

Ionic Thermoplastic Elastomer Based on Maleated EPDM Rubber. I. Effect of Zinc Stearate

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SYNOPSIS

Neutralization of maleated EPDM rubber by zinc oxide results in an ionic elastomer. The rate and extent of the neutralization reaction increase by addition of stearic acid. Although the rubber is not easy processable as such, incorporation of zinc stearate at a loading of 30 phr makes the rubber behave like a thermoplastic during high temperature ($\geq 150^\circ\text{C}$) processing. Furthermore, zinc stearate causes improvement in the physical properties of the rubber under ambient conditions. It is believed that zinc stearate acts as a reinforcing filler under ambient conditions and as a plasticizer for the ionic domains at higher temperature (that is, above its melting point, 128°C). The conclusions are based on the results of dynamic mechanical, rheological, and infrared spectroscopic studies. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymers can be modified by introduction of ionic groups.¹ The ionic polymers, also called ionomers, offer great potential in a variety of applications. Ionic rubbers are mostly prepared by metal ion neutralization of acid functionalized rubbers such as carboxylated styrene-butadiene rubber, carboxylated polybutadiene rubber and carboxylated nitrile rubber.²⁻⁵ Ionic rubbers under ambient conditions show moderate to high tensile and tear strength and high elongation. The ionic crosslinks are thermolabile and thus the materials can be processed like thermoplastics.⁶

Ethylene propylene diene monomer (EPDM) rubber, functionalized by sulfonation and maleation reactions form sulfonated and maleated EPDM rubber respectively. Ionic rubbers based on sulfonated EPDM rubber have been studied by several workers.⁷⁻¹⁰ Maleated EPDM rubber (m-EPDM), on the other hand, has not been exploited as a potential ionomer and has been mostly in use as a component in reactive blending, that is for the impact modification of nylon-66 or polybutadiene terephthalate.^{11,12} Kresge has reported studies on

physical and mechanical properties of m-EPDM based ionomers.¹³

This paper reports the results of studies on the physical, dynamic mechanical, and rheological behavior of zinc oxide neutralized m-EPDM, particularly in the presence of stearic acid and zinc stearate.

EXPERIMENTAL

Details of the materials used are given in Table I. Formulations of different mixes are shown in Table II.

m-EPDM was mixed with zinc oxide and other ingredients in a laboratory size two-roll mill at a nip gap of 2 mm. Cold water was circulated inside the rollers in order to prevent excessive temperature rise during mixing. Mixing schedule was as follows:

Mixing step	Time (min)
Add rubber and band	2
Add ZnO	2
Add stearic acid	2
Add zinc stearate	10
Sheet out	2

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Rheometric studies were done with a Monsanto moving die rheometer MDR-2000. The arc of oscil-

Table I Details of the Materials Used

Material	Supplier	Characteristics
Maleated EPDM (m-EPDM), trade name, Royaltuff 465	Uniroyal Chemical Co., Naugatuck, CT, U.S.A.	E/P ratio, 55 : 45; maleic content, 1%; Mooney viscosity, $ML_{(1+4)}$ 100°C, 80; Specific gravity, 0.89; Molecular weight, $M_w = 3.99 \times 10^5$, $M_n = 1.16$ $\times 10^5$
Zinc oxide (ZnO)	BDH Chemicals, Calcutta, India	Rubber grade; specific gravity, 5.6
Stearic acid	Obtained locally	Rubber grade; melting point, 76°C
Zinc stearate	Obtained locally	Rubber grade; melting point, 128°C
Dicumyl peroxide (DCP)	Obtained locally	40% DCP content
Dimethyl sulfoxide (DMSO)	E. Merck & Co., Calcutta, India	99% pure

lation of the die was $\pm 0.5^\circ$. The mixes were compression molded under a pressure of 10 MPa to form sheets of thickness of 2 mm. Molding temperatures and times are given in Table II.

The hardness was determined as per ASTM D-2240 (1986) and expressed in Shore A. The stress-strain properties were measured using dumbbell shaped specimens according to ASTM D412 (1987) in a Zwick universal testing machine (UTM), model 1445, at a crosshead speed of 500 mm/min. Hysteresis studies were made according to ASTM D412 (1980) by stretching the dumbbell shaped specimens up to an extension of 200%. Tear strength was measured in the Zwick UTM 1445 using a 90° nick cut-rescure sample according to ASTM D 624-86. The tension set at 100% extension was determined as per ASTM D-412 (1987).

Measurement of dynamic mechanical properties was carried out under tension mode using a visco-elastometer, namely, Rheovibron DDV-III-EP of M/s. Orientec Corporation, Tokyo, Japan. Sample size was 3.5 cm \times 6.5 mm \times 2 mm. Testing was carried out at a low amplitude 0.025 mm over a

temperature range of -100°C to $+200^\circ\text{C}$. Heating rate was $1^\circ\text{C}/\text{min}$ and frequency of oscillation was 3.5 Hz or 110 Hz.

Rheological and processability behavior were studied in a Monsanto processability tester (MPT), which is an automatic high pressure capillary viscometer. The entire barrel and capillary are electrically heated with a microprocessor based temperature controller.¹⁴ The capillary length to diameter ratio was 30 : 1. Preheat time for each sample was 5 min. Reprocessability studies were made by repeated extrusions, up to four cycles of the samples, through MPT at different shear rates.

Infrared (IR) spectroscopic studies were made with film specimens in a Perkin Elmer infrared spectrophotometer model 843, attached with a computer for data processing.

RESULTS AND DISCUSSION

Figure 1 shows the Monsanto rheographs of the different mixes. Increase in rheometric torque with

Table II Formulations of Mixes and Molding Conditions

Ingredient	Mix Number						
	EP0	EP1 ^a	EP2	EP3	EP4	EP5	EP6
m-EPDM	100	100	100	100	100	100	100
ZnO	—	10	10	10	10	10	10
Stearic acid	—	—	1	1	1	1	1
Zinc stearate	—	—	—	10	20	30	40
DCP	2.0	—	—	—	—	—	—
Molding temperature, ($^\circ\text{C}$)	150	170	120	120	120	120	120
Molding time, (min)	8	60	20	20	20	20	20

^a Mix No. EP1D is the same as EP1 but also contains 10 phr of DMSO.

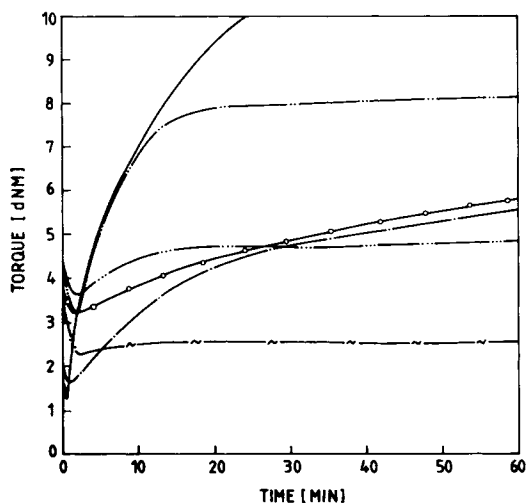


Figure 1 Monsanto rheographs of mixes at different temperatures. (— · — EP1, 120°C), (— · — EP1, 170°C), (— · · — EP2, 120°C), (— · · · — EP3, 120°C), (— ~ — EP5, 120°C), (— EP0, 150°C).

time shows gradual formation of the crosslinked structure which in the present case is attributed to the formation of ionic aggregates due to the metal carboxylate salt ($-\text{COO} \text{Zn}^{+2} \text{OOC}^-$) acting as physical crosslinks. The rate and extent of the reaction of m-EPDM with ZnO at 120°C is low. At 170°C, however, the rate increases and the extent of reaction becomes appreciable (Fig. 1). The increase in the rheometric torque (S') with time shows the occurrence of marching curing. This is understandable since m-EPDM contains both carboxylic acid as well as anhydride groups, as discussed later

under IR spectroscopic studies, and ZnO initially reacts with the carboxylic acid groups. The reaction of ZnO with the anhydride groups starts only after hydrolysis of the anhydride groups by the water liberated from the initial neutralization reaction. The reason of increase in reaction rate of m-EPDM with ZnO at higher temperature (i.e., 170°C) can be explained by taking into account the effect of the matrix viscosity. At 120°C the viscosity of the rubber is much higher compared to that at 170°C. Therefore, diffusion of ZnO is slower at 120°C, resulting in lower rate of the neutralization reaction. That the rate of the reaction in solid rubber is dependent on the matrix viscosity and the rate of diffusion of reactants has been reported earlier.¹⁵

Stearic acid which, is generally accepted as a reagent to prevent scorch in metal oxide-carboxylic rubber systems,^{16,17} greatly increases the rate and extent of the neutralization reaction in the present case even at 120°C.

Incorporation of zinc stearate causes lowering of the torque values as shown in the Monsanto rheographs (Fig. 1). As discussed later, zinc stearate does not prevent formation of ionic crosslinks, but causes plasticization of the ionic aggregates at high temperatures, presumably by solvation mechanism, thereby reducing the rheometric torque.

Physical properties of the different systems are listed in Table III. The m-EPDM-DCP system (mix EP0) was cured to the same level as the m-EPDM-ZnO (mix EP1) by choosing molding times so that the torque increase (that is, the difference between the maximum torque and the minimum torque) is

Table III Physical Properties

Properties	Mix Number						
	EP0	EP1	EP2	EP3	EP4	EP5	EP6
300% modulus (MPa)	0.70 (0.76)	1.70 (1.80)	2.20 (1.90)	2.60 (1.90)	2.80 (2.06)	2.90 (1.80)	2.90 (1.50)
Elongation (%)	580 (512)	850 (422)	620 (503)	880 (303)	800 (422)	760 (431)	710 (440)
Tensile strength (MPa)	0.89 (0.80)	4.40 (2.24)	5.80 (2.20)	7.15 (1.91)	8.54 (2.34)	7.67 (2.42)	6.34 (1.88)
Tear strength (N/cm)	143 (130)	332 (202)	370 (211)	381 (244)	400 (347)	418 (233)	422 (220)
Hysteresis loss (J/m^2) $\times 10^2$	3.3	4.5	7.0	9.0	10.0	10.7	13.9
Permanent set at 100% extension (%)	8	11	10	11	13	13	15
Hardness (Shore A)	40	47	53	56	58	62	64

Values in the parentheses are the results of tests done at 70°C.

same in both cases. As compared to the m-EPDM-DCP system, the m-EPDM-ZnO system shows higher hardness, modulus, tensile strength, and tear resistance presumably due to the presence of ionic clusters discussed later. The higher elongation at break in the m-EPDM-ZnO system is believed to be due to occurrence of stress-induced ion exchange, which causes lowering of stress concentration, resulting in high elongation.¹⁸ Typical plots of hysteresis studies are shown in Figure 2 and the results are summarized in Table III. Hysteresis follow the order $EP0 < EP1 < EP2 < EP3$. Hysteresis of the ionic system (EP1) is higher than that of the DCP-cured system (EP0). Reinforcing fillers in general are known to cause increase in hysteresis of rubbers. Accordingly, it is believed that the ionic aggregates in the m-EPDM-ZnO system act not only as crosslink sites, but also as fillers providing reinforcement to the matrix.¹⁹ The effect becomes more pronounced on addition of stearic acid and zinc stearate. As discussed earlier, incorporation of stearic acid facilitates formation of ion aggregates. It has been reported that at ambient conditions crystalline zinc stearate acts as reinforcing filler in metal oxide crosslinked carboxylic rubbers.²⁰ Results of measurements of physical properties at 70°C reveal that reinforcing ability of zinc stearate diminishes at higher test temperatures, presumably due to the onset of melting of zinc stearate and the consequent plasticization.

Figure 3 shows the variation of dynamic storage modulus (E') with temperature. As compared to the m-EPDM-DCP system, the m-EPDM-ZnO system shows a broad rubbery plateau, due to physical crosslinks arising out of the ionic aggregates. Addition of zinc stearate causes gradual increase in E'

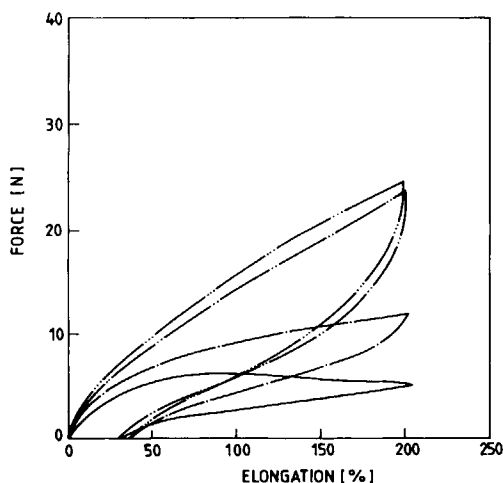


Figure 2 Hysteresis loops for different mixes. (— EP0), (--- EP1), (- · - · EP2), (- · · · - EP3).

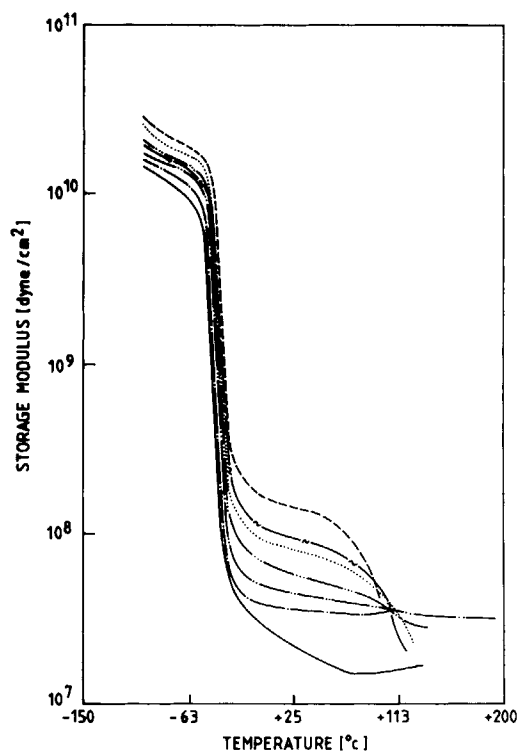


Figure 3 Plots of dynamic storage modulus against temperature at 3.5 Hz. (— EP0), (--- EP1), (- · - · EP2), (- · · · - EP3), (- · · · · EP4), (- ~ - EP5), (--- EP6).

at ambient temperatures, but sharp fall in E' at temperature exceeding 100°C, indicating onset of transition from the rubbery state to the viscous flow state. It is also evident that the rate of fall of E' increases with increase in zinc stearate loading. It is believed that at room temperature zinc stearate strengthens the ionic aggregates causing reinforcement of the matrix resulting in higher E' . But at temperatures approaching its melting point (i.e., 128°C) zinc stearate plasticizes the ionic aggregates, presumably by solvation or exchange reaction, as discussed later. In the absence of zinc stearate, plasticization cannot occur and accordingly the transition from the rubbery state to the viscous flow state is not observable under the conditions of temperature range and strain levels studied. The absence of the transition results in broad rubbery plateau in the m-EPDM-ZnO and m-EPDM-ZnO-stearic acid systems.

Figure 4(a) shows typical plots of $\tan \delta$ versus temperature, wherefrom it is evident that the glass to rubber transition in the m-EPDM-ZnO system occurs at a slightly higher temperature than the m-EPDM-DCP system. Furthermore, incorporation of stearic acid and zinc stearate shifts the glass-rubber transition temperature (T_g) of the m-EPDM-ZnO

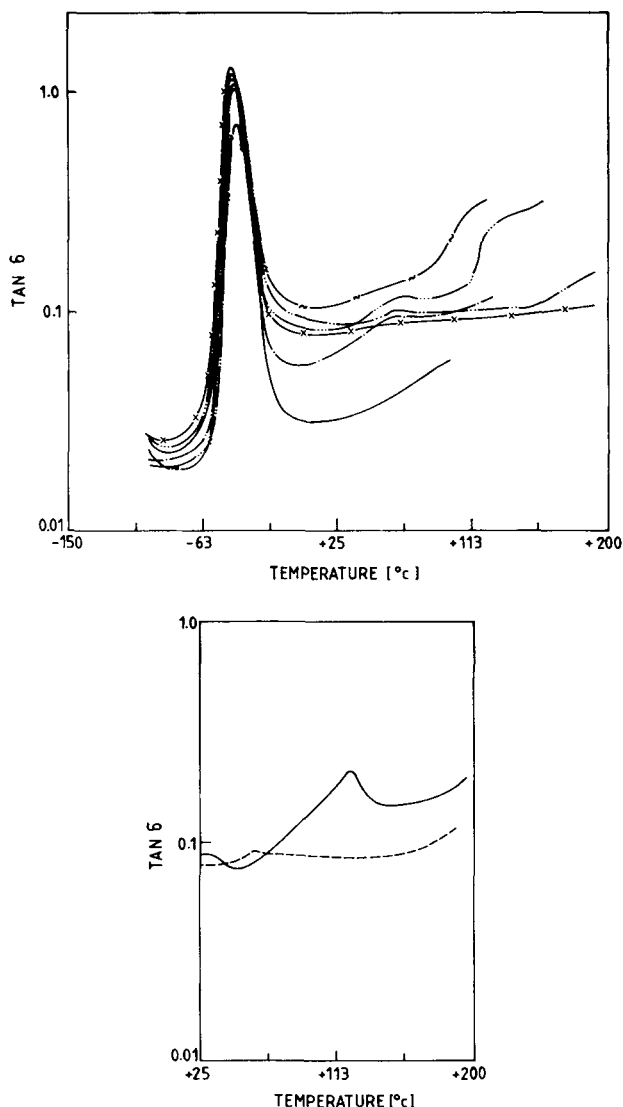


Figure 4 Plots showing variation of $\tan \delta$ against temperature. (a) (— EP0), (— · — EP1), (— × — EP1D), (— · · — EP2), (— · · · — EP3), (— ~ — EP5); (b) Mix EP2, — 110 Hz, --- 3.5 Hz.

system to the higher temperature side. The results are summarized in Table IV. The value of $\tan \delta$ at T_g (that is, $\tan \delta_{\max}$) decreases with the incorporation of stearic acid and zinc stearate. This indicates that with the introduction of stearic acid and zinc stearate, the chains become considerably tightened, and therefore, the backbone relaxation related to T_g occurs at slightly higher temperature with consequent lowering of $\tan \delta$ at T_g . In the high temperature region (that is, above room temperature) a second relaxation occurs, which is, however, not prominent in the m-EPDM-ZnO, and m-EPDM-ZnO-stearic acid systems. The high temperature relaxation becomes prominent in the presence of zinc

stearate. When the experiment with m-EPDM-ZnO-stearic acid system was conducted at a higher frequency (that is, 110 Hz) the transition becomes more prominent and it occurs around 100°C [Fig. 4(b)]. Characteristic features of the second transition is that the transition temperature, designated as T_i , shifts to higher temperature side with the incorporation of zinc stearate and the $\tan \delta$ value at T_i increases. At higher loading of zinc stearate (that is, 30 and 40 phr) $\tan \delta$ at T_i gets overshadowed by the rise in $\tan \delta$ due to early onset of melting of zinc stearate. The high temperature relaxation peak is believed to be due to onset of motion of chain segments firmly held by the ionic aggregates called clusters.^{21,22} Figure 5 is a model proposed for the different types of ionic aggregates in ionomers and the region of restricted mobility in the chain segment causing a biphasic structure.²² Restricted mobility region is separated from the "free" mobility region by a skin layer. Formation of the ionic clusters is favored by higher ion content, provided other factors remain same. That the high temperature relaxation is due to ionic clusters and not by any other relaxation of the base polymer is confirmed by the absence of the peak in the m-EPDM-DCP system and in the dimethyl sulfoxide (DMSO)-treated m-EPDM-ZnO system (mix EP1D). DMSO is known to exert profound solvation effect on the ionic clusters,²³ which counteracts the formation of restricted mobility zone.

Dependence of ratio of storage modulus at room temperature of filled system to gum system (E'_f/E'_g) on volume fraction (ϕ) of zinc stearate is shown in Figure 6. The results can be fitted into the following equations:

At room temperature,

$$\frac{E'_f}{E'_g} = 1.0 + 3.0\phi \quad (1)$$

Equation (1) is qualitatively similar to that proposed earlier by Smallwood.²⁴

Plots of $\tan \delta_f / \tan \delta_g$ versus volume fraction (ϕ) of zinc stearate are shown in Figure 7 and the results can be fitted into the following equations:

At T_g ,

$$\frac{\tan \delta_f}{\tan \delta_g} = 1 - 1.3\phi + 1.5\phi^2 \quad (2)$$

At T_i ,

$$\frac{\tan \delta_f}{\tan \delta_g} = 1 + 1.3\phi \quad (3)$$

Table IV Results of Dynamic Mechanical Studies at 3.5 Hz

Mix No.	Glass-Rubber Transition		Ionic Transition	
	T_g (°C)	$\tan \delta$ at T_g	T_i (°C)	$\tan \delta$ at T_i
EP0	-44.0	1.273	^a	—
EP1	-41.8	1.192	38.0	0.094
EP1D	-42.7	1.208	^a	—
EP2	-40.0	1.084	40.9	0.103
EP3	-38.6	0.944	46.3	0.112
EP4	-38.2	0.934	51.7	0.121
EP5	-36.8	0.837	52.6	0.128
EP6	-37.0	0.820	54.8	0.139

^a Absent.

A relationship similar to that represented by eq. (2) has been observed in the case of polymers filled with reinforcing fillers.²⁵ Equation (3), as proposed, represents strengthening of the ionic domains in the polymer matrix.

Thus, it can be concluded that in the present ionomer system, zinc stearate plays dual role. Firstly, below its melting point it reinforces the matrix and strengthens the ionic aggregates and secondly, at

higher temperature it results in solvation of the ionic aggregates and plasticizes the system thus facilitating the transition from the rubbery state to the viscous flow state²⁰ (Fig. 3).

While studying melt rheology in the MPT, it was observed that the m-EPDM-ZnO and m-EPDM-ZnO-stearic acid systems could not be extruded even at 190°C. This is not unexpected since the material, in the absence of zinc stearate, shows no transition from the rubbery state to viscous flow state (Fig. 3). In the presence of 10 phr of zinc stearate, the m-EPDM-ZnO-stearic acid system could be extruded but melt fracture occurred at lower temperature (150°C) at all shear rates. At 160° and 170°C, however, the extrudates showed melt fracture only at high shear conditions. At 20 phr loading of zinc stearate, melt fracture of the extrudate occurred at high shear conditions at 150°C, but at higher temperature no melt fracture occurred and the extrusion was smooth under all shear conditions. At 30 and 40 phr loadings of zinc stearate, the extrudates were

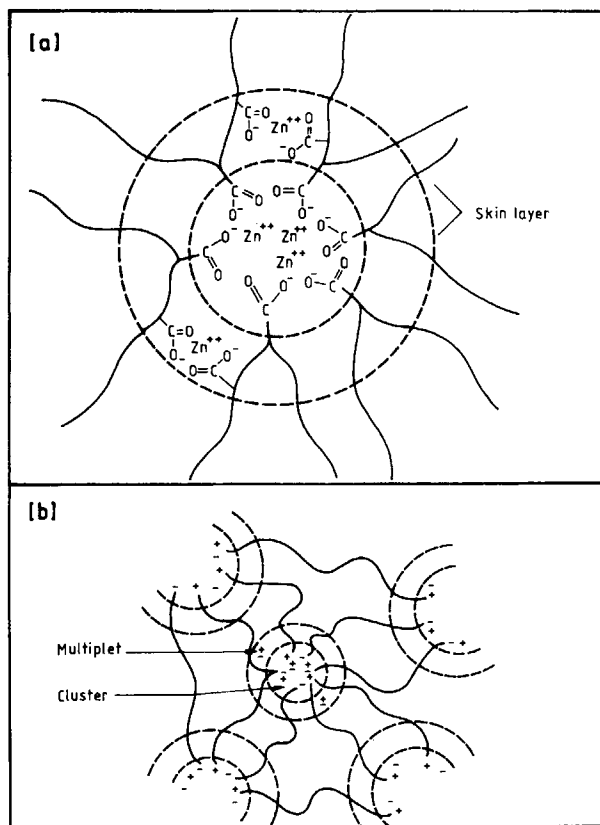


Figure 5 Model of biphasic structure in ionomer.

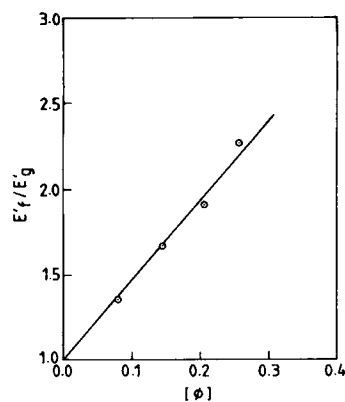


Figure 6 Plot of E_f/E'_g versus volume fraction $[\phi]$ of zinc stearate at room temperature.

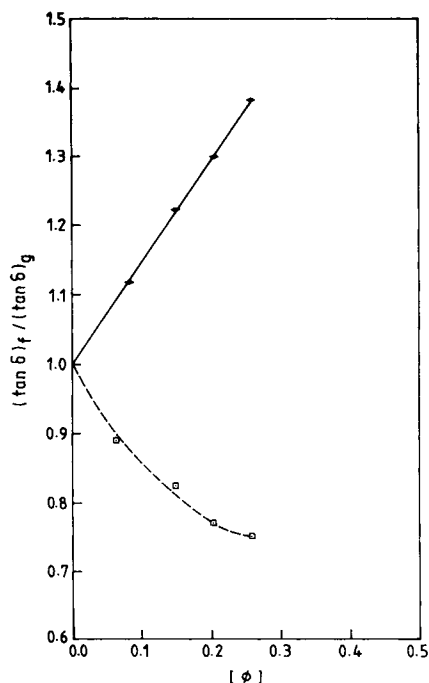


Figure 7 Plot of $\tan \delta_f / \tan \delta_g$ versus volume fraction $[\phi]$ of zinc stearate at T_g (---) and at T_i (—).

smooth under all shear conditions at all temperatures.

Figure 8 shows the plots of apparent viscosity versus shear stress at 170°C for different mixes. Since we have used a relatively long capillary (L/D ratio, 30 : 1) Bagley correction was not applied.²⁶ It is evident that the materials behave as pseudo-plastic fluids, and the viscosity decreases with increasing zinc stearate loading. It is also apparent that the shear stress dependence of viscosity decreases with increasing zinc stearate loading, since higher loading of zinc stearate provides greater extent of plasticization and enhances the flowability of the system.

As expected viscosity decreases with increase in temperature. The activation energy for melt flow was calculated on the basis of Arrhenius–Frenkel–Eyring equation.²⁷

$$\eta = Ae^{\Delta E/RT} \quad (4)$$

Here, η is the apparent viscosity at a temperature T . A is an empirical constant, ΔE is the activation energy required for flow and R is the universal gas constant. Values of activation energy was calculated from the plots of $\ln \eta$ vs. $1/T$ (Fig. 9) and the results are summarized in Table V. It is apparent that ΔE decreases with increase in zinc stearate loading. But the effect of zinc stearate on ΔE decreases with in-

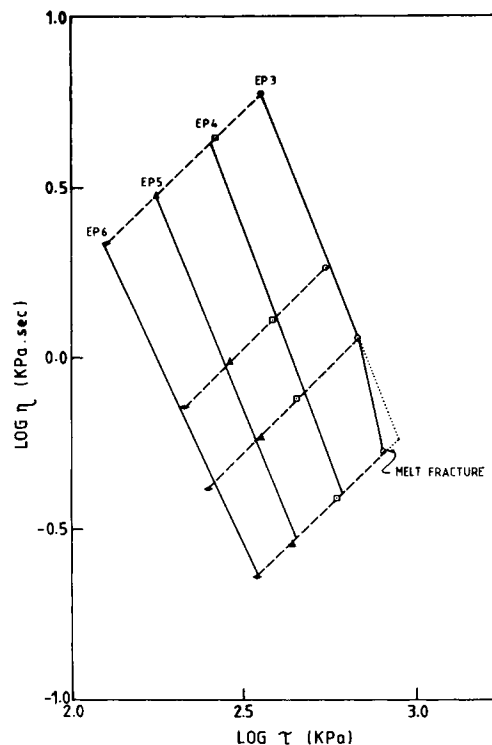


Figure 8 Plots showing dependence of apparent viscosity (η) on apparent shear stress (τ).

creasing shear rate, since high shear rate exerts pronounced influence on lowering of the viscosity.

At high processing temperatures molten zinc stearate is believed to solvate the ionic aggregates (Fig. 10) and high shear force applied may facilitate exchange reactions. Due to the interchange reaction of the intermolecular carboxylate salts (both bridging and nonbridging types) with zinc stearate, the intermolecular metal carboxylate bonds can break and result in formation of a new structure with ionic groups attached to the stearate moiety in one end. Since intermolecular salt bridges cease to exist in the postexchange reaction stage, the chains become

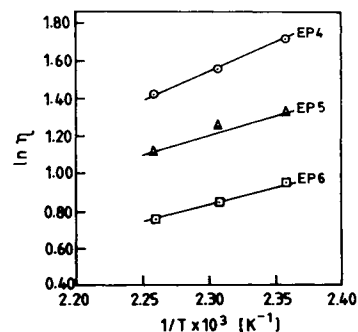


Figure 9 Arrhenius plots showing variation of apparent viscosity (η) with temperature (T) for different mixes.

Table V Activation Energy (ΔE , in kcal/mol) for Viscous Flow

Mix No.	Shear Rate (s^{-1})		
	61	305	610
EP3	6.23	5.53	4.94
EP4	4.72	3.82	3.46
EP5	3.82	2.92	2.24
EP6	3.59	2.69	2.06

free to flow. Results of IR spectroscopic studies, discussed later, give credence to the structures proposed in Figure 10.

Since the system is processible like thermoplastics, its reprocessability was studied under repeated cycles of extrusion in the MPT. Results of reprocessability studies are shown in Table VI. It is evident that after the first cycle viscosity increased slightly, which may be due to the orientation effect. In the subsequent cycles viscosity remained almost

constant. Therefore, it is concluded that the zinc stearate plasticized zinc salt of m-EPDM is melt processible like thermoplastics.

The IR spectra of m-EPDM, m-EPDM-ZnO and m-EPDM-ZnO-stearic acid are shown in Figure 11. In m-EPDM the sharp peak at 1714 cm^{-1} is characteristic of the symmetric stretching of the carboxylic group and the one at 1777 cm^{-1} is due to asymmetric carboxyl stretching. On the other hand, the peak at 1865 cm^{-1} is due to the presence of cyclic anhydride. It is apparent from the spectra of the m-EPDM-ZnO system that the carboxyl peak intensity is reduced due to its reaction with ZnO. A new peak at 1565 cm^{-1} is observed which is broad and diffused and, which is believed to be due to asymmetric stretching of carboxylate ions in bridging type of metal carboxylate.²⁸⁻³¹

Since the intensity of the 1565 cm^{-1} peak is low, it is inferred that the concentration of metal carboxylate formed is low. In the m-EPDM-ZnO system another peak at 1430 cm^{-1} appears as a shoulder to the peak at 1448 cm^{-1} . The peak at 1430 cm^{-1} is

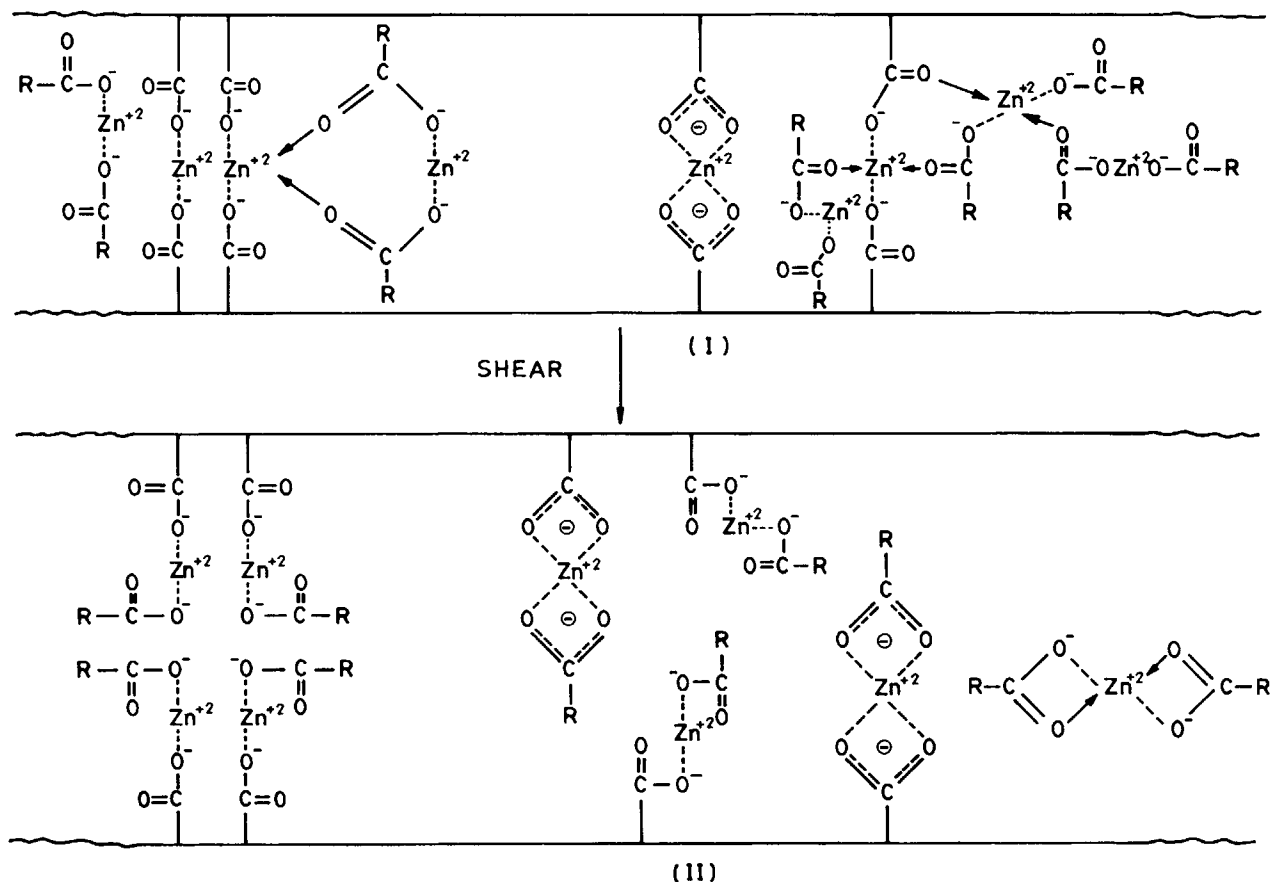


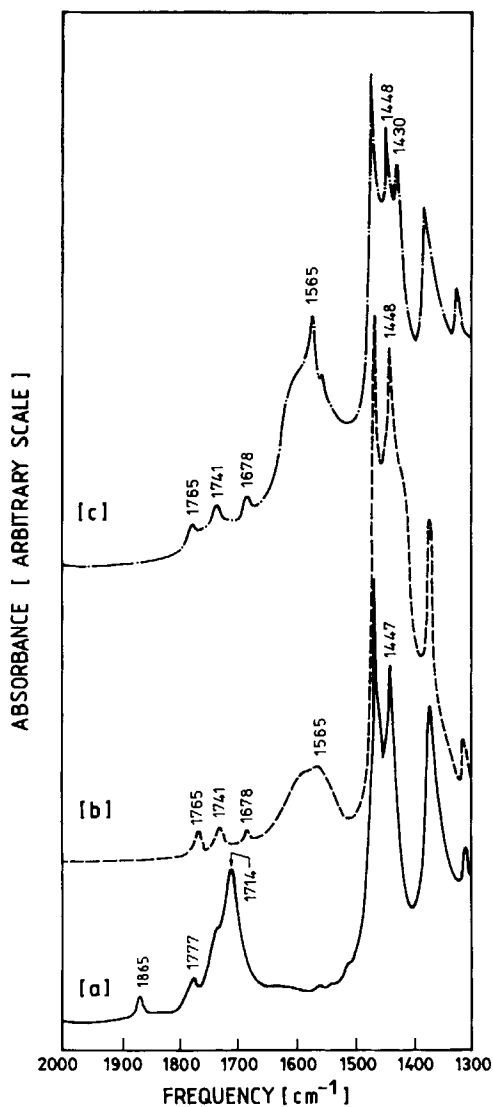
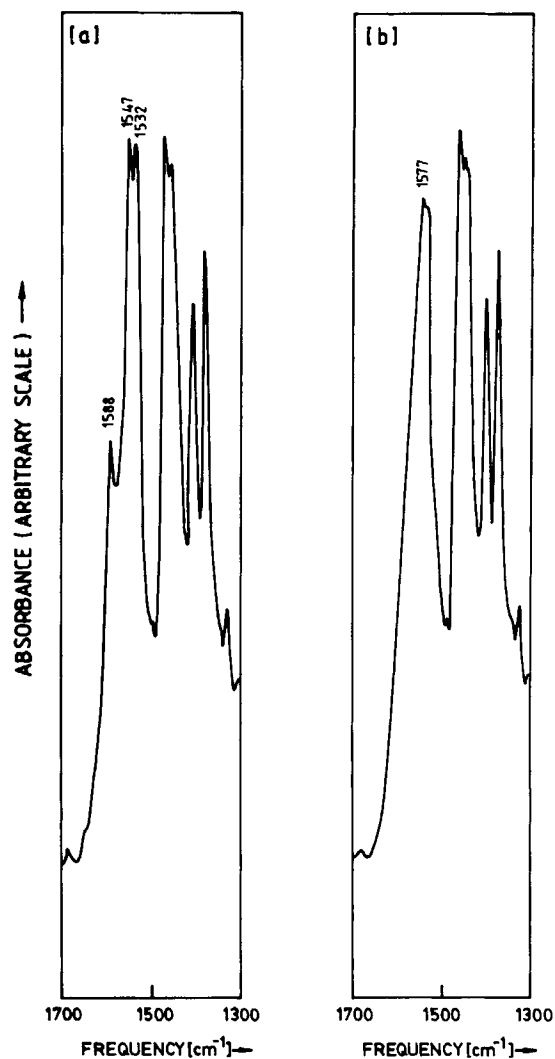
Figure 10 Probable mechanism of shear induced exchange reactions during melt flow process. (I) Interaction of zinc stearate, $(RCOO)_2Zn$, with ionic aggregates before melt flow. (II) Exchange reactions during melt flow.

**Table VI Results of Reprocessability Studies Mix Number, EP5;
Temperature, 170°C; Shear Rate, 159 s⁻¹**

No. of Cycles	Shear Stress (KPa)	Apparent Viscosity (η) KPa s	300% Modulus of Extrudate (MPa)
1	232.6	1.5	2.69
2	253.3	1.7	2.74
3	259.1	1.7	2.87
4	263.2	1.8	2.74

due to symmetric stretching in the carboxylate group and is characteristic of the non-bridging metal carboxylate.²⁸⁻³¹ The 1448 cm⁻¹ peak is due to bending vibration of methyl group.^{29,30} The spectra of mix

EP2 (i.e., m-EPDM-ZnO-stearic acid system) shows strong intensity of the 1565 cm⁻¹ peak, and also a distinct peak at 1430 cm⁻¹ appears, which is indicative of the formation of both bridging and non-bridging type of ionic aggregates.


Figure 11 Infrared spectra of (a) m-EPDM, (b) EP1, and (c) EP2.

Figure 12 IR spectra of (a) mix EP5 and (b) zinc stearate.

In Figure 12 is shown the IR spectra of zinc stearate (taken by KBr disk technique) and that of the ionomer sample containing 30 phr zinc stearate (mix EP5). The spectra of zinc stearate shows a single sharp peak at 1577 cm^{-1} . This is believed to be due to the asymmetric stretching of bridging type of carboxylate groups. Now on the basis of additivity rules, the spectra of EP5 was expected to show the features of the gum system (mix EP2) and that of the zinc stearate. But the spectral features of EP5 is different in the sense that in the carboxylate asymmetric stretching region three sharp peaks are present, at 1588 cm^{-1} , 1547 cm^{-1} , and 1532 cm^{-1} . From this observation we can conclude that there must exist some degree of interaction between zinc stearate and the ionic aggregates, which results in a marked change in the environment of the carboxylate groups. The proposed structural model for the interaction of zinc stearate with ionic aggregates is similar to that proposed by Duvedevani et al.³²

CONCLUSIONS

Neutralization of maleated EPDM rubber by zinc oxide and stearic acid results in an ionic elastomer, which besides showing its glass-rubber transition around -40°C , registers a high temperature transition (that is, $>$ room temperature), due to the ionic domains, in the dynamic mechanical studies. Zinc stearate causes enhancement in physical properties of the rubber under ambient conditions. At high temperature ($>100^\circ\text{C}$), zinc stearate acts as plasticizer for the ionic domains and the composition shows thermoplastic processing behavior.

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