Ionic Thermoplastic Elastomer Based on the Zinc Salt of Sulfonated Maleated EPDM Rubber. I. Effect of Zinc Stearate on Melt-Flow Behavior, and Dynamic Mechanical, Dielectric, and Physical Properties

SWAPAN K. GHOSH, P. P. DE, D. KHASTGIR, S. K. DE*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur-721302, India

ABSTRACT: The effects of zinc stearate on the properties of a new type of ionomer, namely, zinc salt of sulfonated maleated EPDM rubber (Zn-s-m-EPDM), were studied. The activation energy for viscous flow decreases in the presence of zinc stearate. Dynamic mechanical thermal analyses (DMTA) reveal that incorporation of zinc stearate causes an increase in E' at room temperature, but a sharp fall in E' at higher temperature ($>100°C$). While zinc stearate functions as a low reinforcing filler under ambient conditions, it acts as a plasticizer for the ionomer above its melting point ($\geq 128°C$). The ionomer registers two peaks in the tan δ versus temperature plots, the low-temperature peak corresponding to the glass–rubber transition and the high-temperature peak corresponding to the relaxation of the immobile segments of the polymer chains adjacent to the ionic aggregates. Incorporation of zinc stearate strengthens the biphasic structure of the ionomer, as indicated by the increase in tan δ at the high-temperature relaxation temperature (T_i) and decrease in tan δ at the glass–rubber transition temperature (T_g). Dielectric thermal analyses (DETA) reveal that beyond its melting point ($\geq 128°C$) zinc stearate acts as a plasticizer for Zn-s-m-EPDM. Incorporation of zinc stearate increases marginally the physical properties of the ionomer which displays the thermoplastic elastomeric characteristics. Reprocessability studies of the zinc stearate-filled composition show that the ionomer can be recycled without a decrease in properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 743–750, 2000

Key words: sulfonated maleated ionomer; zinc stearate; dynamic mechanical thermal analysis; dielectric thermal analysis; processability, physical properties; ionic thermoplastic elastomer

INTRODUCTION

Modifying a polymer into an ionomer results in a substantial increase in melt viscosity and physical properties.[1–4] This is due to the forma-

tion of physical crosslinks arising out of strong intermolecular ionic interactions. The flow behavior of ionomers is governed by several factors including type of polymer backbone, types of counterions, degree of neutralization, and presence of plasticizers.[5–8] The rheological behavior of carboxylated polystyrene and sulfonated polystyrene was studied by Lundberg et al.[9] They concluded that the sulfonate ionomers are strongly associated and possess higher melt
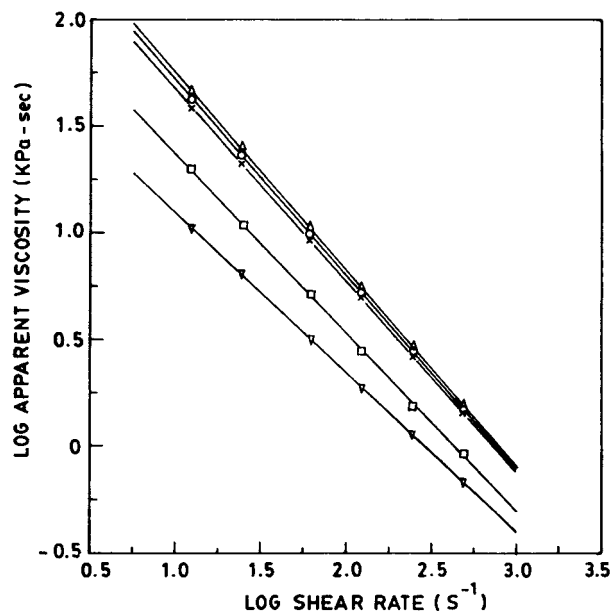

Figure 1   Plots of log apparent viscosity (η) versus log apparent shear rate (s^{-1}) of (—△—) Zn-s-m-EPDM, (—○—) Zn-s-m-EPDM + 10 phr zinc stearate, (—×—) Zn-s-m-EPDM + 20 phr zinc stearate, (—□—) Zn-s-m-EPDM + 30 phr zinc stearate, and (—▽—) Zn-s-m-EPDM + 40 phr zinc stearate.

viscosity than that of the corresponding carboxylated ionomers. They also studied plasticization of metal sulfonated EPDM rubber with various stearic acid derivatives.[10] Duvdevani and coworkers studied the plasticization effect of zinc stearate on the properties of zinc salt of a sulfonated EPDM ionomer.[11] Datta et al. made similar studies on zinc salt of maleated EPDM rubber.[12] Makowski and Lundberg studied the effects of zinc stearate on sulfonated ionomers containing different metal cations.[13] Since a high concentration of the ionic groups in the sulfonate ionomer results in gel formation,[14–16] a combination of carboxylated and sulfonated groups provide an opportunity to increase the concentration of ionic groups without adversely affecting the processing behavior. Sulfonation of maleated EPDM rubber, followed by its neutralization, provides an opportunity to prepare an ionomer containing both sulfonated and carboxylated groups on the same polymer backbone. The present article reports the results of studies on the effect of zinc stearate on the rheological, physicomechanical, and dielectric properties of a new ionomer, namely, zinc salt of sulfonated maleated EPDM rubber, abbreviated Zn-s-m-EPDM.
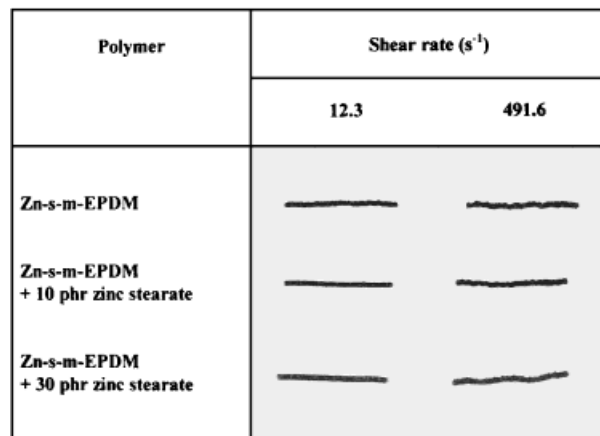

Figure 2   Photomicrographs of representative extrudates at 190°C and at different shear rates.

EXPERIMENTAL

Materials

Maleated EPDM rubber, abbreviated m-EPDM (trade name, Royaltuff 465; Uniroyal Chemical Co., Naugatuck, CT), had a number-average molecular weight (M_n) of 1.16×10^5, and its weight-average molecular weight (M_w) was 3.99×10^5. It contains 55 wt % of ethylene, 45 wt % of pro-
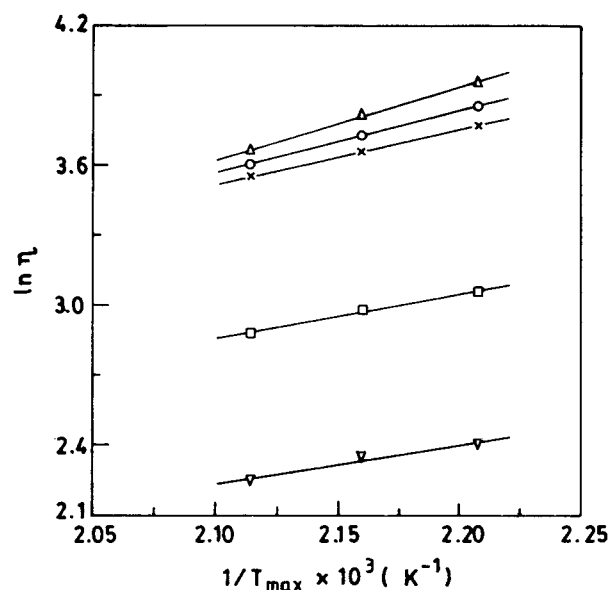
Figure 3   Arrhenius plots showing variation of ln apparent viscosity (η) versus $1/T_{max}$ for (—△—) Zn-s-m-EPDM, (—○—) Zn-s-m-EPDM + 10 phr zinc stearate, (—×—) Zn-s-m-EPDM + 20 phr zinc stearate, (—□—) Zn-s-m-EPDM + 30 phr zinc stearate, and (—▽—) Zn-s-m-EPDM + 40 phr zinc stearate.

Table I   Activation Energy for Viscous Flow (kJ/mol) of Zn-s-m-EPDM

Shear Rate (s^{-1})	Loading of Zinc Stearate (phr)[a]				
	0	10	20	30	40
12.3	26.4	22.2	19.6	15.9	10.9
491.6	21.7	18.8	15.5	12.1	7.9

[a] phr means parts per hundred parts of rubber (by weight).

pylene, and 5 mol % of diene. The maleic anhydride/maleic acid level was 1 mol %. The chemicals used were of analytical grade.

Preparation of Ionomer

Sulfonated maleated EPDM rubber, abbreviated s-m-EPDM, was prepared by the method described elsewhere.[17,18] s-m-EPDM was solubilized in tetrahydrofuran (THF) and neutralized by zinc acetate. The product was steam-stripped, washed thoroughly with boiling water until free from zinc acetate, and dried at 70°C in a vacuum. The product was abbreviated Zn-s-m-EPDM.

Processability Studies

Processability studies were made in a Monsanto processability tester (MPT), which is an automatic high-pressure viscometer. The entire barrel and capillary were electrically heated by a microprocessor-based temperature controller.[19] The capillary length-to-diameter ratio was 30 : 1. The preheat time was 5 min. The melt rheological behavior was studied at six shear rates and at temperatures of 180, 190, and 200°C.

Infrared Spectroscopic Studies

Infrared spectra of compression-molded films (thickness, ~0.4 mm) were taken in a Perkin–Elmer (Model 843) spectrophotometer at a resolution of 3.2 cm^{-1}.

Dynamic Mechanical Analysis

Dynamic mechanical properties were measured in a dynamic mechanical thermal analyzer (MK-II, Polymer Laboratories, UK) in a shear mode at a frequency of 10 Hz and at a 64-μm peak-to-peak strain. The heating rate was 2°C min^{-1}.

Dielectric Thermal Analysis

A dielectric thermal analyzer DEA 2970 from TA Instruments Inc. (USA), coupled with a 2000

thermal analyzer, was used to measure the dielectric properties of the samples. The experiment was carried out at variable frequencies ranging from 1 to 10^5 Hz, using a temperature range of −150 to +200°C at a heating rate of 3°C min^{-1} in a nitrogen atmosphere.

Measurement of Physical Properties

The stress–strain properties of the samples were measured with dumbbell samples according to ASTM D412 (1987) in a Zwick UTM (Model 1445) at a crosshead speed of 500 mm/min. The hardness of the samples was determined as per ASTM D2240 (1986) and expressed in Shore A units. Tear strength was also measured in a Zwick UTM (Model 1445) according to ASTM D624 (1986). The tension set at 100% extension was determined according to ASTM D412 (1987). The swelling experiment was carried out by immersing the polymers in cyclohexane for 48 h at room temperature.

Reprocessability Studies

The reprocessability studies were made by extruding the sample through the MPT device at 190°C and at a shear rate of 61.5 s^{-1}. The extrudate was reextruded under similar conditions and the process was repeated for three consecutive cycles. The preheat time for the sample before each extrusion was 10 min. The tensile strength of the extrudate from each cycle was measured after a resting period of 24 h at 25°C.

RESULTS AND DISCUSSION

Processability Studies

Figure 1 shows the log–log plots of the apparent viscosity versus the apparent shear rate at 190°C. It is evident that the polymers behave as pseudoplastic fluids and the viscosity decreases with increase in the shear rate. The melt vis-

cosity of the ionomer (Zn-s-m-EPDM) is found to decrease gradually with increasing zinc stearate loading. Zinc stearate above its melting point (>128°C) is known to plasticize ionomers and enhances the flowability of the system.[12,20] Photomicrographs of the extrudates at different shear rates are shown in Figure 2. The ionomer in the absence of zinc stearate shows melt fracture at all shear rates. Incorporation of zinc stearate increases the surface smoothness of the extrudates and no melt fracture occurs in the presence of zinc stearate. Expectedly, the viscosity decreases with increase in temperature. The activation energy for melt flow, which is shear-rate-dependent, was calculated on the basis of the Arrhenius equation[21]:

$$\eta = Ae^{E/RT} \tag{1}$$

where η is the apparent viscosity at a temperature T (K); A, the frequency factor; E, the activation energy for melt flow; and R, the universal gas constant. The activation energy was calculated from the plots of ln η versus $1/T$ (Fig. 3) and the results are summarized in Table I. It is apparent that shear-rate-dependent activation energy decreases with increase in the shear rate and zinc stearate loading.

Infrared Spectroscopic Studies

Infrared spectra of the ionomer (Zn-s-m-EPDM), the zinc stearate, and the ionomer composition containing 30 phr of zinc stearate are shown in Figure 4. The ionomer shows an absorbance band at 1585 cm^{-1} which is due to the symmetric stretching vibration of carboxylate anions.[22] However, the bands at 1144 and 1200 cm^{-1} are due to the asymmetric stretching of the sulfonate groups, whereas the absorbance band at 1246 cm^{-1} is due to CH$_2$— wagging motions.[23] The bands at 1030 and 1057 cm^{-1} are due to the symmetric stretching vibration of the sulfonate anions.[24] Zinc stearate shows the characteristic absorbance peak at 1577 cm^{-1}, which is believed to be due to the asymmetric stretching of the bridging type of carboxylate groups.[25] However, the spectra of the zinc stearate-filled ionomer does not show the characteristic features of the neat ionomer and zinc stearate. It shows an absorbance band at 1588 cm^{-1} which is due to the tetrahedral zinc carboxylate salts and the doublet at 1547/1528 cm^{-1} which is believed to be due to the octahedral zinc carboxylate salts.[22] However,
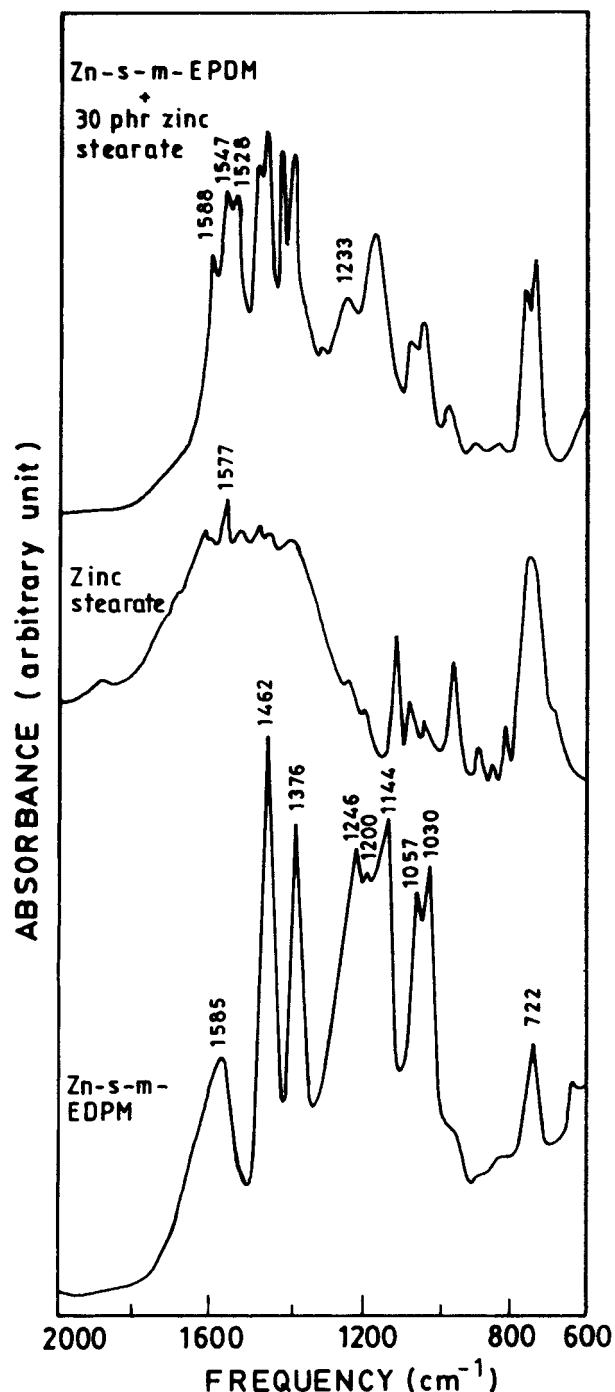

Figure 4 Infrared spectra of Zn-s-m-EPDM, zinc stearate, and Zn-s-m-EPDM + 30 phr zinc stearate.

the absorbance band at 1233 cm^{-1} is due to the asymmetric stretching vibration of the sulfonate anion of the zinc sulfonate groups.[24] Thus, it can be concluded that there exists an ion–ion type of interaction between zinc stearate and the ionic aggregates.
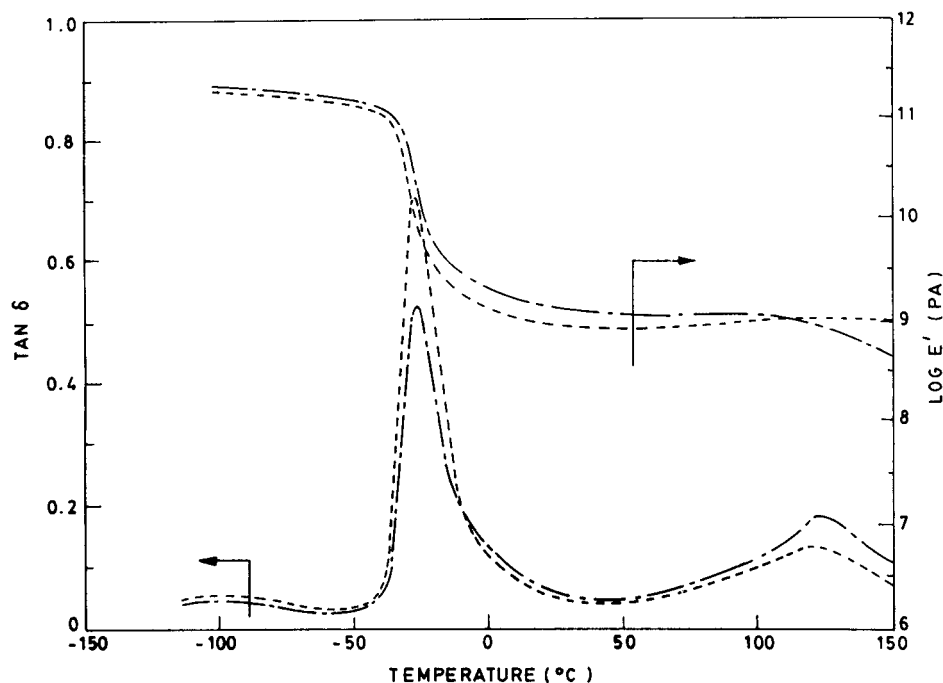
Figure 5 Plots of tan δ and log E' versus temperature for $(----)$ Zn-s-m-EPDM and $(-\cdot-)$ Zn-s-m-EPDM + 30 phr zinc stearate.

Dynamic Mechanical Thermal Analysis

Representative plots of mechanical loss (tan δ) versus temperature are shown in Figure 5. Apart from the glass–rubber transition (the corresponding temperature being abbreviated as T_g), an additional transition in the high temperature region occurs (the corresponding temperature abbreviated as T_i), which is believed to be due to relaxation of the immobile chain segments adjacent to the ionic aggregates.[26-28] The results of dynamic mechanical thermal analyses are summarized in Table II. Since zinc stearate acts as a mild reinforcing filler, it decreases tan δ at T_g, but T_g remains unaltered. Furthermore, zinc stearate is

known to interact strongly with the ionic domains and strengthens the biphasic structure of the ionomer.[10,12] Thus, incorporation of zinc stearate causes increase in tan δ at T_i and T_i shifts to the high-temperature side. Figure 5 also shows the variation of the storage modulus (E') versus the temperature for the polymers. It is evident that the addition of zinc stearate causes an increase in E' at room temperature, but a sharp fall in E' above 100°C occurs, indicating onset of the transition from the rubbery to the viscous flow state. It is known that molten zinc stearate acts as an ionic plasticizer[11,12] and melting of zinc stearate in the presence of the ionic elastomer is likely to

Table II   Results of Dynamic Mechanical Thermal Analyses

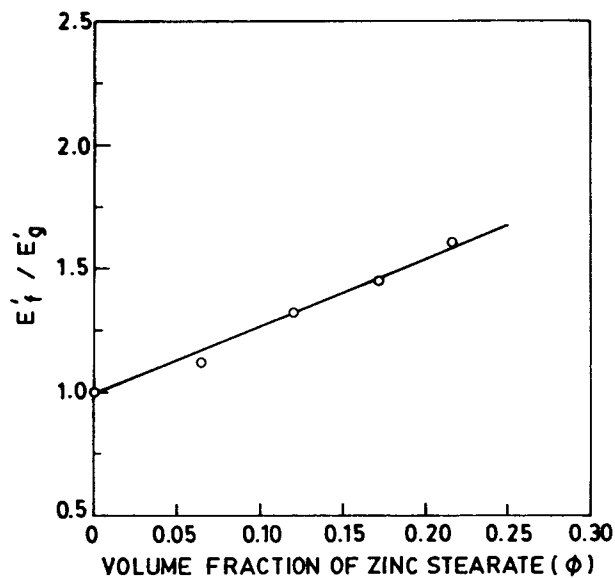| Polymer	T_g (°C)	tan δ at T_g	T_i (°C)	tan δ at T_i	Storage Modulus (Pascal) $\times 10^8$ 25°C	140°C
Zn-s-m-EPDM	−27.4	0.69	119.6	0.14	8.9	9.6
Zn-s-m-EPDM + 30 phr zinc stearate	−26.1	0.52	123.8	0.18	13.1	5.6

[a] No high-temperature (ionic) transition.

Figure 6   Variation of E_f'/E_g' against volume fraction (ϕ) of zinc stearate at 25°C.

occur at a lower temperature (<120°C). It is also observed that the rate of the decrease of E' increases with increase in zinc stearate loading. The dependence of the room-temperature storage modulus on zinc stearate loading is shown in Fig-

ure 6. The results could be fitted by the following equation:

$$E_f'/E_g' = 1.0 + 2.86\phi \qquad (2)$$

where E_f' is the storage modulus of the zinc stearate-filled ionomer and E_g' refers to the storage modulus of the neat ionomer and ϕ is the volume fraction of zinc stearate. The equation is very similar to the relationship proposed by Smallwood in the case of reinforced diene rubbers.[29]

Dielectric Thermal Analysis

The variation of the dielectric constant or permittivity (ε') with temperature for Zn-s-m-EPDM and zinc stearate-filled Zn-s-m-EPDM is shown in Figure 7. It is evident that ε' decreases with increase in the temperature to about 100°C. Also, as the temperature increases, there is an increase in the volume and, consequently, there is a decrease in the number of dipoles per unit volume (dipole density) and so ε' decreases with increase in the temperature, which is a common phenomenon for nonpolar and slightly polar polymers.[30–32] A further increase in temperature causes a decrease in ε' for Zn-s-m-EPDM. This is because the ionic
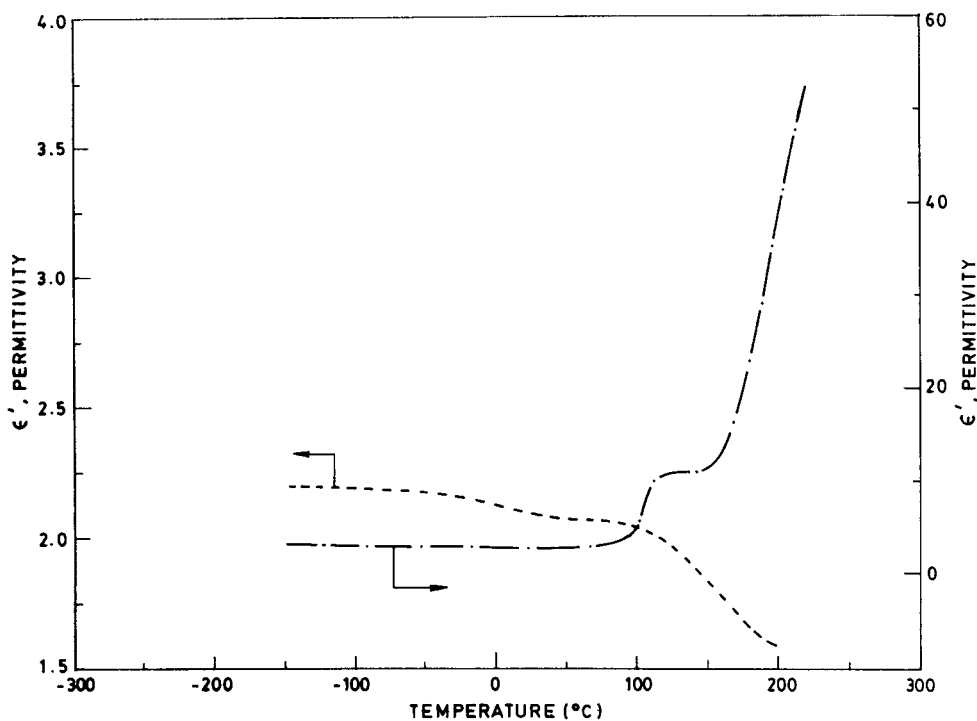

Figure 7   Plots for permittivity (ε') versus temperature for (— — —) Zn-s-m-EPDM and (— · —) Zn-s-m-EPDM + 30 phr zinc stearate.
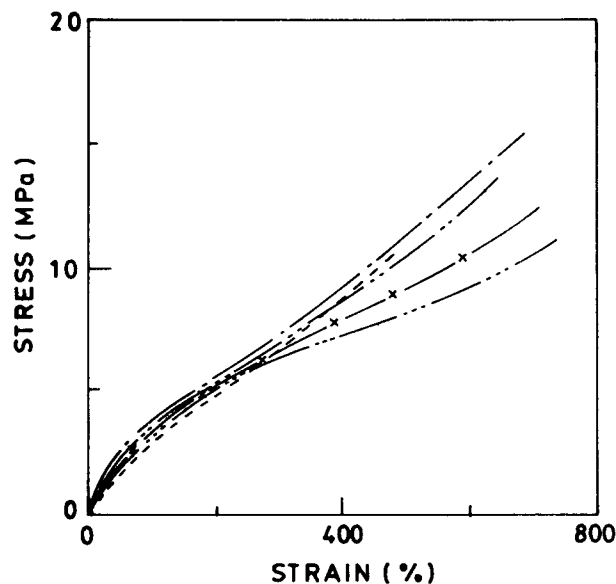
Figure 8 Stress–strain plots of (— — —) Zn-s-m-EPDM, (— – – – —) Zn-s-m-EPDM + 10 phr zinc stearate, (—✕—) Zn-s-m-EPDM + 20 phr zinc stearate, (— – —) Zn-s-m-EPDM + 30 phr zinc stearate, and (— – – —) Zn-s-m-EPDM + 40 phr zinc stearate.

groups present act as physical crosslinks and restrict the chain mobility which hinders the process of dipole orientation under the electric field. However, at higher temperature, zinc stearate melts and plasticizes the ionic aggregates, thereby breaking down the physical crosslinks. Thus, the zinc stearate-filled system shows an appreciable increase in ε' against temperature in the high-temperature region.

Physical Properties

Stress–strain plots of the polymers at room temperature are shown in Figure 8, and their physi-

cal properties are summarized in Table III. As the loading of zinc stearate increases, the following properties gradually increase to 30 phr and then decrease: tensile strength, modulus, tear resistance, hardness, and elongation at break. At room temperature, zinc stearate facilitates the formation of ionic aggregates through interionic interaction, thus strengthening the physical crosslinks and reducing the percent of volume swell in the solvent. The increase in elongation at break and tension set are probably due to the occurrence of the stress-induced ion-exchange reaction, slippage of the polymer chains over zinc stearate surface, and ion hopping.[9,33–36]

Reprocessability Studies

Since the polymer exhibits thermoplastic flow behavior, reprocessability studies were carried out with the ionomer filled with 30 phr of zinc stearate and the results are shown in Figure 9. Viscosity values during repeated extrusions and the tensile strength of the corresponding extrudates remain constant up to three cycles of extrusion through MPT.

CONCLUSIONS

Incorporation of zinc stearate causes a dramatic reduction in the melt viscosity of the ionomer (Zn-s-m-EPDM). While zinc stearate acts as an ionic plasticizer above its melting point ($\geq 128°C$), it functions as a low reinforcing filler at ambient conditions. The zinc stearate-filled ionomer can be reprocessed and behaves like a thermoplastic elastomer.

Table III   Physical Properties of Zn-s-m-EPDM

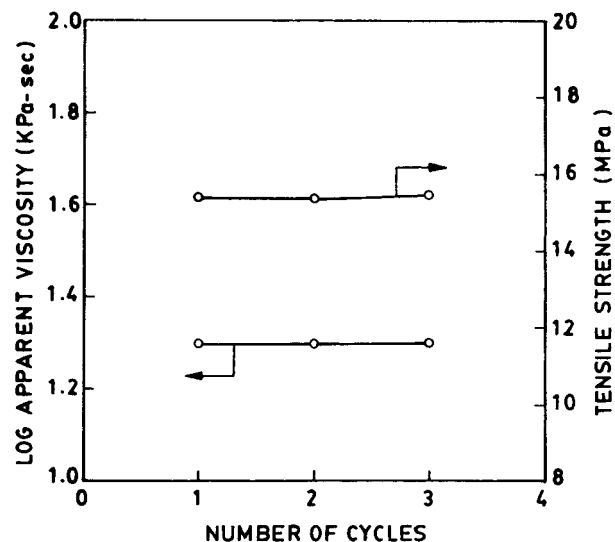| Properties	Zinc Stearate Loading (phr)				
	0	10	20	30	40
100% modulus (MPa)	2.5	3.1	3.4	3.8	3.6
200% modulus (MPa)	4.9	5.4	5.3	5.6	5.4
300% modulus (MPa)	6.9	6.2	6.7	7.3	7.0
Tensile strength (MPa)	10.5	11.4	12.6	15.4	13.8
Elongation at break (%)	491	749	716	690	651
Tear strength (kNm^{-1})	58	60	61	63	64
Tension set at 100% extension (%)	11	13	13	14	15
Hardness (Shore A)	59	61	63	63	66
Volume swell in cyclohexane (%)	58	53	49	29	26

Figure 9 Plots of log apparent viscosity (η) and tensile strength versus number of cycles of extrusion for Zn-s-m-EPDM + 30 phr zinc stearate.

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