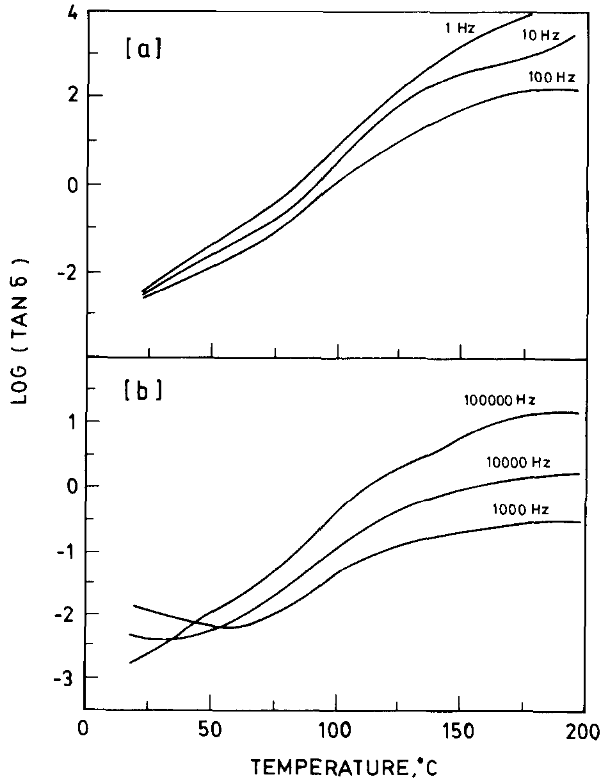

Figure 6 Frequency dependence of dielectric loss tangent (tan δ) for zinc sulfonated EPDM containing 10 phr DMSO at: (a) 1–100 Hz; (b) 1–100 kHz

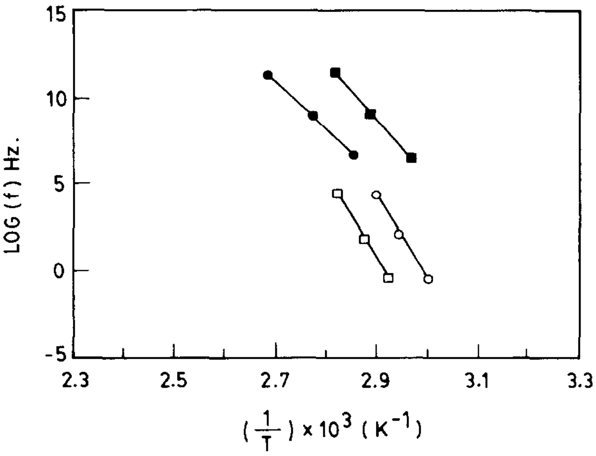

Figure 7 Plots of log (frequency) vs. $1/T_{max}$ for: (–○—○—○–) zinc sulfonated EPDM, 1–100 Hz; (–●—●—●–) zinc sulfonated EPDM, 1–100 kHz; (–□—□—□–) zinc sulfonated EPDM + 10 phr paraffin oil, 1–100 Hz; (–■—■—■—■–) zinc sulfonated EPDM + 10 phr paraffin oil, 1–100 kHz

Table 2 Activation energies of the ionic transitions obtained from d.e.t.a. studies[a]

Sample	E_{act} (kcal mol^{-1}) Frequency range; 1–100 Hz	Frequency range; 1–100 kHz
Zinc sulfonated EPDM	90.9	54.1
SE + Paraffin oil (10 phr)	92.2	65.4
SE + DMSO (10 phr)	No transition	No transition

[a] SE = zinc sulfonated EPDM

[b] Calculated from the plots of log(frequency) vs. $1/T_{max}$

The thermal activation of dipolar relaxation often follows the well known Arrhenius law, where the activation energy (E_{act}) can be calculated from the slope in the plot of $\log f$ *versus* $1/T_{max}$, where f represents the measurement frequency and T_{max} the temperature corresponding to the maximum in the log(tan δ) *versus* temperature plot at that particular frequency[19,20]. Arrhenius plots of log (frequency) *versus* $1/T_{max}$, obtained from the corresponding ionic peaks in the log(tan δ) *versus* temperature plots are shown in *Figure 7*. Since the Arrhenius plots show two slopes, both in the case of zinc sulfonated EPDM and the compound containing paraffin oil, it can be inferred that there exists two types of ionic transition, one occurring in the frequency range from 1 to 100 Hz and the other in the range from 1 to 100 kHz. The activation energies of the ionic transitions calculated from the slopes of the Arrhenius plots are given in *Table 2*. The transitions at lower frequencies show higher activation energy values than those at higher frequencies.

These observations can be explained on the basis of the 'shell–core model' for the distribution of salt groups in ionomers[21–23]. The shell–core model postulates that in the dry state a cluster of ~0.1 nm in radius is shielded from the surrounding matrix ions that are not incorporated into the clusters by a shell of hydrocarbon chains. The surrounding matrix ions which cannot approach the cluster more closely than the outside of the hydrocarbon shell will be attracted into the cluster by electrostatic forces. The matrix ions associate to form multiplets which act as ionic crosslinks and affect the properties of the matrix. The low-frequency transitions for the ionic groups at low temperatures, which were observed to occur in the case of zinc sulfonated EPDM and the oil-containing compound might be attributed to the polar groups (multiplets) present in the matrix and the high-frequency transition occurring at higher temperatures might be originating

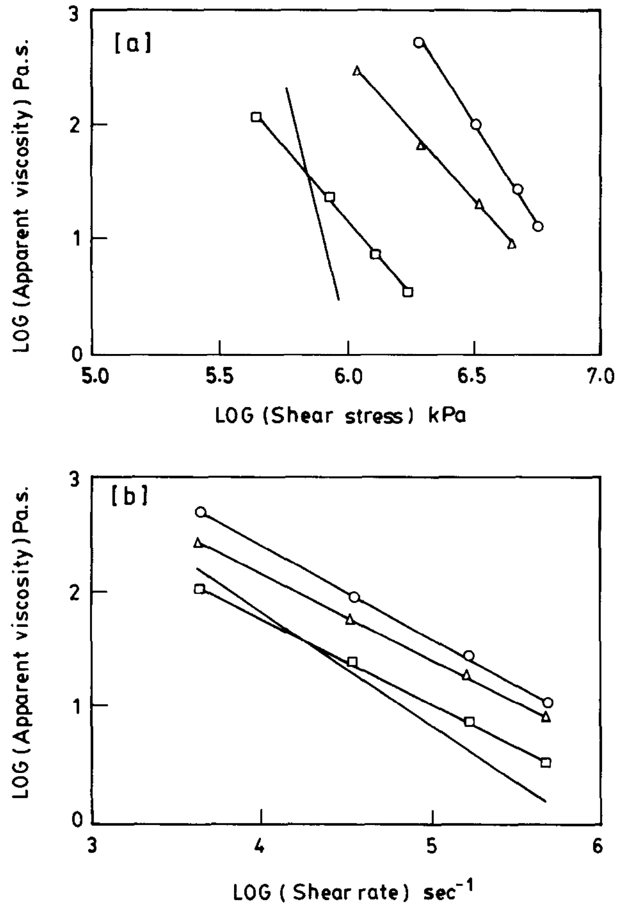

Figure 8 Plots of apparent viscosity *versus* (a) shear stress and (b) shear rate at 170°C: (———) EPDM; (-o—o—o-) zinc sulfonated EPDM; (-△—△—△-) zinc sulfonated EPDM + 10 phr paraffin oil; (-□—□—□-) zinc sulfonated EPDM + 10 phr DMSO

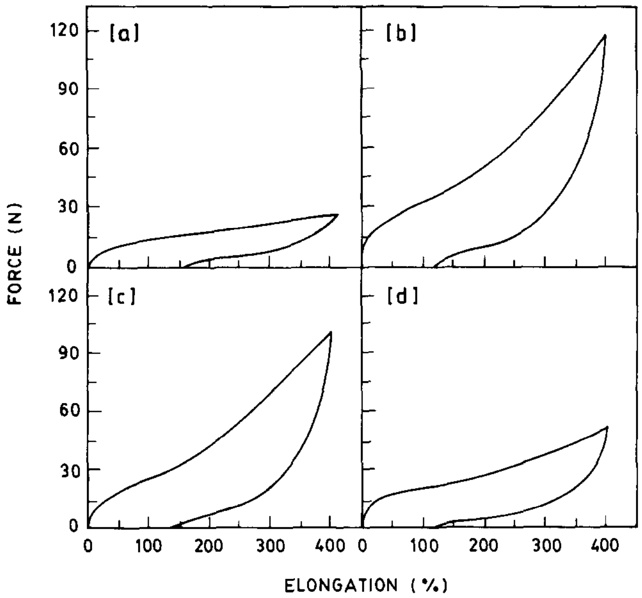

Figure 9 Hysteresis plots for: (a) EPDM; (b) zinc sulfonated EPDM; (c) zinc sulfonated EPDM + 10 phr paraffin oil; (d) zinc sulfonated EPDM + 10 phr DMSO

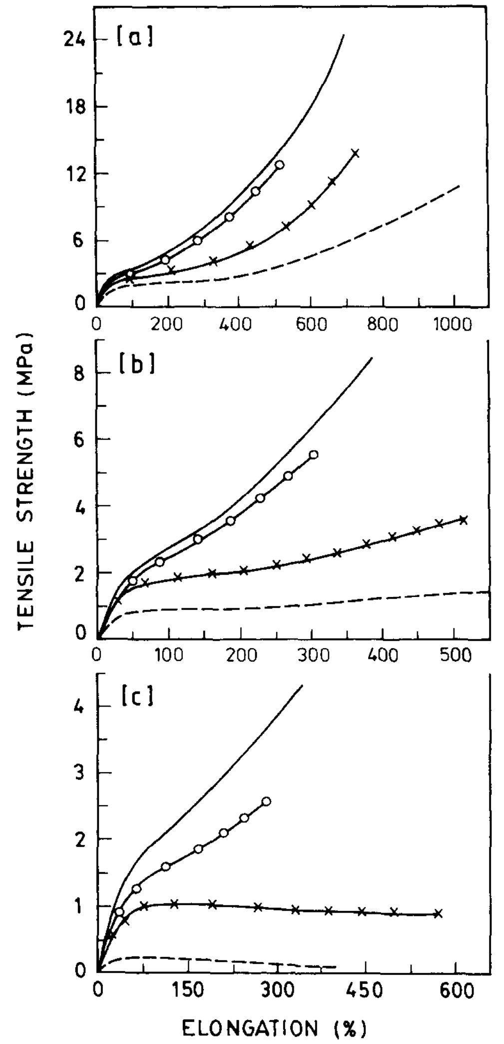

Figure 10 Stress–strain plots at (a) 25, (b) 50, and (c) 70°C for: (- - - - - -) EPDM; (———) zinc sulfonated EPDM; (–o—o—o–) zinc sulfonated EPDM + 10 phr paraffin oil; (–x—x—x–) zinc sulfonated EPDM + 10 phr DMSO

from the larger aggregates or clusters. In the presence of paraffin oil, the activation energy of the high-frequency transition increases, while the activation energy of the low-frequency transition remains almost unchanged. Although the reason for such behaviour is not fully understood, it appears that the presence of non-polar oil may alter the environment around the clusters, while the more aggregated multiplets remain unaffected by its presence.

Processability

Figure 8 shows the log–log plots of apparent viscosity *versus* shear stress and shear rate. The reduction in viscosity with increasing shear stress is due to the pseudoplastic nature of the compounds. At all shear stresses and shear rates the plasticized compounds show lower viscosities than the unplasticized zinc sulfonated EPDM, with the viscosity values following the order, unplasticized > oil > DMSO. In conformity with the results of d.m.a. and d.e.t.a. studies, disruption of the ionic aggregates of the zinc sulfonated EPDM by DMSO causes a sharp fall in the viscosity. It is apparent that the plasticization of ionic domains by 10 phr of DMSO is more efficient than the plasticization of the backbone hydrocarbon by 10 phr of paraffin oil.

Physical properties

The results of hysteresis studies are shown in *Figure 9*. The area under the hysteresis curve is lowest for EPDM and highest for zinc sulfonated EPDM. Although the plasticized compounds show a lower hysteresis than the neat zinc sulfonated EPDM, the compound containing DMSO shows a lower hysteresis than the compound containing paraffin oil. The high value of the hysteresis shown by zinc sulfonated EPDM compared to EPDM is due to the additional energy dissipation mechanisms operating in the former[24], because the ionic aggregates may be considered to behave as ultrafine particles of a reinforcing filler in the host polymer, in addition to acting as multifunctional crosslinks[25]. The reduction in

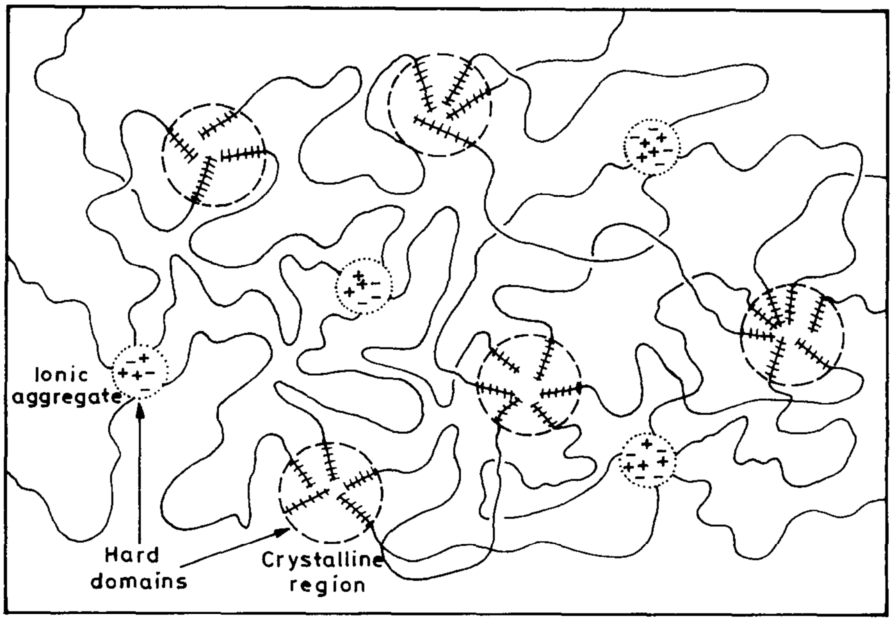

Figure 11 Schematic representation of the morphological structure of zinc sulfonated EPDM containing 75 wt% ethylene

hysteresis shown by the compounds containing paraffin oil and DMSO may be attributed to the plasticization of the hydrocarbon backbone, and the ionic aggregates, respectively.

Figure 10 shows the tensile stress–strain behaviour of EPDM, zinc sulfonated EPDM and the plasticized compounds, at 25, 50, and 70°C. Modulus and tensile strength values are higher in the case of the zinc sulfonated EPDM, when compared to EPDM, at all three temperatures. Zinc sulfonated EPDM showed less reduction in tensile strength at higher temperatures compared to EPDM. This is attributed to the presence of physical crosslinks or hard domains in the polymer which arise out of the ionic aggregates and crystalline regions. The presence of the ionic aggregates makes the matrix rigid, therefore enabling the crystalline regions to exert their influence, which is not observable in the case of EPDM. The morphological structure in zinc sulfonated EPDM is believed to be similar to that of conventional thermoplastic elastomers, i.e. a combination of hard domains and soft segments, as depicted in *Figure 11*. Both the plasticizers cause a reduction in the physical properties at the three test temperatures, which is due to plasticization of the main chain in the case of paraffin oil and disruption of ionic structure in the case of DMSO. When compared to the paraffin oil, DMSO causes a greater reduction in the physical properties at higher temperatures.

CONCLUSIONS

Zinc sulfonated EPDM containing 75 wt% ethylene behaves as an ionic thermoplastic elastomer. Dynamic mechanical analysis of zinc sulfonated EPDM shows two transitions in addition to the T_g, which are ascribed to the presence of ionic aggregates and the melting of the crystallites. Paraffin oil acts as the backbone plasticizer and DMSO acts as the ionic domain plasticizer. Results from dielectric thermal analysis indicate the existence of two types of ionic aggregates in zinc sulfonated EPDM. Studies involving the Monsanto processability tester show that both paraffin oil and DMSO reduce the melt viscosity of the zinc sulfonated EPDM, with the reduction being higher in the case of DMSO. Zinc sulfonated EPDM shows a higher hysteresis when compared to EPDM. Although oil and DMSO cause a reduction in the hysteresis, modulus and tensile strength of zinc sulfonated EPDM, this reduction is more pronounced in the case of DMSO, due to plasticization of the ionic domains.

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