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Reinforcement of EPDM-based ionic thermoplastic elastomer by precipitated silica filler

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Incorporation of up to 20 phr of precipitated silica filler into a thermoplastic elastomer of composition 100 phr maleated EPDM rubber, 10 phr zinc oxide, 1 phr stearic acid, 30 phr zinc stearate, results in an improvement of physical properties such as modulus, tensile strength and tear resistance. While the glass–rubber transition temperature (T_g) of the thermoplastic elastomer occurring around −37°C remains unaltered in the presence of the filler, the ionic transition (T_i) occurring around +50°C is shifted to higher temperature on filler incorporation. Furthermore, the filler causes a decrease in tan δ at T_g, but an increase in tan δ at T_i. It is believed that, besides the dispersive-type forces operative in the interaction between the backbone chains and the filler particles, the ionic domains in the thermoplastic elastomer interact strongly with the polar sites on the filler surface. Reprocessability studies in the Monsanto Processability Tester (MPT) show that the silica-filled polymer can be reprocessed like a thermoplastic, there being no reduction in properties even after four cycles of extrusion through the MPT. Copyright © 1996 Elsevier Science Ltd.

(Keywords: precipitated silica; ionic thermoplastic elastomer; rubber–filler interaction)

Introduction

Metal oxide neutralization of the acid groups in functionalized polymers like maleated and sulfonated EPDM (ethylene propylene diene monomer) rubbers produces ionic crosslinks or domains that are heat-fugitive[1–4]. The resulting ionic polymers or ionomers behave as thermoplastic elastomers, abbreviated as TPE[5]. Zinc stearate is known to act as a plasticizer for the ionic domains and facilitate processing of the ionic polymers above its melting point (>128°C)[6,7]. Although reinforcing fillers in general are known to adversely affect the strength properties of TPEs[8], there are reports of reinforcement of ionic thermoplastic elastomers by carbon black[9–12].

Precipitated silica is known to act as a reinforcing filler for rubbers. The presence of polar silanol groups on the filler surface is likely to promote its interaction with the ionic groups of the ionomer. The present investigation was undertaken in order to study the effect of precipitated silica on the properties of ionic TPE, based on maleated EPDM rubber (m-EPDM). Preliminary results indicated that, in the presence of ZnO and stearic acid, m-EPDM showed good strength and the rubber was easily processable in the presence of zinc stearate.

Experimental

Details of the materials used are given in *Table 1*. Formulations for the different mixes are given in *Table 2*; these are given in phr, i.e. parts per 100 parts of rubber, by weight.

Mixing was done in a laboratory-size two-roll mill at 2 mm nip gap. In order to ensure uniform mixing of the ingredients, the mixing schedule outlined in *Table 3* was followed. The speed of the front roll was less than the speed of the back roll to prevent bagging of the base polymer; the speed ratio was 1:1.2. Cold water was circulated through the rolls to prevent excessive heat generation during mixing. Each sample was moulded to form 2 mm thick sheets at a pressure of 10 MPa at 120°C for 20 min.

The hardness was determined as per ASTM D2240 (1986) and expressed in terms of a Shore A value.

The stress–strain properties were studied in a Zwick universal testing machine (UTM), model 1445, according to ASTM D412 (1980) specification. The tension set at 100% elongation was determined as per ASTM D412 (1987).

Tear strength was measured in the Zwick UTM 1445 using a 90° nick-cut crescent sample (die C) according to ASTM D624-86. Measurement of hysteresis under tension mode was made in the same instrument according to ASTM specification D412 (1980), by stretching the dumb-bell shaped specimens up to an extension of 200%.

Dynamic mechanical studies were performed in a Rheovibron viscoelastomer DDV-III-EP of M/s Orientec Corporation, Tokyo, Japan, at a frequency of 3.5 Hz in the temperature range −100° to 200°C. The heating rate was 1°C min^{-1}.

The processability studies were carried out in a Monsanto Processability Tester (MPT) with a capillary having a length-to-diameter ratio of 30:1. The processing temperatures were 150, 160 and 170°C. Shear rates chosen were in the range 10^1 to 10^3 s^{-1}.

Infra-red (i.r.) spectroscopic studies were conducted

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Table 1 List of materials used

Material	Source	Characteristics
Maleated EPDM rubber (m-EPDM), trade name Royaltuf 465	Uniroyal Chem. Co., Naugatuck, CT, USA	E/P ratio, 55/45; maleic content, 1%; Mooney viscosity, $ML(1+4)$ 100°C, 60; M_w, 3.99×10^5; M_n, 1.16×10^5
Zinc oxide (ZnO)	BDH Chemicals, Calcutta, India	98% pure; rubber grade
Stearic acid	Obtained locally	99% pure; rubber grade; melting point, 76°C
Zinc stearate	Obtained locally	Rubber grade; melting point, 128°C
Precipitated silica, trade name Ultrasil VN-3	Degussa AG, Germany	Specific gravity, 2.2

Table 2 Formulation of mixes

	Mix number			
Ingredient	S0	S1	S2	S3
m-EPDM	100	100	100	100
ZnO	10	10	10	10
Stearic acid	1	1	1	1
Zinc stearate	30	30	30	30
Silica	0	10	20	30

Table 3 Mixing schedule

	Mixing step	Time of mixing (min)
i)	Add rubber and band	2
ii)	Add ZnO	1
iii)	Add stearic acid	1
iv)	Add 1/3 zinc stearate	3
v)	Add 1/2 filler	3
vi)	Add 1/3 zinc stearate	3
vii)	Add 1/2 filler	3
viii)	Add 1/3 zinc stearate	3
ix)	Sheet out	1

Table 4 Physical properties[a]

	Mix number			
	S0	S1	S2	S3
Hardness (Shore A)	62	65	67	69
300% Modulus (MPa)	2.90 (1.82)	3.26 (2.58)	3.64 (2.35)	4.49 (3.13)
Tensile strength (MPa)	7.60 (2.42)	10.30 (3.10)	14.35 (3.59)	10.43 (4.00)
Elongation at break (%)	760 (431)	1370 (400)	1340 (530)	1000 (440)
Tear strength ($\mathrm{N\,cm^{-1}}$)	418 (233)	436 (256)	449 (296)	424 (283)
Hysteresis work ($\mathrm{J\,m^{-2}}$) $\times 10^3$	80.1	98.0	112.0	110.2
Tension set at 100% extension (%)	17	20	22	22

[a] Values in parentheses are the results of tests carried out at 70°C

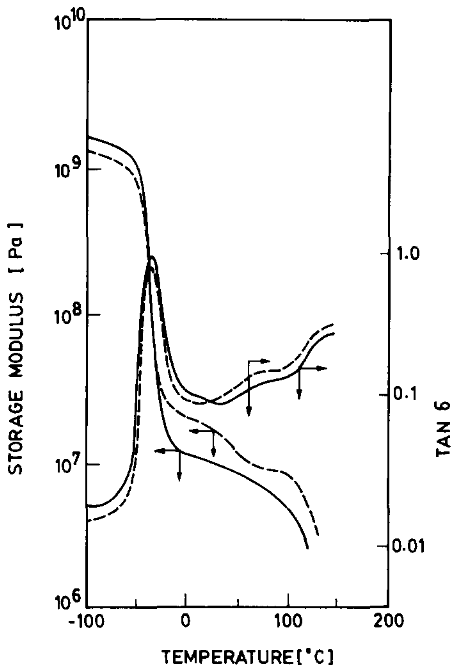

Figure 1 Typical plots from dynamic mechanical thermal analysis showing storage modulus and tan δ variation with temperature. ——, S0; – – –, S2

with melt-cast film specimens in a Perkin–Elmer infra-red spectrophotometer, model 843, attached to a computer for data processing.

Results and discussion

The physical properties of the different mixes are summarized in *Table 4*. As expected, both hardness and modulus increase with increase in filler loading. Incorporation of silica causes a gradual increase in tensile strength up to 20 phr of filler, when the strength is almost twice that of the unfilled system. At 30 phr of filler loading the tensile strength decreases to the level of 10 phr, but it is still 1.5 times the value of the unfilled system. The increase in elongation at break on filler incorporation is believed to be due to slippage of the polymer chains over the silica surface[13]. Because of the thermo-reversible nature of the ionic crosslinks, tensile strength dropped at elevated test temperature (that is, 70°C), but the silica-filled system registers higher strength than the unfilled system even at 70°C. Both tear resistance and hysteresis increase on incorporation of silica, but the effect is less pronounced compared with the stress–strain properties. Tension set of the ZnO-neutralized m-EPDM system is low (around 20%) and incorporation of filler causes only marginal increase in set due to chain slippage over the filler surface, as discussed earlier. Measurement of physical properties reveals that an interaction occurs between the filler surface and the polymer. Results of dynamic mechanical studies, discussed below, support the conclusions derived from other physical properties.

Typical plots of the storage modulus *versus* temperature and mechanical loss (tan δ) *versus* temperature are shown in *Figure 1*. It is clear that, apart from the glass–rubber transition (T_g) occurring around −37°C, an ionic transition (T_i) occurs at high temperature (>50°C) which, in the presence of silica, becomes prominent and is shifted to the higher temperature side. The high-temperature transition is believed to be due to relaxation of the restricted chain segments arising from ionic aggregates such as multiplets and clusters[14–16], as depicted in *Figure 2*. It is shown that the skin layer

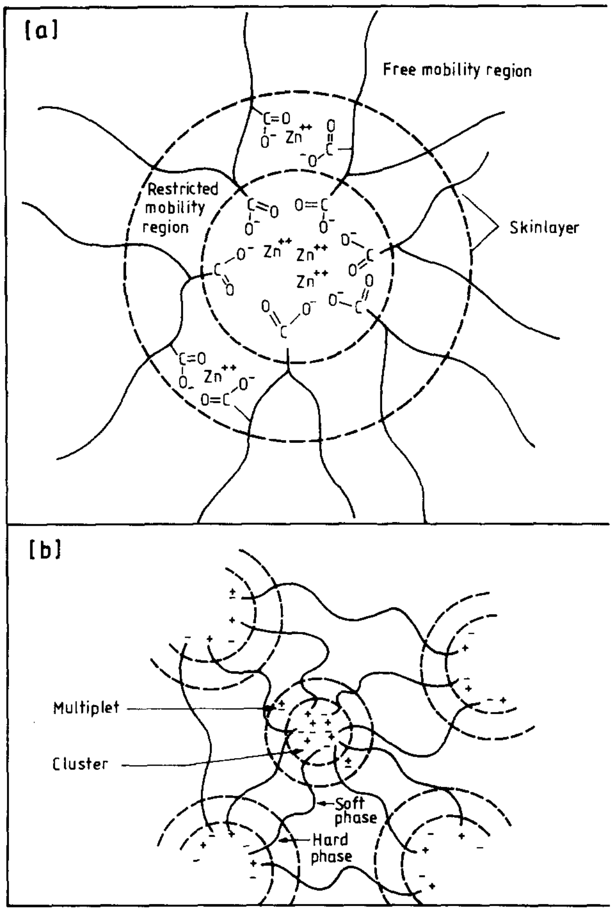

Figure 2 Model of ionomer showing formation of biphasic structure

Table 5 Results of dynamic mechanical studies

Mix number	T_g (°C)	Tan δ at T_g	T_i (°C)	Tan δ at T_i
S0	−36.8	0.837	+52.6	0.128
S1	−37.0	0.814	+60.6	0.139
S2	−36.4	0.715	+62.9	0.148
S3	−35.5	0.692	+72.8	0.166

separates the restricted mobility region from the free mobility region, which constitutes the bulk of the chain segments. Results of dynamic mechanical studies are summarized in *Table 5*. The values of tan δ at different temperatures were obtained from the data stored in the instrument's computer.

The variation in room-temperature storage modulus on filler incorporation is shown in *Figure 3*. The results could be fitted with the following equation:

$$\frac{E'_f}{E'_g} = 1 + 12.1\phi \tag{1}$$

where E'_f is the storage modulus of the silica-filled system and E'_g refers to the modulus of the gum or unfilled system, and ϕ is the volume fraction of silica. This is very similar to the relationship proposed by Smallwood in the case of diene rubbers[17]. The greater slope of the plot in *Figure 3*, compared with that of conventional rubber systems, is ascribed to the strong interaction between the polymer chains containing ionic aggregates and the active sites on the filler surface.

Figure 3 also shows the plots of $\tan\delta_f/\tan\delta_g$ *versus* volume fraction of filler (ϕ) at T_g and T_i. Here 'f' stands for the silica-filled system and 'g' denotes the gum or unfilled system. The results could be fitted with the following relations.

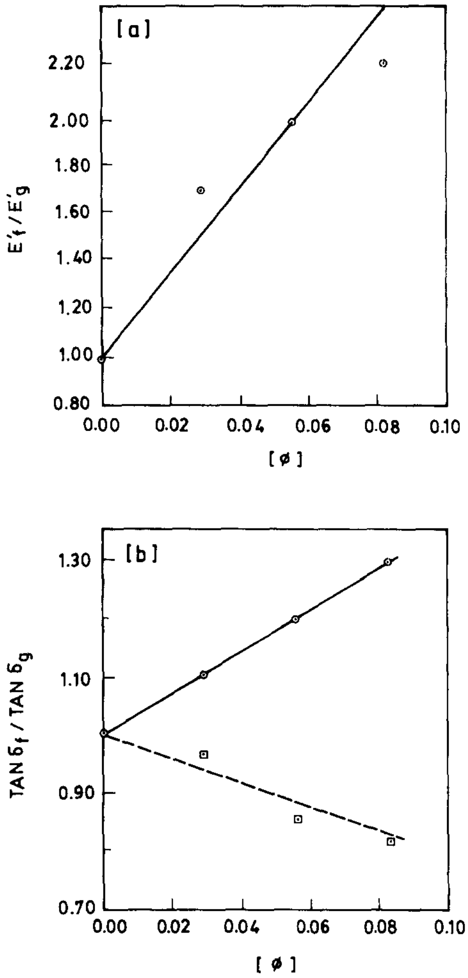

Figure 3 Variation of (a) E'_f/E'_g with volume fraction (ϕ) of filler at room temperature, and (b) $\tan\delta_f/\tan\delta_g$ with volume fraction (ϕ) of filler: – – –⊡– – –, at T_g; ——⊙——, at T_i

At T_g:

$$\frac{\tan\delta_f}{\tan\delta_g} = 1 - 2.6\phi \tag{2}$$

Equation (2) is similar to that obtained in the case of conventional rubber systems and depicts weak rubber–filler interaction[18–20], involving the backbone chains of the polymer.

At T_i:

$$\frac{\tan\delta_f}{\tan\delta_g} = 1 + 3.1\phi \tag{3}$$

This indicates that the occurrence of the high-temperature relaxation of the restricted mobility zones of the chain segments is facilitated by the filler, thereby implying strong bonding between the ionic aggregates and the polar sites of the filler. From the above results, it can be inferred that the rubber–filler interaction in the case of silica-filled ionic rubber is of two types: (1) the interaction between the filler particles and the non-ionic segments of the polymer backbone, which is similar to

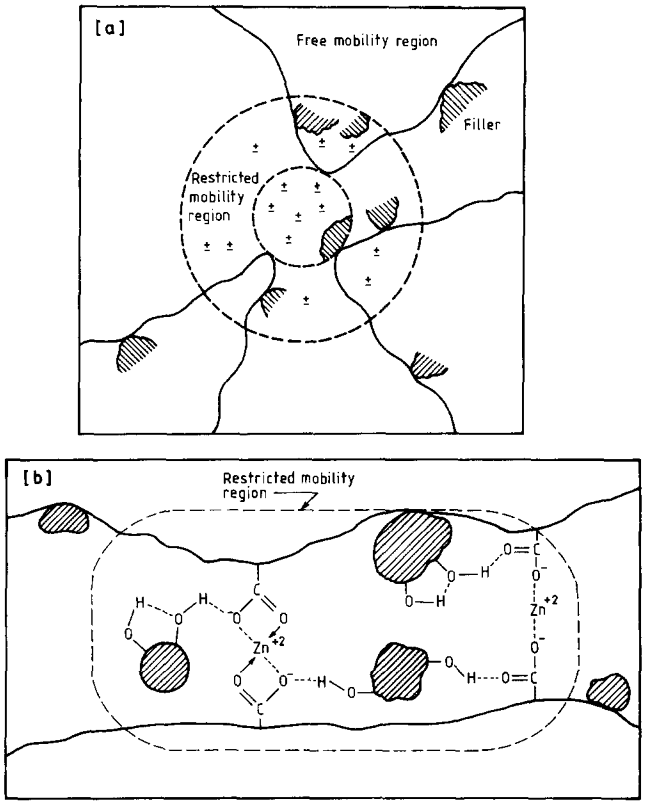

Figure 4 (a) Schematic diagram showing distribution of fillers in different parts of an anionic elastomer. (b) Proposed structural model showing the interaction of silanol groups on silica surface with carboxylate groups

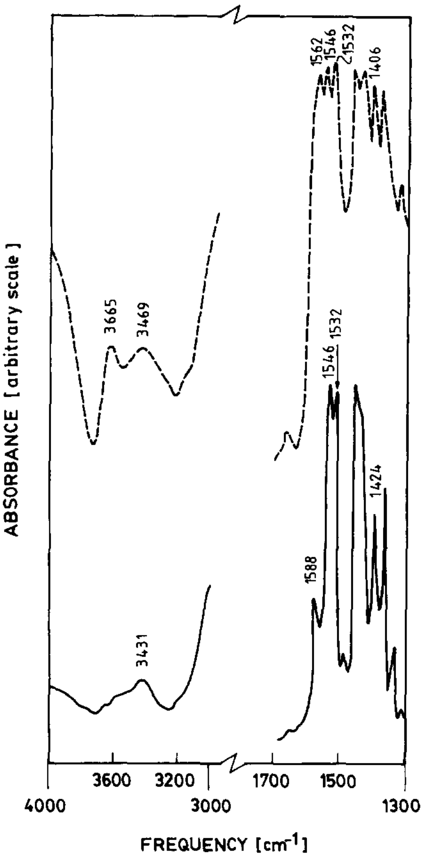

Figure 5 Infra-red spectra: ——, S0; – – –, S1

the interaction involving diene rubbers and reinforcing fillers, as manifested in the lowering of tan δ at T_g; and (2) the interaction between the ionic groups of the polymer and the polar sites (silanol groups) present on the filler surface, which is manifested in an increase in tan δ at T_i. At T_i the slope in the plot of equation (3) is positive, thereby inferring that increase in filler loading strengthens the high-temperature relaxation, presumably by increasing the ionic-cluster-induced chain rigidity. While the rubber–filler interaction involving the non-ionic polymer backbone is of a weak Van der Waals' type, the same due to ionic aggregates can be of both the hydrogen-bonded type involving polar sites on the filler surface[13] and the Van der Waals' type, as depicted in *Figure 4*. The results of i.r. spectroscopic studies, discussed below, are in conformity with the proposed hydrogen-bonded interaction shown in *Figure 4*.

Figure 5 shows the i.r. spectra of both unfilled and silica-filled samples (mixes S0 and S1). In the case of the unfilled sample, the peak at 3431 cm^{-1} is possibly due to the hydrogen-bonded structure involving –OH and –COOH groups (not shown in *Figure 4*), while the three peaks at 1588, 1546 and 1532 cm^{-1} are due to carboxylate asymmetric stretching vibration and ascribed to the bridging type of metal carboxylate[21–24]. The peak at 1424 cm^{-1} is believed to be due to symmetric stretching of the carboxylate anion and is ascribed to the non-bridging type of metal carboxylate[21–24]. Therefore, it is assumed that both bridging and non-bridging types of metal carboxylates are present in the ionic aggregates. In the case of the silica-filled system, the peak at 3469 cm^{-1} is believed to be due to hydrogen-bonded structure in vicinal silanol groups[25] and the peak at 3665 cm^{-1} is ascribed to the hydrogen-bonded structure involving silanol groups with carboxylate anions (*Figure 4*). The peaks in the carboxylate asymmetric stretching region occur at 1562, 1546 and 1532 cm^{-1} and the carboxylate symmetric stretching peak occurs at 1406 cm^{-1}. Since both bridging and non-bridging types of metal carboxylates participate in hydrogen bond formation, the respective stretching vibration bands are shifted to lower frequencies compared with the unfilled system.

Figure 6 shows the variation of apparent viscosity with apparent shear stress. It is evident that the mixes are pseudoplastic in nature. Furthermore, as expected, viscosity increases with increasing filler loading.

The activation energy (ΔE) for viscous flow was calculated according to the following equation[26]:

$$\eta = A\,\mathrm{e}^{\Delta E/RT} \tag{4}$$

where η is the apparent viscosity at temperature T, R is the universal gas constant and A is an empirical constant. The activation energy values for different systems and at different shear rates are summarized in *Table 6*. It is evident that the activation energy for flow increases with filler loading, but decreases with increase in shear rate.

At high processing temperature zinc stearate plasticizes the matrix and solvates the ionic clusters[27,28], thus facilitating polymer flow. In the silica-filled systems, however, the flow is hindered due to the presence of silica particles anchoring the chain segments both in the regions of free mobility and restricted mobility, thereby increasing the free energy of activation. Furthermore, under high shear conditions, it is likely that the loosely

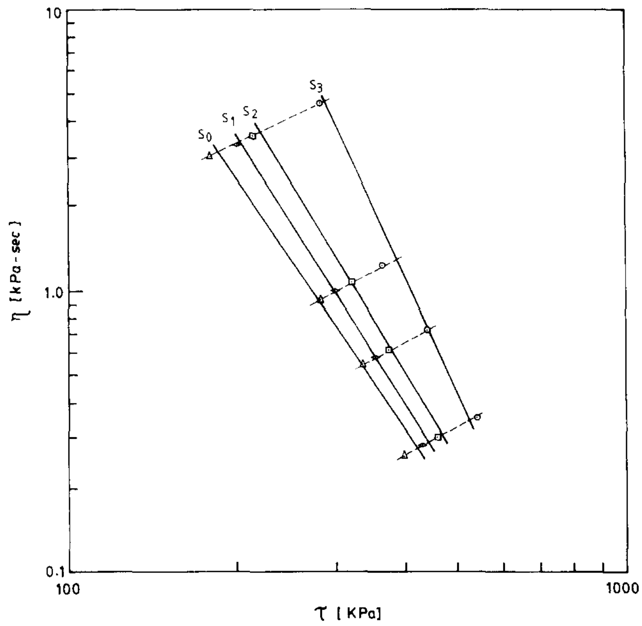

Figure 6 Variation of apparent viscosity (η) with shear stress (τ)

Table 6 Activation energy (ΔE) for viscous flow in kJ mol^{-1}

	Mix number			
Shear rate (s^{-1})	S0	S1	S2	S3
61	16.0	28.1	31.8	39.5
305	12.2	20.5	24.3	28.2
610	9.4	15.6	16.9	18.6

Table 7 Results of reprocessability studies. Mix no., S2; temperature, 70°C; shear rate, 121 s^{-1}

Cycle	Shear stress (kPa)	300% Modulus of extrudate (MPa)
1	285.71	3.82
2	293.27	3.98
3	296.40	4.00
4	297.29	3.91

held silica aggregates are broken down, causing a reduction in the apparent activation energy of flow.

Since the system exhibits thermoplastic behaviour, its reprocessability was studied in the MPT and the results are given in *Table 7*. Viscosity during repeated extrusions and the modulus of the corresponding extrudates remain constant up to four cycles of extrusion, thereby confirming the thermoplastic elastomeric nature of the silica-filled m-EPDM/ZnO/stearic acid/zinc stearate composition.

Conclusions

The zinc salt of maleated EPDM rubber in the presence of stearic acid and zinc stearate behaves as a thermoplastic elastomer which can be reinforced by the incorporation of precipitated silica filler. It is believed that, besides the dispersive type of forces operative in the interaction between the backbone chains and the filler particles, the ionic domains in the polymer interact strongly with the polar sites on the filler surface through the formation of hydrogen-bonded structures.

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