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Dynamic mechanical and infra-red spectroscopic studies on interaction between carbon black and ionic thermoplastic elastomer based on maleated EPDM rubber

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Incorporation of up to 30 phr of high abrasion furnace (HAF) carbon black into a thermoplastic elastomer of composition 100 phr maleated EPDM rubber, 10 phr ZnO, 1 phr stearic acid and 30 phr zinc stearate, improves its physical properties like modulus 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. Furthermore, $\tan\delta$ at T_g decreases but $\tan\delta$ at T_i increases due to filler incorporation. It is believed that, besides the interaction between the backbone chains and the filler particles, the ionic domains in the thermoplastic elastomer interact with the polar sites of the filler particles presumably by hydrogen bond formation. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ionic thermoplastic elastomer; carbon black; matrix–filler interaction)

Introduction

Functionalization of ethylene–propylene diene monomer (EPDM) rubber by carboxylation or sulfonation reaction produces carboxylated or sulfonated EPDM rubber respectively, and neutralization of the acid groups by suitable bases such as zinc oxide or magnesium oxide leads to the formation of ionic crosslinks[1–4] that are thermolabile. The resulting ionic polymers behave as thermoplastic elastomers (TPEs)[5]. Zinc stearate is known to act as a plasticizer for the ionic domains and facilitates processing of the ionic polymers above its melting point (> 128°C)[6,7].

It has been reported that zinc oxide neutralized maleated EPDM rubber (abbreviated as m-EPDM) in the presence of stearic acid and zinc stearate behaves as a thermoplastic elastomer[8].

Precipitated silica has been reported to act as reinforcing filler for m-EPDM based ionic elastomer[9]. The presence of polar silanol groups on the filler surface is believed to promote its interaction with the ionic groups of the rubber. Since reinforcing carbon black contains polar groups on its surface, the present investigation was undertaken in order to study the effect of HAF carbon black on the properties of the ionic elastomer. Although reinforcing fillers in general are known to adversely affect the strength properties of TPEs[10], there are reports of reinforcement of ionic thermoplastic elastomers by carbon black[11–14].

This communication reports the results of studies on the interaction between HAF carbon black and ionic thermoplastic elastomer based on m-EPDM, with special reference to dynamic mechanical and Fourier transform infra-red (*FT*i.r.) spectroscopic studies.

Experimental

Details of the materials used are given in *Table 1*. Carbon black used was high abrasion furnace type (grade N330). Formulations for the different mixes are given in *Table 2*.

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 detailed in *Table 3* was followed. Cooling 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.

Stress–strain properties were studied in a Zwick universal testing machine (UTM), model 1445, according to ASTM D412 (1980) specification. Tear strength was measured in the Zwick UTM 1445 using a 90° nick-cut crescent sample according to ASTM D624-86. Hysteresis studies under tension were 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 (M/s Orientec Corporation, Tokyo, Japan) at a frequency of 3.5 Hz in

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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, $ML_{(1+4)}$ at 100°C, 60
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
HAF Carbon black (N-330)	Philips Carbon Black Limited, Durgapur, India	Specific gravity, 1.8

Table 2 Formulation of mixes[a]

	Mix number			
Ingredient	B0	B1	B2	B3
m-EPDM	100	100	100	100
ZnO	10	10	10	10
Stearic acid	1	1	1	1
Zinc stearate	30	30	30	30
HAF carbon black	0	10	20	30

[a] Values given in phr (parts per hundred of rubber, by weight)

Table 3 Mixing schedule

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

Table 4 Physical properties at 25°C[a]

	Mix number			
	B0	B1	B2	B3
300% modulus (MPa)	2.78 (1.82)	3.01 (1.95)	3.64 (2.24)	4.04 (2.38)
Hardness (Shore A)	62	67	71	74
Tensile strength (MPa)	7.42 (2.47)	7.64 (2.48)	8.12 (2.90)	7.45 (3.01)
Elongation at break (%)	760 (431)	730 (504)	710 (520)	692 (517)
Tear strength ($N\,cm^{-1}$)	400 (233)	485 (256)	510 (303)	530 (321)
Hysteresis work ($J\,m^{-2}$) × 10^3	80.1	87.3	112.6	133.0
Tension set at 100% extension (%)	13	13	14	16

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

the temperature range from −100 to 200°C. The heating rate was 1°C min^{-1}.

Rheological properties were measured 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 were chosen as 61, 305, 610 and 1525 s^{-1}.

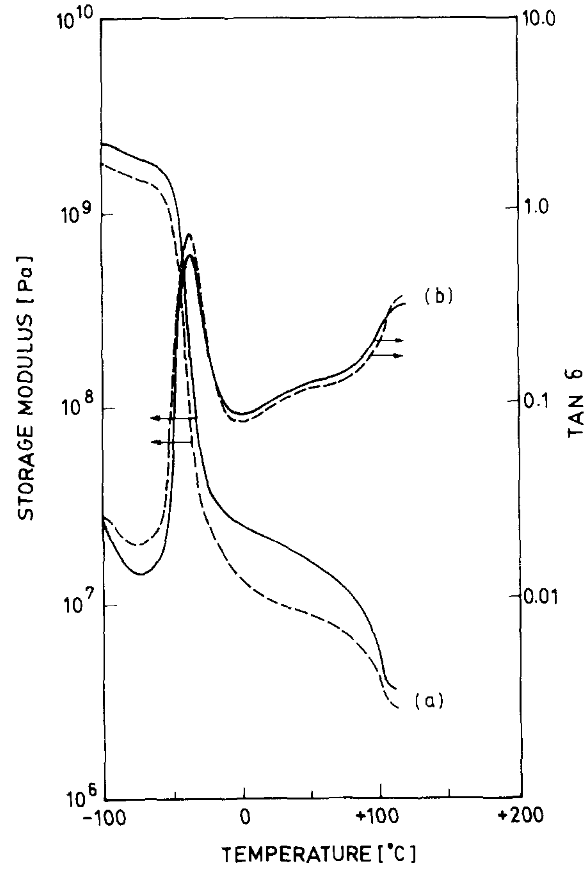

Figure 1 (a) Storage modulus *versus* temperature plots; (b) tan δ *versus* temperature plots. - - - -, B0; ······, B2

The infra-red spectra were taken in a Brüker FTIR spectrometer model IFS-66, at a resolution of 4 cm^{-1}, using an MCT cryogenic detector for signal enhancement. Spectra of carbon black (in powder form) were taken by a DRIFT attachment using a KBr support. For this sample 2000 scans were signal averaged. For sample numbers B0 and B1 thin compression moulded films (~ 0.4 mm thick) were used. For these samples the attenuated total reflection (ATR) technique was used. Spectral data were collected after taking the average of 200 scans.

Results and discussion

Physical properties are summarized in *Table 4*. While ultimate tensile strength is only marginally affected, incorporation of HAF carbon black causes increases in

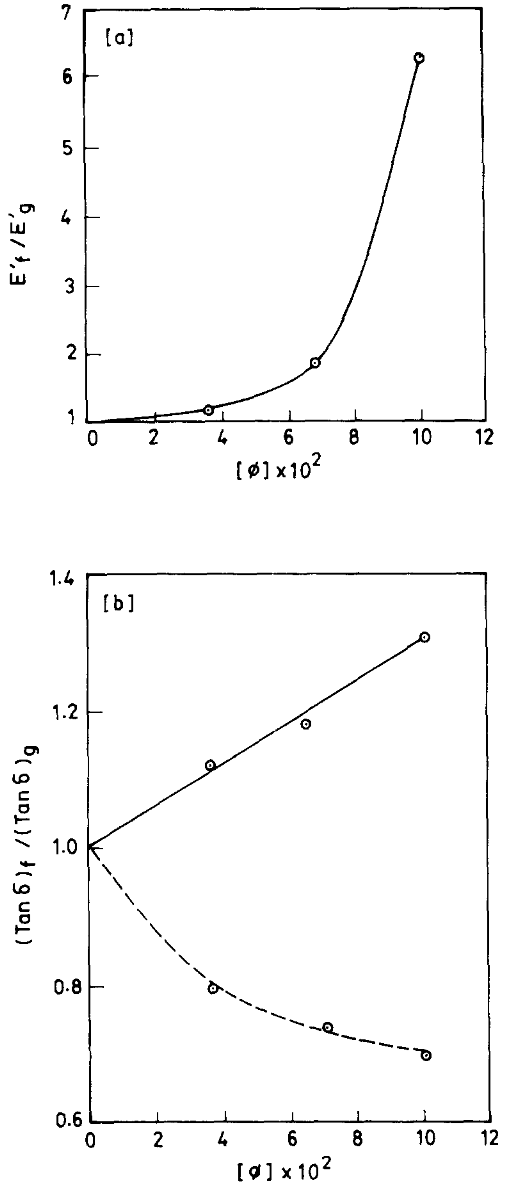

Figure 2 (a) Variation of E'_f/E'_g with volume fraction of the filler (ϕ) at room temperature. (b) Variation of $(\tan\delta)_f/(\tan\delta)_g$ with volume fraction of filler (ϕ) at T_g (- - - -) and T_i (——)

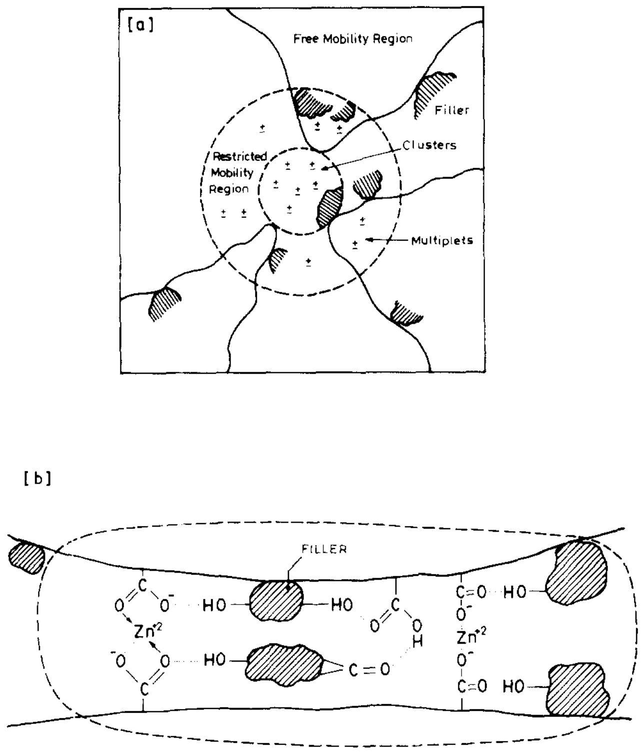

Figure 3 (a) Proposed model showing attachment of the filler particles in different regions of the ionomer. (b) Probable mechanism of interaction between filler particles and ionic groups in the restricted mobility region

hardness and modulus and a decrease in elongation at break. Furthermore, tear strength increases with increasing carbon black loading. The increase in tear resistance is accompanied by an increase in hysteresis loss. Although tensile strength values at room temperature remain almost unaffected, retention of strength at higher test temperature increases on filler incorporation. The results reveal that an interaction occurs between the elastomer and the filler, the effect of which is particularly manifested during measurement of physical properties at elevated temperature.

Variation of storage modulus (E') and $\tan\delta$ with temperature is shown in *Figure 1a*. It is evident that E' increases with increasing filler loading under ambient temperatures. However, at higher temperatures, E' decreases and the decrease is sharp at temperatures exceeding 90°C. It has been reported that, above its melting point (128°C), zinc stearate plasticizes the ionic aggregates in an ionic polymer[10]. In the polymer matrix and in the presence of carbon black filler, melting of zinc stearate is likely to occur at lower temperatures and, hence, plasticization of the matrix and occurrence of the transition from the rubbery state to the viscous flow state occurs around 90°C. That at room temperature carbon black reinforces the rubber is evident from the variation of the ratio (E'_f/E'_g) with filler concentration, as shown in *Figure 2a*. The plot shows that (E'_f/E'_g) is related to volume fraction of filler (ϕ) by the following relation:

$$\frac{E'_f}{E'_g} = 1 + 1.3\phi + 14.3\phi^2 \qquad (1)$$

where E'_f is the storage modulus of the filled system and E'_g is the storage modulus of the unfilled samples. Similar behaviour has been observed in the case of diene rubbers cured by conventional vulcanizing agents and filled with reinforcing fillers[15].

Variation of $\tan\delta$ with temperature, as shown in *Figure 1b*, reveals that besides the low-temperature glass–rubber transition, there occurs a second transition above room temperature, i.e. around +40 to +60°C. The high-temperature transition, denoted as T_i, is believed to be due to relaxation of restricted chain segments arising from ionic aggregates such as multiplets and clusters[16–18], as depicted in *Figure 3*. That the second relaxation is due to ionic aggregates and not due to crystallinity has been confirmed by the absence of the relaxation in the case of neat m-EPDM and the corresponding neat EPDM[8]. Furthermore, it has been reported that EPDM containing 55% ethylene is essentially amorphous[5].

While the glass–rubber transition temperature (T_g) remains unaltered on filler incorporation, $\tan\delta$ at T_g decreases. However, T_i and $\tan\delta$ at T_i increase with

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
B0	−36.8	0.837	+52.6	0.128
B1	−38.0	0.670	+57.1	0.137
B2	−37.7	0.650	+58.0	0.140
B3	−36.4	0.625	+60.2	0.152

increase in filler loading (*Table 5*). The values of T_g, tan δ at T_g, T_i and tan δ at T_i were collected from the data stored in the computer attached to the instrument. Plots of $(\tan\delta)_f/(\tan\delta)_g$ *versus* volume fraction of the filler are shown in *Figure 2b*. Here $(\tan\delta)_f$ is the tan δ value for the filled system and $(\tan\delta)_g$ is the tan δ value for the unfilled system.

At T_g,

$$\frac{(\tan\delta)_f}{(\tan\delta)_g} = 1 - 5.8\phi + 34.6\phi^2 \tag{2}$$

At T_i,

$$\frac{(\tan\delta)_f}{(\tan\delta)_g} = 1 + 1.5\phi \tag{3}$$

At T_g, the negative slope of the plot is similar to that for conventional rubber–filler systems showing strong rubber–filler interaction[19]. At T_i, the slope is positive thereby inferring that increase in filler loading strengthens the high-temperature relaxation. *Figure 3* is a schematic model showing the attachment of the filler particles in different regions of the ionomer. It is evident that the rubber–filler interaction in the present case is of two types: (1) interaction between the filler particles and the backbone chains, which is similar to the interaction involving diene rubbers and reinforcing fillers and which is manifested in lowering of tan δ at T_g; and (2) interaction between the ionic aggregates and the filler particles, which is manifested in an increase in the tan δ value at T_i. The filler particles seem to enhance the ionic-cluster-induced chain rigidity responsible for the high-temperature transition (T_i)[11,20,21]. While the rubber–filler interaction involving the backbone chains is of Van der Waals' type, the same due to ionic aggregates can be of both the hydrogen-bonded type (which is discussed later) and the Van der Waals' type, as proposed in *Figure 3*.

Infra-red spectra of the carbon black, mix B_0 (i.e. the base ionic elastomer) and mix B_1 (i.e. carbon-black-filled ionic elastomer) are shown in *Figure 4*. In the high-frequency range, carbon black shows three peaks: (1) the peak at 3730 cm^{-1} is believed to be due to O–H groups in substituted phenolic compounds; (2) the peak at 3653 cm^{-1} is ascribed to free O–H groups in phenols and alcohols; (3) the broad peak at 3162 cm^{-1} is attributed to composite absorption of hydrogen-bonded OH groups from alcohols, phenols and enols[22-25]. The base ionomer shows an absorption at 3424 cm^{-1} arising from O–H stretching of free carboxylic acids. The carbon-black-filled ionomer shows a very broad absorption at 3217 cm^{-1} which is believed to be due to composite absorption by the hydrogen-bonded O–H groups present in both carbon black and ionomer[23,24].

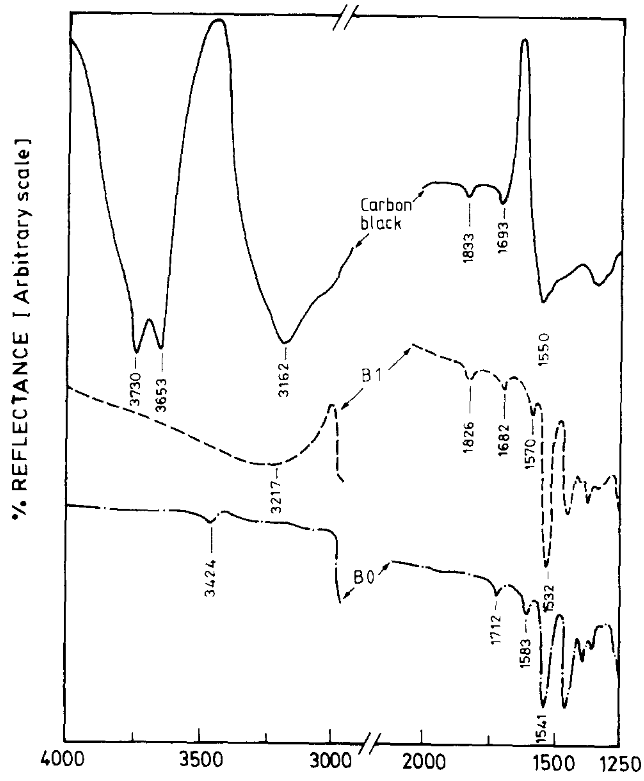

Figure 4 Infra-red spectra of HAF carbon black, mix B0 and mix B1

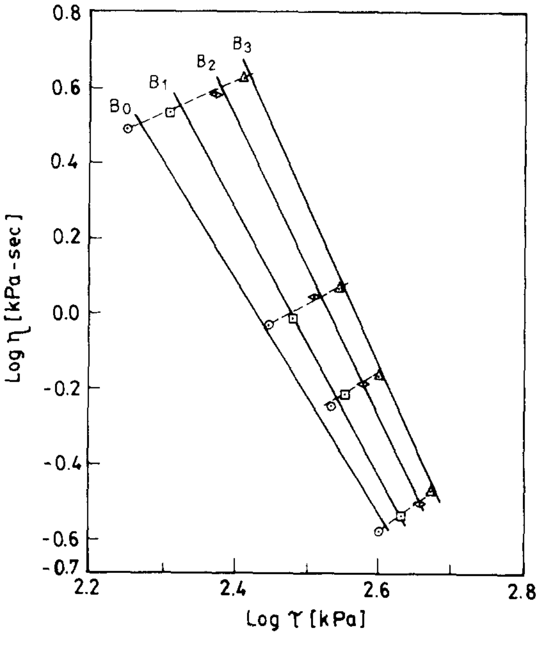

Figure 5 Variation of apparent viscosity (η) with shear stress (τ)

In the low-frequency region, carbon black shows three peaks: (1) the peak at 1833 cm^{-1} is ascribed to β-lactone; (2) the peak at 1693 cm^{-1} is believed to be due to carboxyl stretching vibration; (3) the peak at 1550 cm^{-1} is possibly due to the enol form of a β-dicarbonyl compound. The base ionomer, on the other hand, shows peaks at 1583 and 1541 cm^{-1}, possibly due to asymmetric stretching vibration of carboxylate anions, and a peak at 1712 cm^{-1} arising from carbonyl stretching of carboxylic acids[22,23,25-28]. The carbon-black-filled ionomer shows different peaks: (1) the peak at 1826 cm^{-1} is due to the hydrogen-bonded β-lactones; (2) the peak at 1682 cm^{-1}

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

	Mix number			
Shear rate (s^{-1})	B0	B1	B2	B3
61	16.0	24.5	28.3	34.9
305	12.3	15.0	17.0	22.4
610	9.4	12.4	13.0	15.8

Table 7 Results of reprocessability studies. Mix no., B2; temperature, 160°C; shear rate, 121 s^{-1}

Cycle	Shear stress (kPa)	300% modulus of extrudate (MPa)
1	218.4	3.65
2	224.7	3.71
3	225.2	3.87
4	225.2	3.85

is believed to be due to hydrogen-bonded carbonyl groups; (3) the peaks at 1570 and 1532 cm^{-1} arise from hydrogen-bonded carboxylate anions. Results of i.r. spectroscopic studies reveal that O–H groups on the filler surface interact with the carboxylate anions of the ionomer, presumably through hydrogen bond formation. Similarly, carbonyl groups on the filler surface interact with the carboxyl groups of the polymer.

Figure 5 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[29]:

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

where η is apparent viscosity, R is the universal gas constant and T is absolute temperature. 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 it decreases with increasing shear rate.

At high processing temperature zinc stearate plasticizes the matrix and solvates the ionic clusters[30], thus facilitating the polymer flow. In the black-filled systems, however, the flow is hindered due to the presence of filler particles anchoring the free chains of the backbone and also the immobile segments in the neighbourhood of the ionic zones, thereby increasing the free energy of activation. Furthermore, under high shear conditions, loosely held carbon black aggregates are broken down, causing a reduction in activation energy of flow.

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

Conclusions

HAF carbon black improves the physical properties of the thermoplastic elastomer based on the formulation 100 phr m-EPDM, 10 phr ZnO, 1 phr stearic acid and 30 phr zinc stearate. The filler plays a dual role in the sense that it reinforces the backbone chains of the polymer and strengthens the high-temperature ionic transition.

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