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Reinforcement of an ionic thermoplastic elastomer based on a zinc-sulfonated ethylene–propylene–diene terpolymer by precipitated silica

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Precipitated silica improves the physical properties of a zinc-sulfonated ethylene–propylene–diene terpolymer (SEPDM) of high (i.e. 75 wt%) ethylene content. The properties studied include hardness, stress–strain characteristics, tear strength, abrasion resistance and hysteresis. Processability studies carried out by using the Monsanto Processability Tester (MPT) show that silica increases the melt viscosity of the zinc-sulfonated EPDM. Results obtained from dynamic mechanical analysis (d.m.a.) show that silica reinforces the backbone chain and weakens the ionic associations. The results obtained from dielectric thermal analysis (d.e.t.a.) confirm the d.m.a. results and suggest that the formation of multiplets and clusters present in the SEPDM are adversely affected by silica. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ionic thermoplastic elastomer; precipitated silica; reinforcement)

INTRODUCTION

The zinc salt of the sulfonated ethylene–propylene–diene terpolymer elastomer, hereafter abbreviated as SEPDM, is a new type of potentially useful elastomeric ionomer[1–4]. The ionomer differs from conventional vulcanized rubbers in that the presence of metal sulfonate groups provides strong physical crosslinks at ambient temperature, but the material becomes thermoplastic at elevated temperatures, thus permitting melt processing[5]. The effect of fillers on the mechanical properties of elastomers is of great interest because fillers could be used very effectively to enhance the ultimate properties[6,7]. While studying the effect of fillers on the properties of the zinc-sulfonated EPDM, we observed an improvement in the physical properties on the incorporation of precipitated silica. This present paper reports the results of studies on the effect of precipitated silica on the physical properties and processability of SEPDM of high ethylene content.

EXPERIMENTAL

Materials

The polymers used in this study are (i) thermoplastic EPDM (M_n, 52 000 and M_w, 151 000) containing 75 wt% ethylene, 20 wt% propylene and 5 wt% 5-ethylidine-2-norbornene and (ii) SEPDM (level of sulfonation, 30 (milliequivalent) per 100 g polymer) formed by sulfonation of the pendent unsaturated groups in the thermoplastic EPDM, followed by neutralization of the resultant EPDM sulfonic acid by using the procedure described by Makowski *et al.*[8]. Both polymers were supplied by Exxon Research and Engineering Company, New Jersey, USA. The silica used was Ultrasil VN3, manufactured by Degussa, Germany, and its characteristics were as follows: surface area, 234 $m^2 g^{-1}$; oil absorption, 240 g per 100 g; pH, 6.0.

Sample preparation

The rubber compounds were prepared in a Brabender Plasticorder (Model PLE-330) using a cam-type rotor. Mixing was carried out for 6 min at a rotor speed of 80 rpm and a temperature of 150°C. The neat polymers were also masticated under the same conditions. Test specimens were prepared by moulding in an electrically heated hydraulic press for 5 min at 160°C under a pressure of 10 MPa.

Determination of physical properties

Hardness was determined as per ASTM D2240 (1986) and expressed in Shore A units. The stress–strain properties were determined at 25, 50 and 70°C according to ASTM D412 (1987) by using dumb-bell shaped specimens in a Zwick Universal Testing Machine (UTM), Model 1445, fitted with a temperature controlled cabinet, using a cross-head speed of 500 mm min^{-1}.

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The tear resistance was determined as per ASTM D624 (1986) using unnicked 90°C angle test pieces (die C) at 25°C at a cross-head speed of 500 mm min^{-1} in a Zwick UTM model 1445. The abrasion resistance was determined in a Du Pont abrasion tester (BS 903: Part A9, 1957, method C) and expressed as abrasion loss, which is the volume in cm^3 abraded from a test specimen per hour. The hysteresis loss was determined under strain mode according to ASTM D412 (1980) by stretching dumb-bell shaped specimens to a strain level of 200% in a Zwick UTM Model 1445.

Determination of processability

The processability studies were carried out by using a Monsanto Processability Tester (MPT) at shear rates of 36, 90, 181 and 289 s^{-1}, and a temperature of 190°C. The capillary length (29.77 mm) to diameter (1.50 mm) ratio was 20, with entrance angles of 45 and 60° (compound). The pre-heating time for each sample was 10 min.

Dynamic mechanical analysis

The dynamic mechanical properties were measured 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 a temperature range from -100 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 with dimensions of $25 \times 25 \times 0.5\,\mathrm{mm}^3$ were used. The measurements were carried out over the frequency range from 1 to 10^5 Hz and temperature range from 20 to 200°C, at a heating rate of 5°C min^{-1}.

RESULTS AND DISCUSSION

Physical properties

The physical properties of the neat polymers and the SEPDM compound containing 20 parts per hundred parts of rubber (phr) silica are summarized in *Table 1*. The SEPDM showed a greater hardness than the thermoplastic EPDM. Hardness is a measure of the modulus of elasticity at low strain[9]. The higher hardness of the SEPDM is due to the presence of ionic aggregates[10]. Silica increased the hardness of the SEPDM.

The stress–strain properties of the neat polymers and the silica-filled compound at 25, 50, and 70°C are shown in *Figure 1*. At room temperature, the SEPDM showed a higher modulus and tensile strength and a lower elongation at break when compared to the EPDM, due to the presence of ionic domains which act as physical cross-links[11]. A schematic representation of the morphological structure of the SEPDM containing 75 wt% of ethylene is shown in *Figure 2*. The incorporation of silica caused an increase in the modulus and a decrease in the elongation at break, but the tensile strength, however, remained constant.

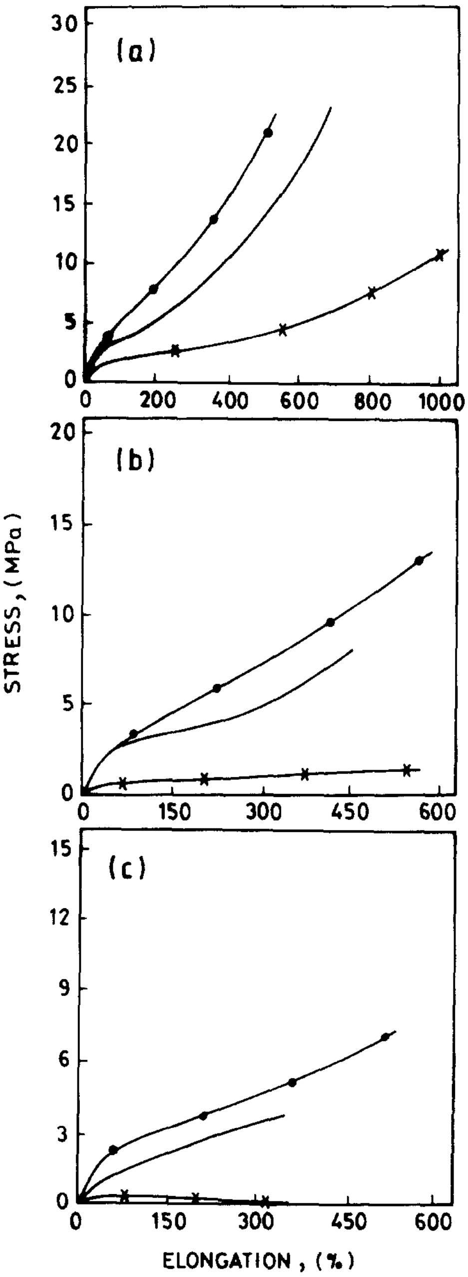

Figure 1 Stress–strain plots of: (-x-x-x-) EPDM; (——) SEPDM; (-●-●-●-) SEPDM + 20 phr silica at various temperatures: (a) 25; (b) 50; (c) 70°C

Although the tensile strength and modulus of the

Table 1 The physical properties at room temperature of the materials used in this study

Composition of the mix	Hardness (Shore A)	Modulus at 300% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength ($\mathrm{kN\,m^{-1}}$)	Hysteresis loss ($\times 10^3$) ($\mathrm{J\,m^{-2}}$)	Abrasion loss ($\mathrm{cm^3\,h^{-1}}$)
EPDM	56	2.7	11.0	1036	62	82	0.29
Zinc-sulfonated EPDM (SEPDM)	69	7.3	23.0	691	115	146	0.21
SEPDM + 20 phr silica	77	11.8	21.7	520	177	241	0.03

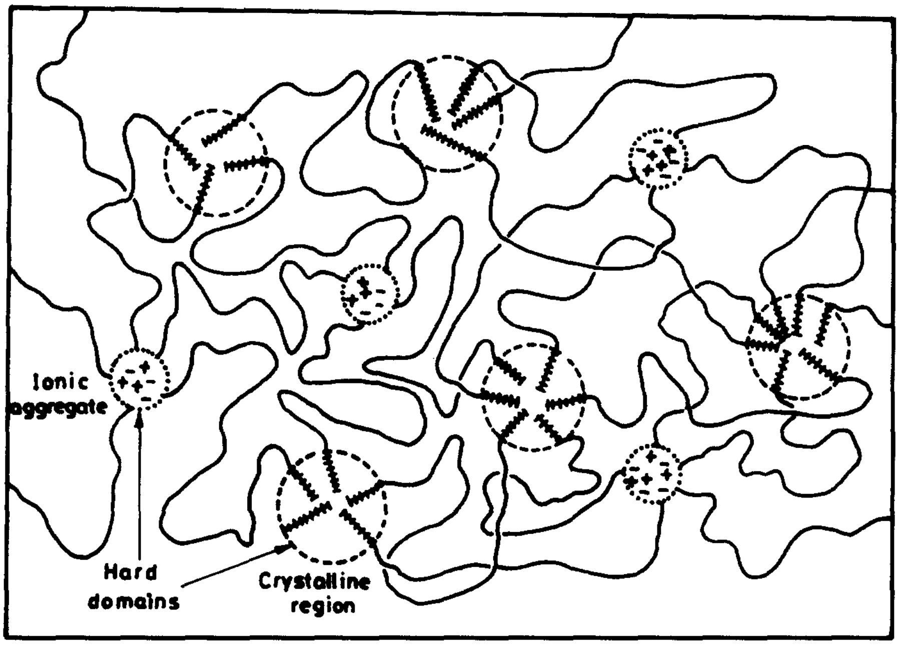

Figure 2 Proposed schematic representation of the morphological structure of the SEPDM containing 75 wt% ethylene

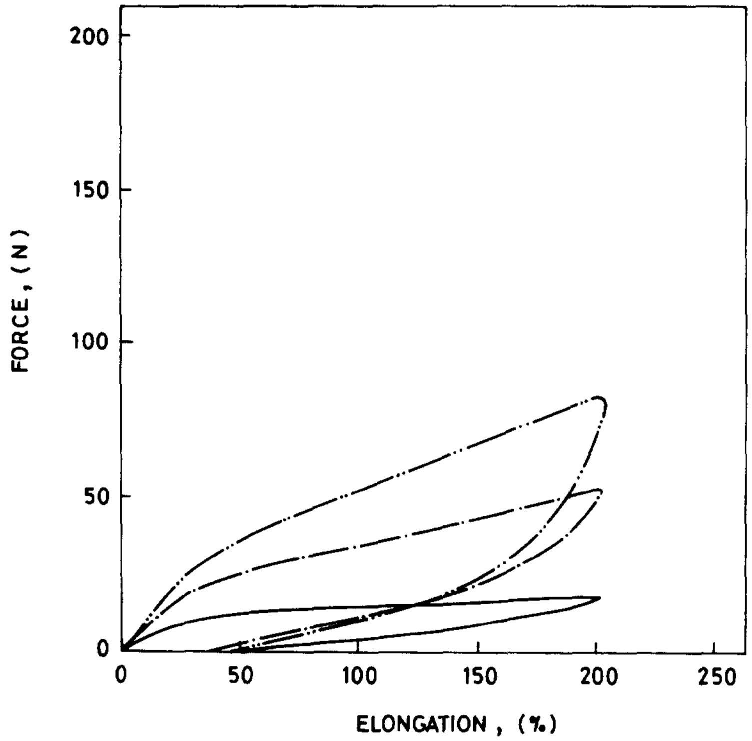

Figure 3 Hysteresis plots at 25°C of: (——) EPDM; (— · — · —) SEPDM; (— ·· — ·· —) SEPDM + 20 phr silica

thermoplastic EPDM (used as the control), dropped drastically at elevated test temperatures (50 and 70°C), the SEPDM showed a greater retention of properties under similar conditions. Incorporation of silica increased the ability to retain strength at higher test temperatures. Unlike SEPDM, the control thermoplastic EPDM does not contain any physical crosslinks, and accordingly the retention of properties at higher test temperatures is low. In the case of SEPDM, silica seems to interact with the main backbone chain, therefore increasing the strength at elevated temperatures.

SEPDM showed a higher tear strength and lower abrasion loss, when compared to the control thermoplastic EPDM. The tear resistance of an elastomer is a measure of the crack propagation. The ionic domains of the SEPDM may be acting as tear deviators or arrestors[12]. Incorporation of silica improved the tear resistance of the SEPDM, thus suggesting a possible reinforcement of the matrix. The higher abrasion resistance of the SEPDM could be attributed to the higher strength of the matrix, as is evident from its higher modulus when compared to the EPDM[13]. The incorporation of silica causes a reduction in the abrasion loss.

The results obtained from hysteresis studies are shown in *Figure 3*. The SEPDM shows a higher hysteresis than the thermoplastic EPDM, thus suggesting an additional

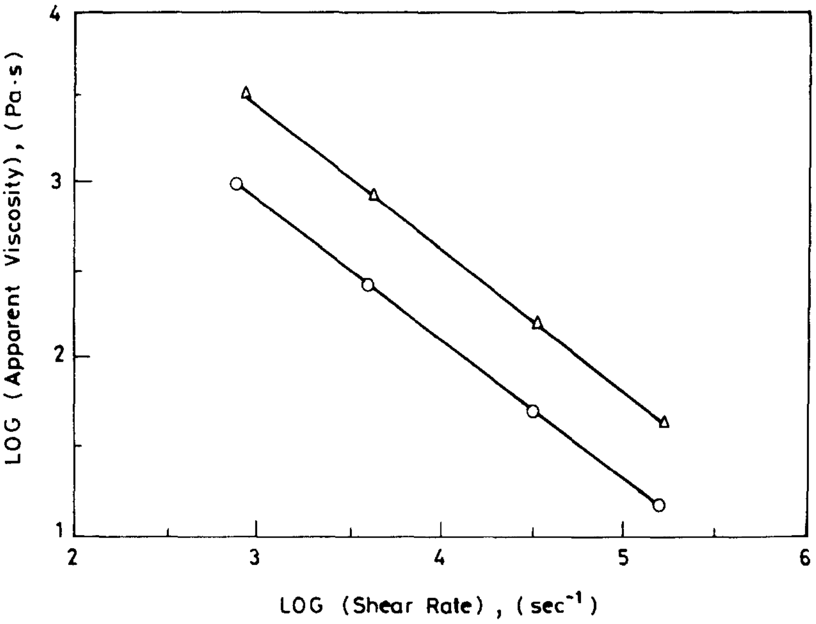

Figure 4 Apparent viscosity vs. shear rate at 190°C of: (-○—○—○-) SEPDM; (-△—△—△-) SEPDM + 20 phr silica

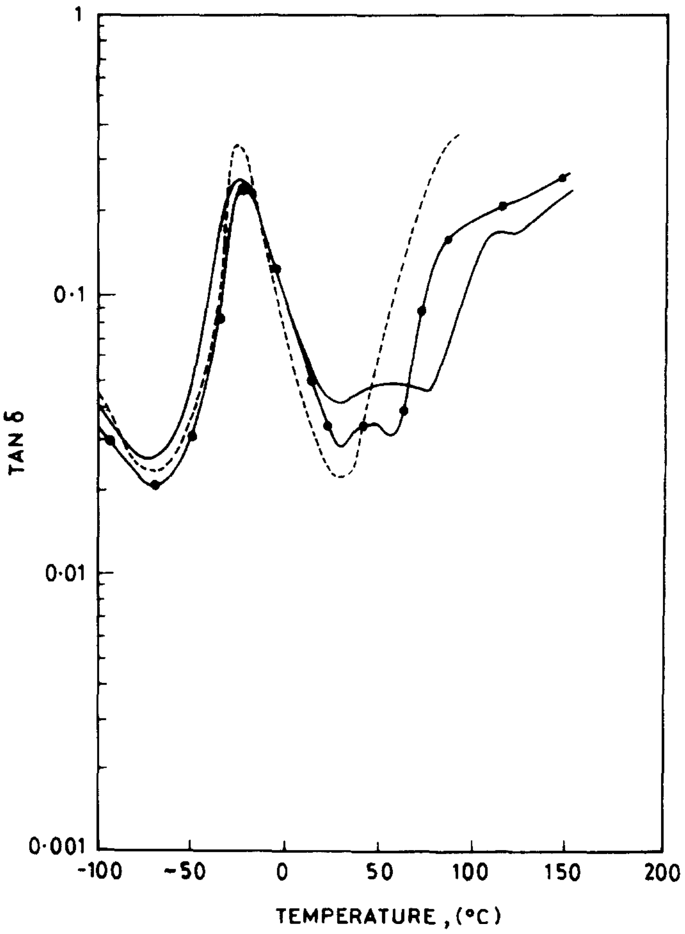

Figure 5 Semilogarithmic plots of tan δ vs. temperature of: (- - - -) EPDM; (——) SEPDM; (-●—●—●-) SEPDM + 20 phr silica

energy dissipation mechanism in the former, arising out of the ionic aggregates. The latter may be considered to behave as ultrafine reinforcing filler particles in the host polymer in addition to acting as multifunctional crosslinks[10,12]. An increase in the hysteresis of SEPDM on the addition of filler indicates additional energy dissipation mechanisms, such as motion of filler particles, chain slippage or breakage and dewetting at high strain levels[12]. The results suggest that silica acts as a reinforcing filler for the zinc-sulfonated EPDM.

Processability

The log–log plots of apparent viscosity *versus* shear rate in the case of the SEPDM and the compound containing silica are shown in *Figure 4*. At all of the shear rates, the silica-filled compound showed a higher viscosity when compared to the corresponding neat SEPDM.

Dynamic mechanical properties

Figure 5 shows the plot of loss tangent ($\tan\delta$) against temperature, obtained from the dynamic mechanical analysis of the neat polymers and the silica-filled SEPDM. The glass–rubber transition occurs at around −26°C (i.e. T_g) in the case of both EPDM and SEPDM. The incorporation of silica caused a slight increase in the T_g (from −26 to −23°C) due to a stiffening of the backbone chain. The $\tan\delta_{max}$ (i.e. the $\tan\delta$ value at T_g) was lower in the case of SEPDM when compared to EPDM, because of the stiffening imparted by the ionic domains in SEPDM[14]. Incorporation of silica results in a further decrease in $\tan\delta_{max}$ due to the formation of an adsorbed polymeric shell on the active filler surface[15].

Apart from the T_g, the SEPDM and its silica-filled compound show two other transitions, namely one at around +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 transition of a hard phase arising out of the ionic aggregates. The transition due to the ionic aggregates has been found to occur in a similar temperature range in the case of rubbery ionomers[16,17]. In the case of crystalline ionomers, the transition due to ionic aggregates has been reported to occur at a temperature which is lower than the crystalline melting temperature[18–20]. The incorporation of silica caused a marginal reduction in $\tan\delta$ at the high-temperature ionic transition (T_i), thus suggesting that the formation of the hard phase is reduced in the presence of silica. The results obtained from dynamic mechanical analysis are summarized in *Table 2*.

Dielectric thermal properties

Figure 6 shows the variation of $\tan\delta$ with temperature observed from the dielectric thermal analyses of the EPDM and SEPDM. The transition at +115°C observed

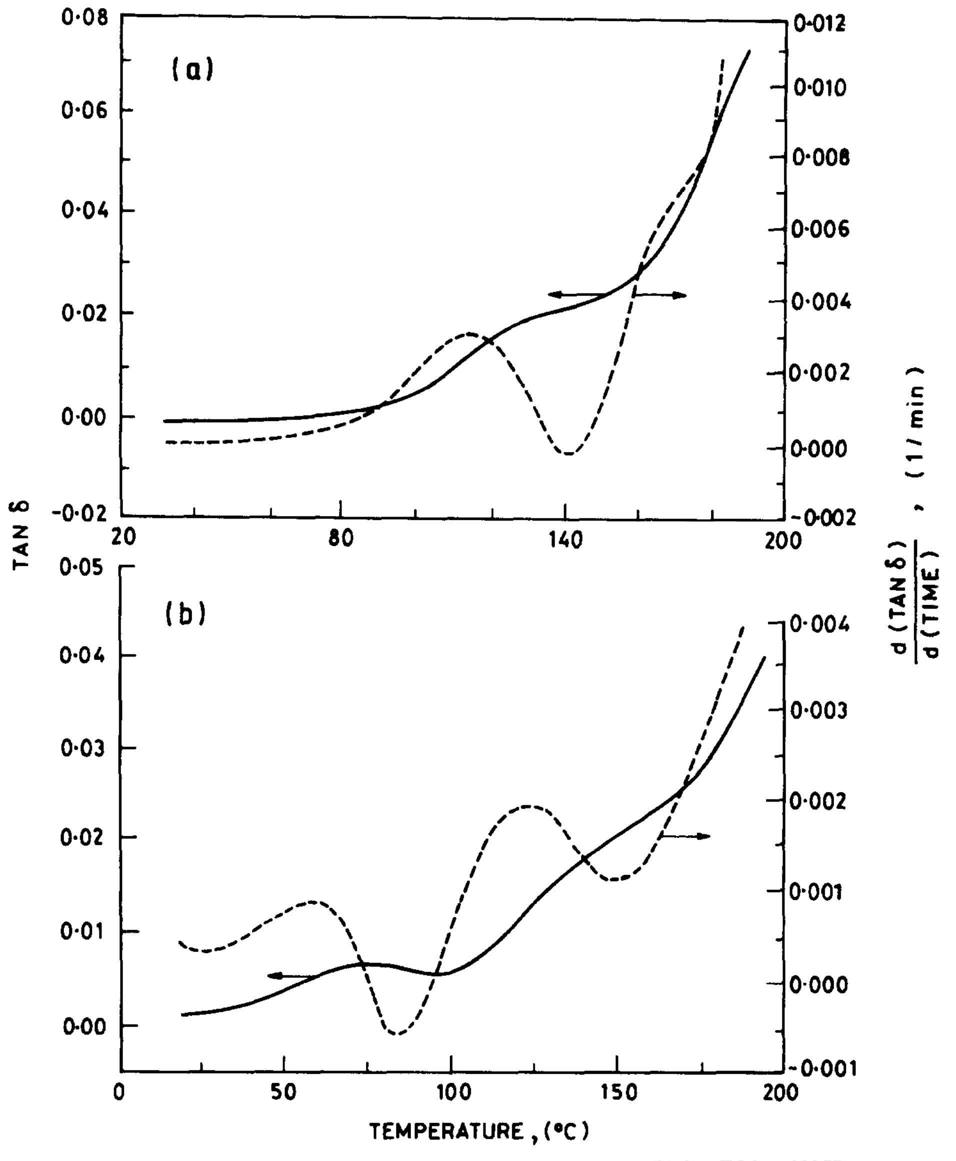

Figure 6 Temperature dependence of dielectric loss tangent ($\tan\delta$) for: (a) EPDM at 1 Hz; (b) SEPDM at 100 Hz

Table 2 Results obtained from dynamic mechanical analysis of the materials used in this study

Composition of the mix	T_g [a] (°C)	Tan δ at T_g, tan δ_{max}	Transition due to ionic aggregates, T_i [b] (°C)	Tan δ at T_i	Transition due to melting of crystallites[b] (°C)
EPDM	−26	0.365		–	–[c]
Zinc-sulfonated EPDM (SEPDM)	−26	0.257	+27 to +80	0.040	+119
SEPDM + 20 phr silica	−23	0.244	+27 to +63	0.035	+118

[a] From (tan δ)$_{max}$ in the plot of tan δ vs. temperature
[b] From tan δ vs. temperature plot
[c] Not detectable

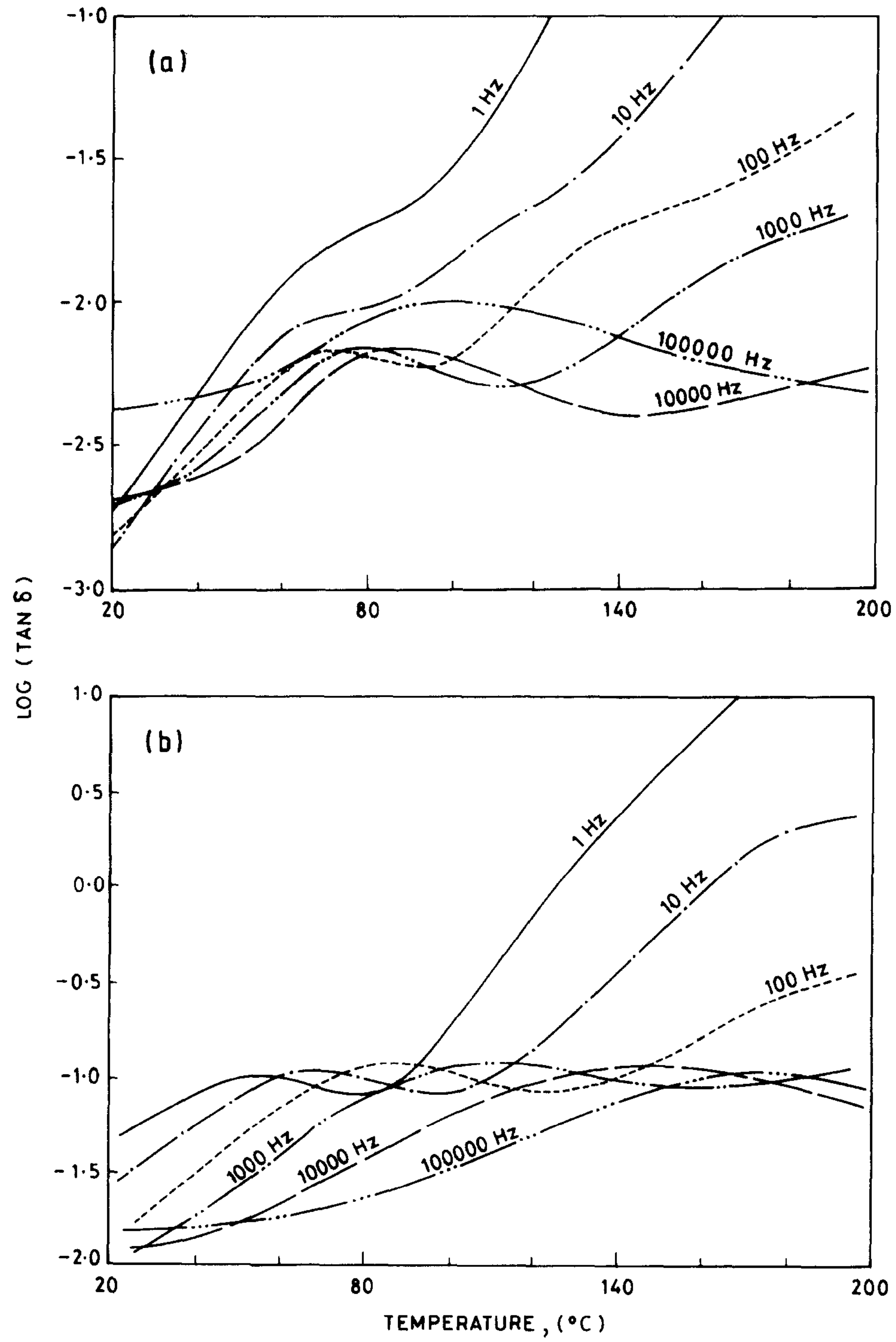

Figure 7 Semilogarithmic plots of dielectric loss tangent (tan δ) vs. temperature for: (a) SEPDM; (b) SEPDM + 20 phr silica

in the case of the EPDM is due to the melting of the crystalline zone of the polyethylene block. SEPDM shows two transitions, namely one at +123°C, and the other at a lower temperature (+57°C). While the high-temperature transition is believed to be due to the melting of the crystalline polyethylene block, the low-temperature transition is believed to be due to the ionic aggregates[18–20].

The frequency dependence of the log tan δ *versus* temperature plots obtained from the dielectric thermal analyses of SEPDM and the corresponding compound containing silica are shown in *Figure 7*. The latter compound exhibits both transitions, as was observed in the case of the neat SEPDM. Arrhenius plots[21,22] of log (frequency) *versus* $1/T_{\max}$, where $T_{\max}$ represents the temperature corresponding to the maximum in tan δ in the plot of log(tan δ) *versus* temperature, for the neat SEPDM and the silica-filled compound, and the corresponding activation energies of the ionic transitions, are shown in *Figure 8*. Since the Arrhenius plots show two slopes, it could be inferred that there exists two types of ionic transitions, with one occurring in the frequency range from 1 to 100 Hz, and the other occurring in the range from 10^3 to 10^5 Hz. In the case of both neat SEPDM and its silica-filled compound, the transitions at lower frequencies show higher activation energies than those at higher frequencies.

These observations could be explained on the basis of the models for the distribution of salt groups in ionomers, which postulate the existence of multiplets and

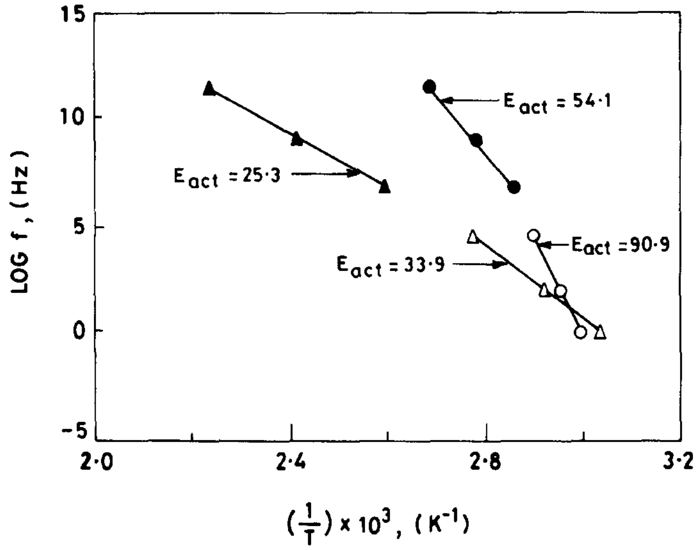

Figure 8 Plots of log (frequency) vs. $1/T_{\max}$ for: (-○-○-○-) SEPDM, 1–100 Hz; (-●-●-●-) SEPDM, 10^3–10^5 Hz; (-△-△-△-) SEPDM + 20 phr silica, 1–100 Hz; (-▲-▲-▲-) SEPDM + 20 phr silica, 10^3–10^5 Hz. E_{act} is the activation energy (kcal mol^{-1}) of ionic transitions calculated from the slope of the plots

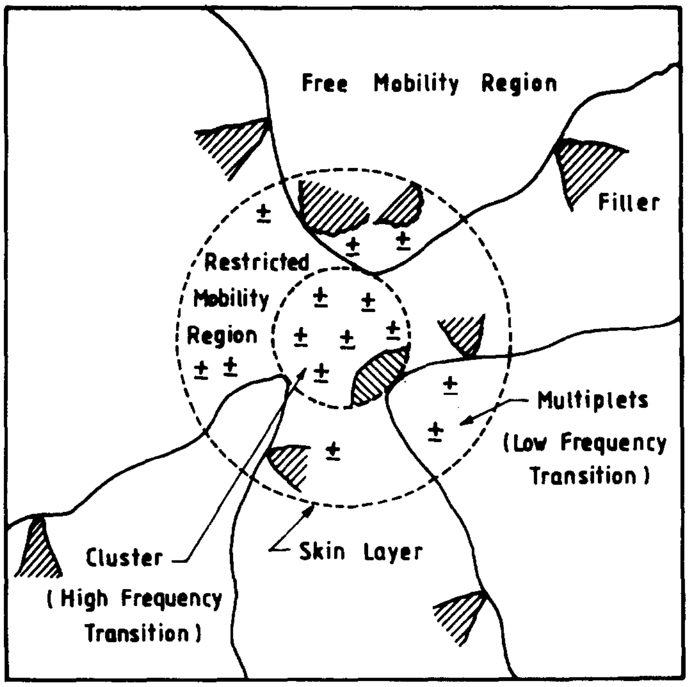

Figure 9 Proposed schematic representation of the attachment of silica particles to the backbone chains and ionic aggregates of SEPDM

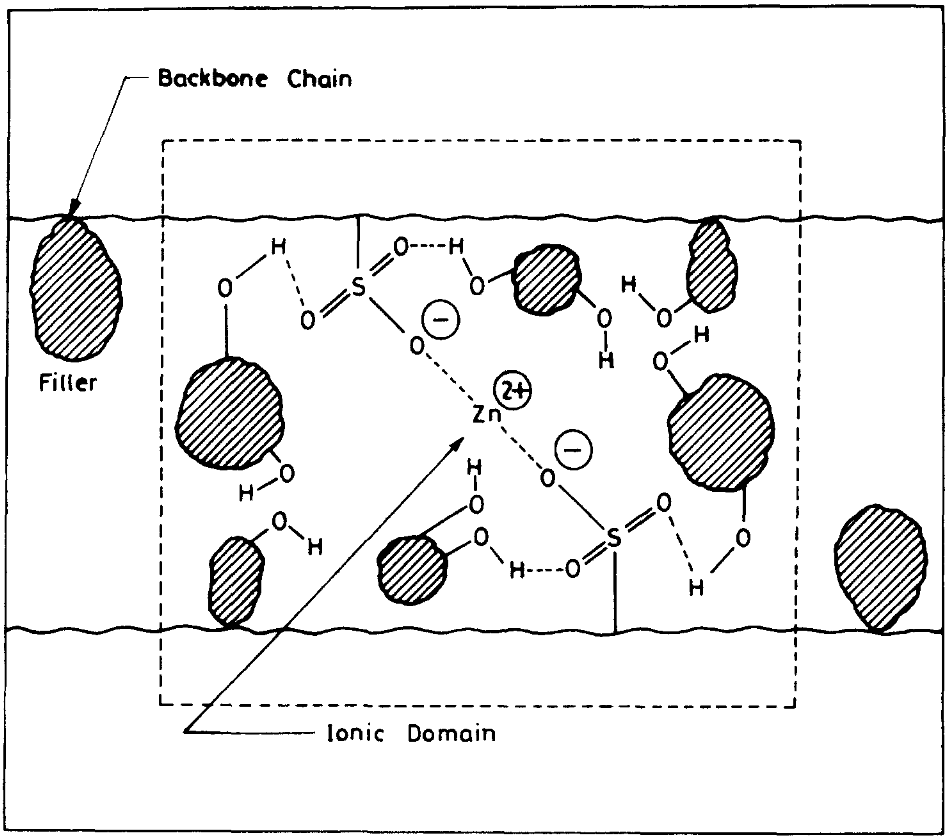

Figure 10 Proposed schematic representation of the interaction between the silanol groups of silica and ionic aggregates of SEPDM

clusters[23-26]. Multiplets are aggregates consisting of ion pairs distributed in the matrix. When sufficient numbers of multiplets are close enough together to form a contiguous region of restricted mobility, the region constitutes a cluster and exhibits its own separate T_g. The low-frequency transitions for the ionic groups at low temperatures which are observed to occur in the case of SEPDM and its silica-filled compound might be attributed to the multiplets present in the matrix, while the high-frequency transitions occurring at higher temperatures might be originating from the larger aggregates or clusters[26]. *Figure 9* suggests a model for the morphological structure of the ionic rubber which shows the attachment of the silica particles in different regions. In the presence of silica, the activation energies of both the low- and high-frequency transitions decreased. The ionic interactions present in the ionomers are dependent on various factors[4]. In this present case silica seems to facilitate the dipolar relaxation of the polymer, thus resulting in a lowering of the activation energy. The silanol groups in silica seem to interfere in the formation of ionic aggregates, the exact mechanism of which is not clearly understood. *Figure 10* shows a representation of the probable mechanism of interaction between the silanol groups of the filler and the ionic aggregates. The results obtained from the dielectric thermal analysis are in conformity with the observed reduction in tan δ at T_i in the case of the dynamic mechanical studies (*Table 2*).

CONCLUSIONS

Precipitated silica increases the hardness, modulus, tear strength, abrasion resistance and hysteresis of SEPDM of high ethylene content. Although the room-temperature tensile strength of the silica-filled compound is similar to the neat polymer, incorporation of silica improves the retention of the stress–strain properties of the polymer at elevated test temperatures. Processability studies in the Monsanto Processability Tester indicate the increase in melt viscosity of the polymer in the presence of silica. Dynamic mechanical analysis shows that in addition to the T_g, the ionic transition occurs at a high temperature for both SEPDM and its silica-filled compound. The results indicate a stiffening of the polymer backbone and a weakening of the ionic transitions in the presence of silica. The results obtained from dielectric thermal analysis suggest that the filler weakens formation of both the multiplets and clusters present in the ionomer.

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