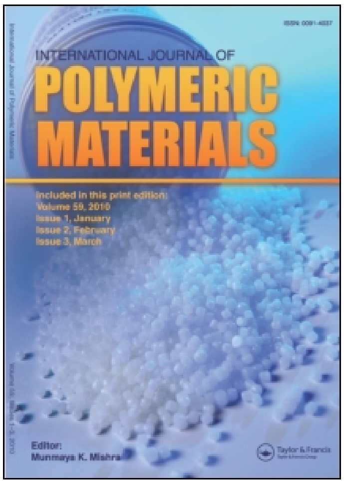

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Dynamic Mechanical Properties of Carbon Black Filled Ethylene Vinyl Acetate Rubber

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The dynamic mechanical properties of ethylene vinyl acetate (EVA) rubber filled with different loadings of carbon black and at different degrees of crosslinking were studied over a wide range of temperatures (−150° to +200°C). The loss tangent (tan δ) versus temperature plots indicated presence of different transitions. The α-transition (or the glass-rubber transition) corresponding to the maximum in tan δ value, occurred at −17°C, which is the principal glass-transition temperature (abbreviated as T_g) of EVA rubber. The γ-transition occurred in the temperature region of −125° to −135°C, while the β-transition appeared as a shoulder in the temperature region of −65° to −75°C. Besides, there was also a high tempeature transition around +62°C which is known as liquid to liquid transition ($T_{l,l}$). Incorporation of carbon black filler did not cause any shift of T_g, while the tan δ peak values at T_g decreased sequentially with increase in filler loading. The γ- and β-relaxations were found to be insensitive to filler loading. The $T_{l,l}$ transition, however, was found to be suppressed by incorporation of carbon black filler particularly at high loading. Extent of crosslinking did not influence the T_g. But, the $T_{l,l}$ transition, which was prominent with the lightly crosslinked system was found to be suppressed at high level of crosslinking. Strain dependent dynamic mechanical properties under isothermal conditions showed that the secondary structure breakdown of carbon black filler under the effect of strain amplitude is influenced by the degree of crosslinking of EVA rubber.

KEY WORDS Dynamic mechanical properties, filled elastomer, carbon black, ethylene vinyl acetate rubber.

1. INTRODUCTION

Several investigators have studied the effect of different fillers on the dynamic mechanical properties of rubbers.[1–9] Recently, dynamic mechanical studies of ethylene vinyl acetate rubber filled with silica filler have been reported.[10,11] The present work deals with the results of our studies on the dynamic mechanical properties of carbon black filled EVA rubber over a wide range of temperatures (−150° to +200°C). The effect of degree of crosslinking of EVA rubber on its dynamic mechanical properties has also been studied.

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2. EXPERIMENTAL

2.1 Materials

The EVA rubber used was levaprene 450 (45% vinyl acetate content), manufactured by Bayer, Germany. The filler used was HAF-LS carbon black, manufactured by Philips Carbon Black Limited, India. Its characteristics were as follows: specific gravity, 1.8; BET surface area 82 m^2/gm; DBP absorption, 102 $cm^3/100$ gm; particle size, 29 nm. The peroxide used for crosslinking of EVA rubber was dicumyl peroxide (96% pure), manufactured by Bayer, Germany. The coagent used for the peroxide crosslinking was triallyl cyanurate, manufactured by Degussa, Germany.

2.2 Sample Preparation

Mixing was done in a laboratory size two-roll mixing mill (330 mm × 152.5 mm) at room temperature according to ASTM D 3182. The rubber compounds were vulcanized to their respective optimum cure times determined by Monsanto Rheometer R-100S at 160°C.

2.3 Test Method

The dynamic mechanical studies of the vulcanizates were carried out using the Dynamic Viscoelastometer. Rheovibron (model DDV-III-EP) of Orientec Corporation, Japan. Experiments were carried out in tension mode over a temperature range of $-150°$ to $+200°C$ at a frequency of 11 Hz and double strain amplitude (DSA) of 0.1%. DSA is defined as:

$$\mathrm{DSA} = \frac{2 \times \text{amplitude}}{\text{length of the test piece}} \qquad (1)$$

The rate of temperature rise was 1°C per minute.

Isothermal strain dependent properties were studied at room temperature (27°C) by changing the amplitude and length of the test pieces, with DSA values ranging from 0.07% to 5%.

2.4 Solvent Swelling

The volume fraction of rubber in the swollen vulcanizate, V_r, which can be taken as a measure of degree of cross-linking was calculated using the following equation.[12]

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}} \qquad (2)$$

where T is the weight of the test, D the deswollen weight of the specimen, F the weight fraction of insoluble components of the vulcanizate and ρ_r and ρ_s are the specific gravities of EVA rubber and chloroform, respectively. $A_0 = S_x - D$, where S_x is the swollen weight of the specimen.

3. RESULTS AND DISCUSSION

Formulations of the mixes are given in Table I. EBO is the formulation for the unfilled compound. EB1, EB2, EB3 and EB4 are the mixes containing different loadings of carbon black. EB4L and EB4H contain the same filler loading as EB4, but different curative concentrations. Accordingly, the extent of crosslinking of the three vulcanizates (EB 4, EB4L and EB4H) measured by V_r (volume fraction of rubber in solvent swollen vulcanizate) follows the order, EB4L < EB4 < EB4H (Table I).

3.1 Temperature Dependent Dynamic Mechanical Properties

3.1.1 Storage Modulus. Figure 1 illustrates the storage modulus (E') of EVA vulcanizates containing different loadings of carbon black filler over a temperature range of $-150°$ to $+200°C$. The filled EVA vulcanizates in general exhibited characteristic sigmoidal variation of the storage modulus with temperature. The modulus values at any temperature increased with increasing filler loading and this may be attributed to the increase in apparent crosslink density due to increased polymer-filler interaction. Similar observations have also been reported recently by other investigators.[13,14]

In order to quantify the extent of interaction between carbon black and EVA rubber, the term σ/η called the carbon black-rubber interaction parameter[15,16] has been calculated and the results shown in Table II. The parameters σ and η were derived from static and dynamic modulus measurements, respectively. The σ term

TABLE I

Compound formulations[a]

	Mix No.						
	EB0	EB1	EB2	EB3	EB4	EB4L	EB4H
Levaprene 450[b]	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Accinox DN[c]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Rhenogran P50[d]	3.0	3.0	3.0	3.0	3.0	3.0	3.0
HAF Black (LS)[c]	—	15.0	30.0	45.0	60.0	60.0	60.0
Dicumyl peroxide	1.8	1.8	1.8	1.8	1.8	0.6	3.6
Triallyl cyanurate	2.5	2.5	2.5	2.5	2.5	1.0	5.0
Mooney viscosity ML_{1+4}, 120°C	8	11	15	24	30	29	30
Optimum cure time at 160°C, min[f]	18.5	19.0	20.0	20.0	21.0	25.0	20.5
Volume fraction of rubber, V_r[g]	0.114	0.133	0.153	0.165	0.205	0.120	0.225

[a] Composition in 100 parts by weight of rubber.
[b] Ethylene vinyl acetate rubber (vinyl acetate content, 45%).
[c] para-phenyl-beta-napthylamine.
[d] Polycarbodiimide.
[c] High abrasion furnace black-low structure.
[f] Monsanto rheometry results.
[g] Solvent swelling results.

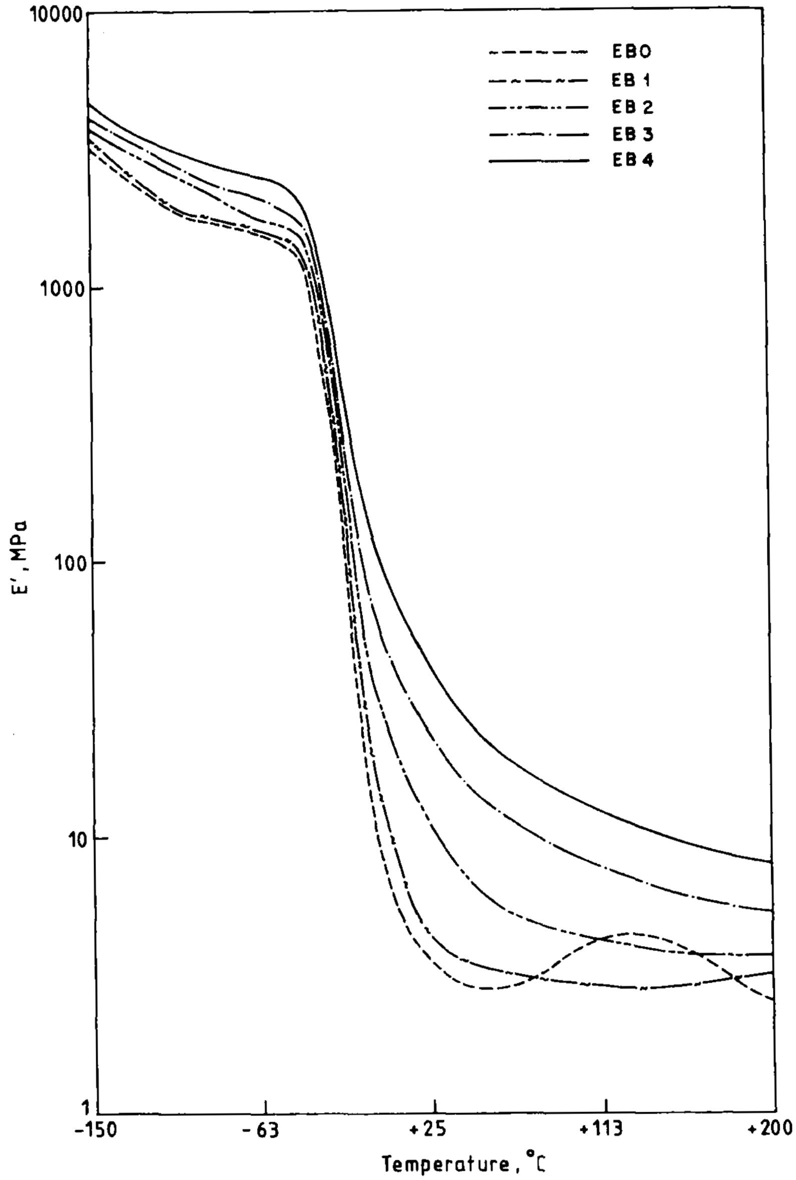

FIGURE 1 Effect of carbon black filler on the temperature dependent storage modulus of EVA vulcanizates.

relates to the filler-rubber interaction and is measured from the slope of the stress-strain plot at the extension ratio ranging from 1 to 3 where the modulus is supposed to be dependent on the adhesion between the carbon black surface and the rubber.[17,18] The η value is a measure of filler-filler interaction (secondary structure). In the present study this value was calculated from the ratio of storage modulus at low DSA (0.07%) to that at high DSA (5%). It is evident from Table II that the interaction parameter σ/η increased gradually with increase in carbon black

TABLE II

δ,[a] η,[b] and σ/η[c] values for carbon black filled EVA vulcanizates

Vulcanizate designation	σ	η	σ/η
EB0	0.9	1.14	0.78
EB1	1.25	1.28	0.97
EB2	2.38	1.74	1.37
EB3	3.27	2.21	1.48
EB4	5.06	2.74	1.85
EB4L	3.01	2.32	1.30
EB4H	5.92	2.67	2.22

[a] Slope of stress-strain plots at the extention ratio ranging from 1 to 3.

[b] Ratio of the storage modulus at 0.07% DSA to the same at 5% DSA.

[c] Carbon black-rubber interaction parameter.[15,16]

loading. Extent of crosslinking also was found to affect the interaction parameter and higher is the degree of crosslinking (V_r in Table I), higher is the value of the ratio σ/η (Table II).

The gum EVA vulcanizate showed a broad peak in the temperature region of 110°–120°C. In the filled vulcanizates, however, this peak did not appear. This phenomenon may be ascribed to the crystalline aspect of the polymer.[19,20] Other polymers like polyethylene[21] and polybutadiene[22] were also found to register similar peak at high temperature due to crystalline phase. Incorporation of carbon black filler caused interruption in crystallinity and thus this peak was not present in the case of filled vulcanizates.

The effect of the degree of crosslinking on the storage modulus versus temperature plots is shown in Figure 2. It is interesting to note that while in the glassy state the storage modulus increased in the order of decreasing crosslink density (that is, EB4L > EB4 > EB4H), the reverse is true in the rubbery and high temperature regions. The effect of crosslinking on the storage modulus in the glassy region could be interpreted by the fact that, increase in degree of crosslinking causes decrease in the number of free chains available leading to the reduction in strain induced crystallinity. Eventually, in the glassy state the elastic moduli decrease in the order of increasing extent of crosslinking. In the rubbery and high temperature regions the restricted flow characteristics is the determining factor for the variation of moduli under the effect of temperature. Eventually, the moduli in these temperature regions showed expected rise with increase in degree of crosslinking.

Figure 3 shows the plots of relative modulus of EVA vulcanizates as a function of temperature. The relative modulus is defined as E'_f/E'_m, where E'_f is the elastic modulus of the filled vulcanizate and E'_m is that of the gum vulcanizate. The nature of the plots for all compositions is identical. It is seen that in the glassy region, the relative moduli of all the vulcanizates are independent of temperature. Relative moduli increased sharply in the transition zone. In the rubbery and high temperature regions relative moduli of all vulcanizates decreased sharply until about 100°–125°C above which relative moduli registered an increase. It can also be noticed from Figure 3 that the relative moduli of vulcanizates at any given temperature increased

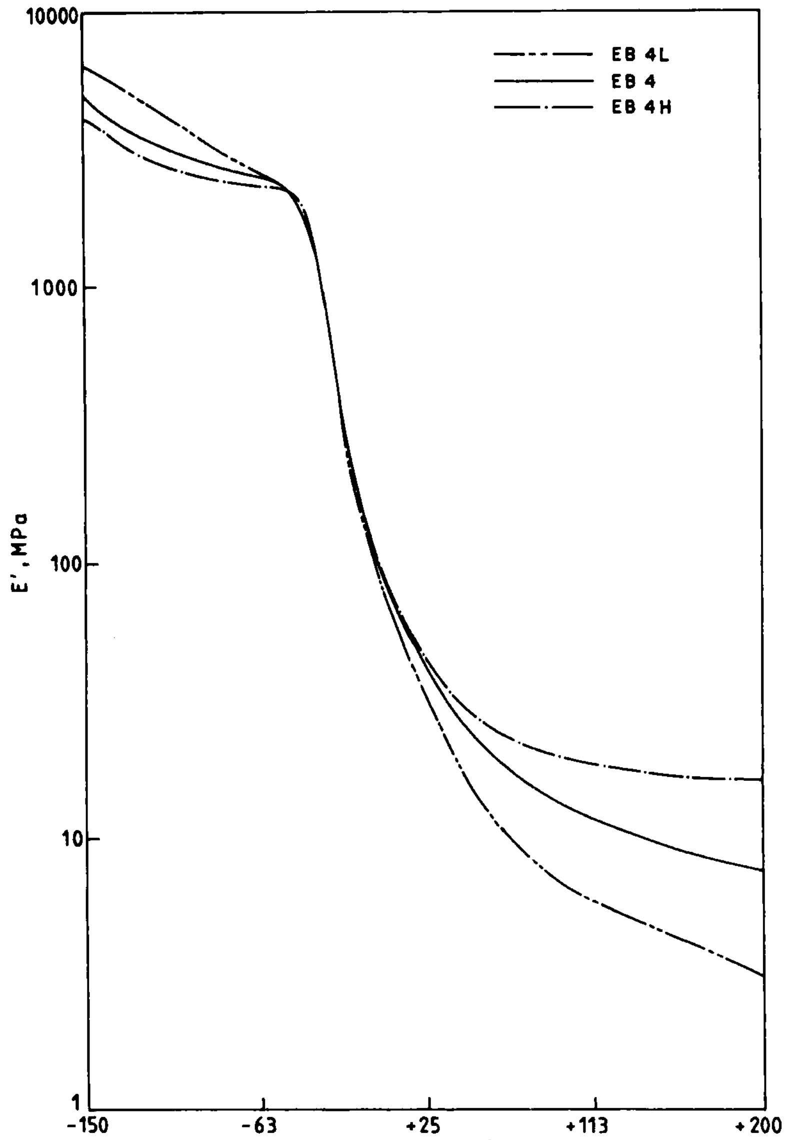

FIGURE 2 Effect of the degree of crosslinking on the temperature dependent storage modulus of EVA vulcanizates (volume fraction of carbon black, 0.234).

with increase in carbon black loading. However, the increase was much higher in the rubbery and high temperature regions than that in the glassy region. This phenomenon indicates that the effect of carbon black filler on the storage modulus is more prominent in the rubbery and high temperature regions than in the glassy state. Similar observations have been reported recently in case of filled rubbers.[10,14] Figure 3 also shows that increase in degree of crosslinking, in the order EB4L < EB4 < EB4H, caused decrease in relative moduli in the glassy state and increase in the rubbery and high temperature regions.

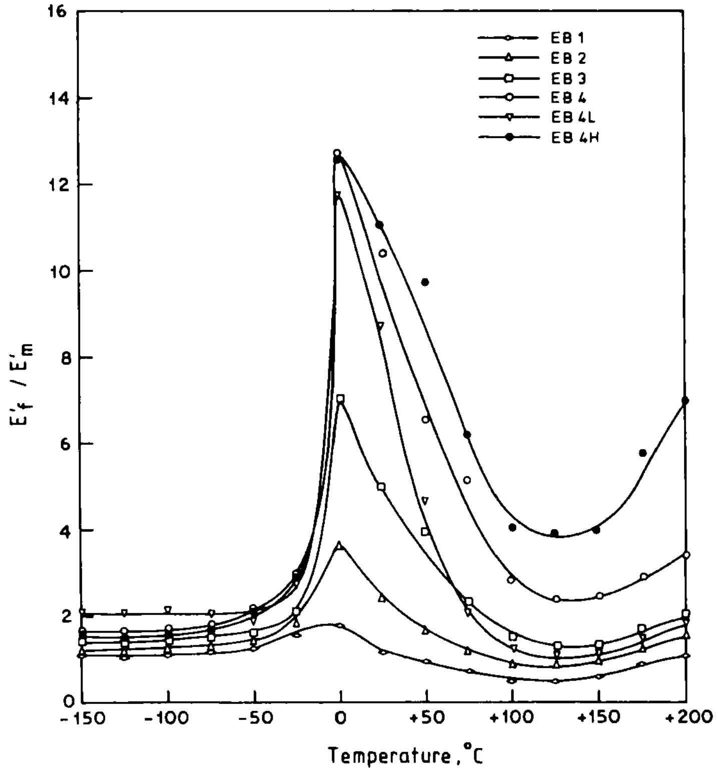

FIGURE 3 Relative storage modulus (E'_f/E'_m) of carbon black filled EVA vulcanizates as a function of temperature.

Figure 4 shows the variation of the storage modulus above T_g (at 0°C) with the concentration of carbon black filler. The experimental plot was compared with the modified Kerner equation.[23] The Kerner equation was simplified by restricting its applicability to the rubbery state of the filled compounds (that is, above T_g) and assuming that the dynamic modulus of the filler greatly exceeds that of the polymer matrix. Assuming the Poisson ratio for the rubber as 0.5, at a given volume fraction of filler (ϕ), the Kerner equation can be written as[23]

$$E'_f/E'_m = \frac{1 + 1.5A\phi}{1 - A\phi} \tag{3}$$

where A is the filler-rubber interaction parameter which is related to loss moduli by the following equation,[23]

$$E''_m/E''_f = 1 - A\phi \tag{4}$$

where E''_m and E''_f are the loss moduli of the gum and the filled matrices, respectively, at the reference temperature. Figure 5 shows the plot of E''_m/E''_f (at 0°C) versus the volume fraction of carbon black. A linear decrease in the E''_m/E''_f values with

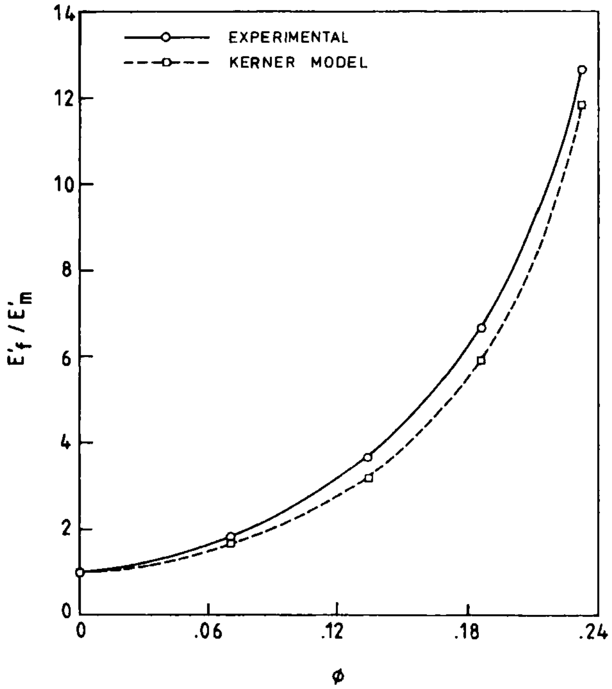

FIGURE 4 Relative storage modulus (E'_f/E'_m) at 0°C as a function of carbon black concentration.

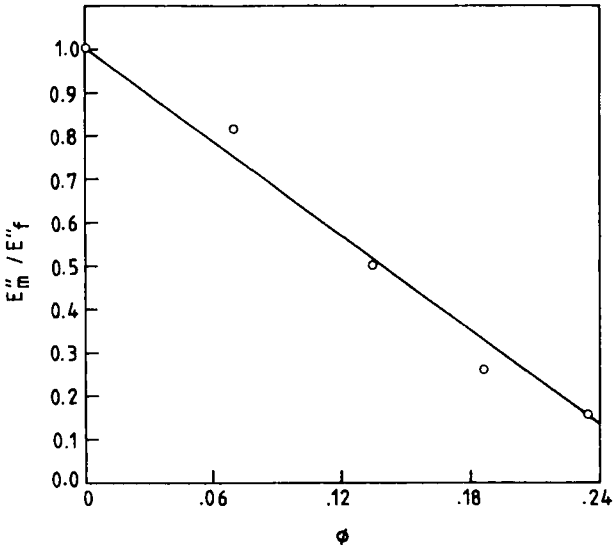

FIGURE 5 E''_m/E''_f at 0°C as a function of carbon black concentration.

the volume fraction of carbon black was observed. The slope of the straight line gives the value of A (Equation 4), which was found to be 3.5. Using $A = 3.5$ in Equation 3, the theoretical plot according to the modified Kerner equation (Equation 3) was found to follow closely the experimental plot (Figure 4).

Low temperature flexibility is an important property for a polymer in low temperature applications. The temperature at which the elastic modulus reaches 69 MPa has been used as a measure of low temperature stiffness.[24] The low temperature stiffness characteristics of different EVA vulcanizates containing increased loading of carbon black have been shown in Figure 6. The effect of degree of crosslinking of filled EVA vulcanizate (at volume fraction of carbon black of 0.234) on the low temperature flexibility is also shown in Figure 6. It can be seen that the low temperature flexibility decreased with increase in carbon black loading. The molecular mobility of the rubber decreased in the vicinity of filler surfaces[25,26] leading to decrease in flexibility at the desired temperature. Increase in crosslink density also causes restriction in chain mobility causing deterioration in low temperature flexibility.

3.1.2 Loss Tangent. ' The variation of low tangent with temperature for the different filled vulcanizates is shown in Figure 7. All the compositions exhibited α and γ-transition characteristics of ethylene vinyl acetate copolymer as reported earlier.[10,27–29] The principal glass-rubber transition temperature was found to occur at −17°C, which is known as the α-transition temperature (or dynamic glass transition temperature, T_g) of EVA rubber. This transition is attributed to the segmental motion of isolated —CH_2—$CH(OCOCH_3)$—CH_2— groups. The γ-transi-

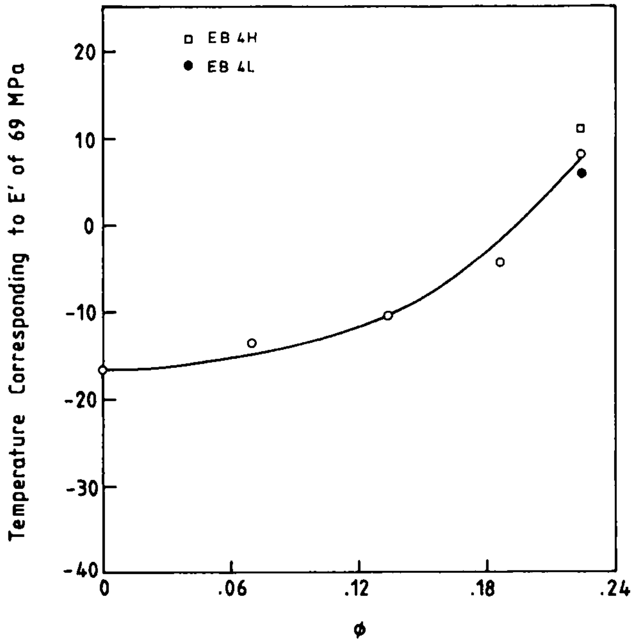

FIGURE 6 Effect of carbon black concentration on the low temperature flexibility (that is, temperature corresponding to E' of 69 MPa) of EVA vulcanizates.

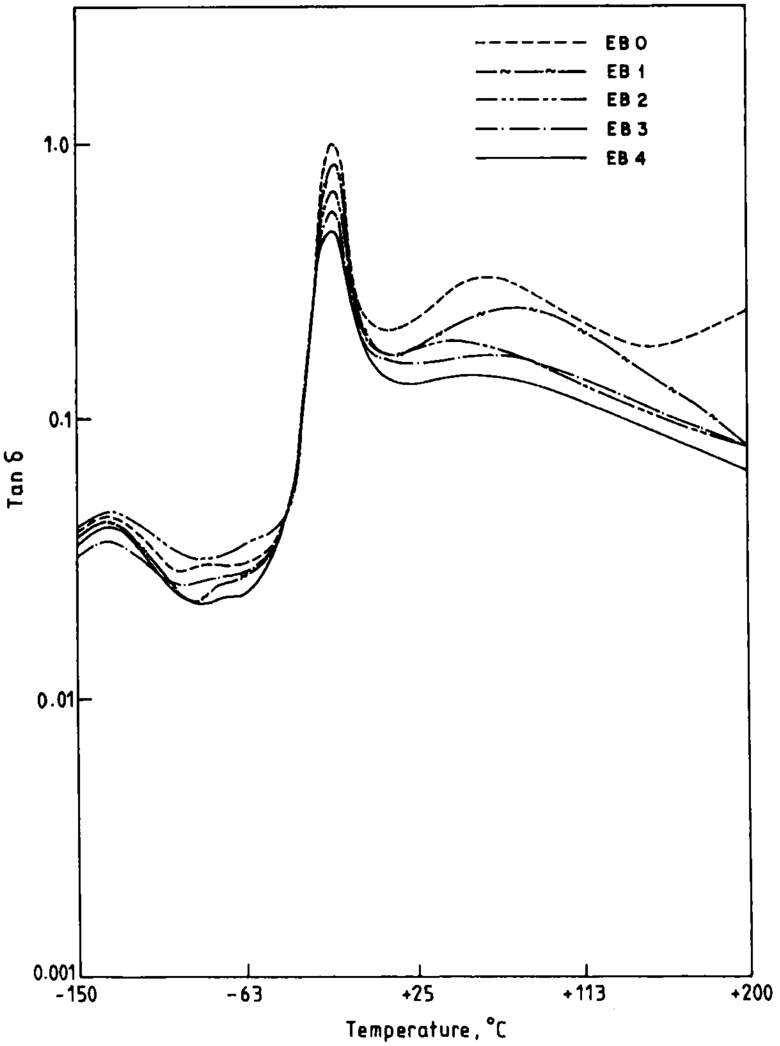

FIGURE 7 Loss tangent (tan δ) as a function of temperature at different loadings of carbon black filler.

tion occurred in the temperature region of −125°C to −135°C. This transition is ascribed to motion of —CH_2— groups in either main or pendant chains. The motion occurs due to the presence of limited number of —CH_2— groups (maximum four —CH_2— groups in sequence).[27] The gum and the filled vulcanizates also registered a distinct "shoulder" in the temperature region of −65° to −75°C. This is known as the β-relaxation peak which occurred due to motion of acetoxy side groups. Similar relaxation due to motion of the side groups was also observed in other ethylene copolymers.[27,28] It is also interesting to note that both γ and β relaxations are independent of the carbon black filler. There was no definite sequence in the variation of these relaxations, both in magnitude and in the temperature region at which these maxima occurred, with the variation of carbon black concentration.

In contrast to γ and β relaxations, the α-transition (or T_g), registered a sharp peak. Although the glass transition temperature did not shift its position with the incorporation of carbon black filler, the magnitude of the tan δ peak decreased and broadness increased systematically with increase in carbon black concentration.

Figure 8 shows the influence of carbon black concentration on tan δ peak values at the α-transition. The relative damping values of carbon black filled EVA vulcanizates, tan δ_f/tan δ_m, where tan δ_f and tan δ_m represent loss tangent values of the filled and gum vulcanizates, respectively, at the α-transition temperature have been plotted as a function of the volume fraction of filler. A linear decrease in relative damping with carbon black concentration according to the following equation[30] was observed,

$$\tan \delta_f = \tan \delta_m(1 - B\phi) \tag{5}$$

where B is the slope of the straight line plot, the value of which was found to be 2.25. Figure 8 also shows the theoretical plot of the relative damping versus volume fraction of carbon black according to Nielsen model[31]:

$$\tan \delta_f = \tan \delta_m(1 - \phi) \tag{6}$$

The deviation of the experimental plot from the theoretical one occurs due to the filler-rubber interaction. The slope B of Equation 5 was introduced as the correction parameter for the filler-rubber interaction.[30] The correction parameter B is related to the effective thickness of the particle-matrix interphase according to the equation[30]:

$$B = (1 + \Delta R/R)^3 \tag{7}$$

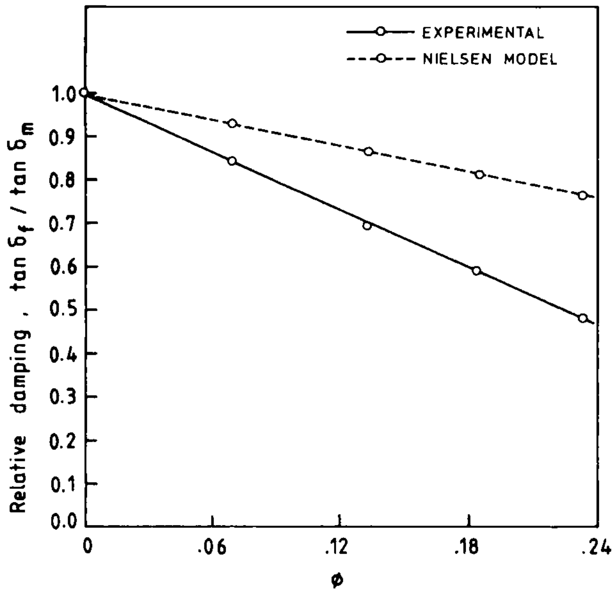

FIGURE 8 Relative damping (tan δ_f/tan δ_m) at T_g as a function of carbon black loading.

where R is the radius of the dispersed particles and ΔR is the thickness of the immobilized polymer layer. The value of ΔR was found to be 93A°, by assuming the average particle diameter as 29 nm. This value agree well with the thickness of immobilized polymer layers reported in the case of glass bead and mica filled polystyrene and polymethylmethacrylate[30] and rutile-filled chlorinated polyethylene rubber.[32] In carbon black filled EVA vulcanizates, there is significant interaction between rubber and filler which tends to immobilize a layer of rubber around each filler particle. The rubber-filler interaction, however, is not strong enough to bring about any change in the glass transition temperature. The position of the T_g thus remains unaffected with incorporation of carbon black filler.

The damping behaviour of different carbon black filled composites in the rubbery and high temperature regions exhibit interesting results. It can be seen from Figure 7 that, the unfilled EVA vulcanizate registered a damping peak around +62°C. This phenomenon may be attributed to the mobility of amorphous phase of EVA rubber. This is referred to as $T_{1,1}$ transition (liquid to liquid transition), as has been reported in other polymers.[19,29] Incorporation of carbon black (as in the case of EB1 vulcanizate) caused broadening of this peak and further increase in filler loading caused gradual disappearance of the peak. The filler effect on the $T_{1,1}$ transition may be ascribed to the reduced mobility of the amorphous phase by the filler-rubber interaction.

Figure 9 shows the effect of crosslink density on the damping behaviour of EVA rubber over the temperature range of −150° to +200°C. It is evident from the figure that in the γ and β-relaxation regions the tan δ peak magnitudes increased with increase in crosslink density, whereas in the α-transition temperature (that is, at T_g) the tan δ peak magnitudes decreased and the tan δ peaks slightly broadened with increase in crosslink density. The glass-transition temperature, however, did not show any significant shift in its position. The γ and β relaxation temperatures were also found to be largely unaffected by the effect of crosslink density. The reduced crystallinity of the highly crosslinked systems might cause the increase in loss parameters of these vulcanizates in the glassy regions. In the glass transition and rubber regions the lightly crosslinked vulcanizate, by virtue of its greater mobility shows higher tan δ than the highly crosslinked systems. Moreover, the $T_{1,1}$ transition peak was found to be very prominent in the case of the lightly crosslinked vulcanizate (EB4L). When the extent of crosslinking increased, as in the case of EB4 and EB4H, the $T_{1,1}$ transition was not observable. Similar suppression of $T_{1,1}$ peak by crosslinking of EPDM rubber has been reported.[19]

3.2 Effect of Strain Amplitude on the Dynamic Mechanical Properties

Figure 10 illustrates the isothermal variation of storage modulus as a function of double strain amplitude (DSA, 0.07–5%) at 27°C for unfilled and carbon black filled EVA vulcanizates. The elastic modulus decreased with increasing DSA and the effect was more pronounced at higher carbon black concentration. The difference in elastic modulus between the maximum or limiting value at low amplitude E'_0 and the limiting value at high amplitude E'_∞ (when there is no further change

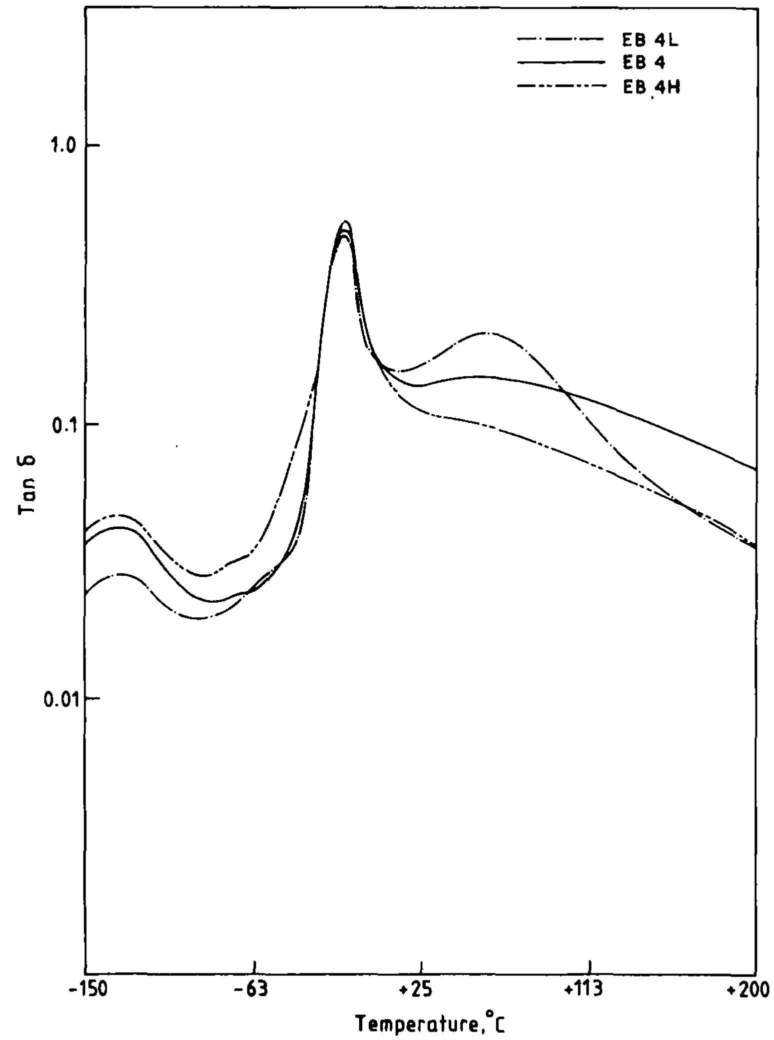

FIGURE 9 Effect of the degree of crosslinking on the loss tangent (tan δ) versus temperature plots of EVA vulcanizates (volume fraction of carbon black, 0.234).

of modulus with increasing strain) is referred to as $\Delta E'$. The quantity $\Delta E'$ in the present case can thus be defined as,

$$\Delta E' = E'_0 - E'_5$$

where E'_0 is the storage modulus at low strain (DSA, 0.07%) and E'_5 is the same at high strain (DSA, 5%). The term $\Delta E'$ is a quantitative measure of the amplitude effect in the highly filled rubber vulcanizates[33] and is attributed to the properties of the filler particles. The increase of $\Delta E'$ is believed to be due to the breakdown of secondary or physical forces dissociating the carbon black interaggregates under the effect of strain amplitude.[5] In the present case $\Delta E'$ can be taken as a measure

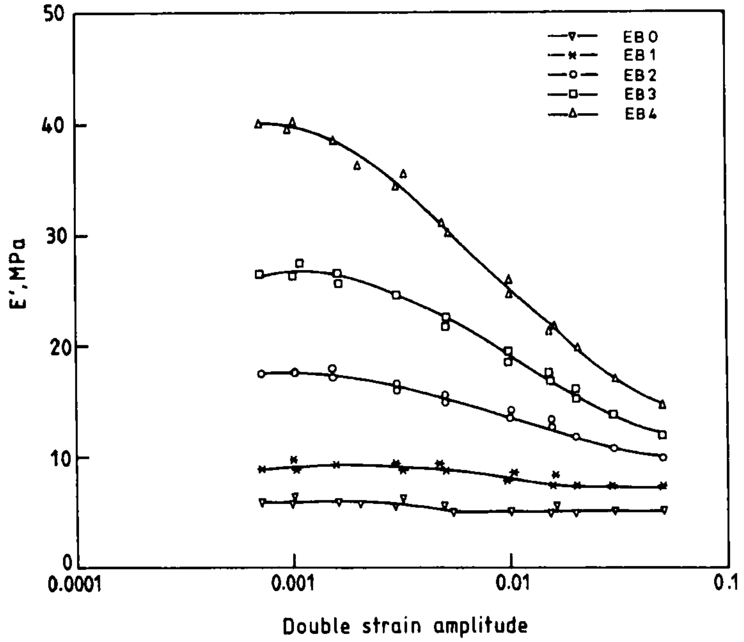

FIGURE 10 Storage modulus (E') at 27°C as a function of double strain amplitude for EVA with different loadings of carbon black filler.

of agglomeration breakdown of carbon black filler. The highly filled vulcanizate, EB4 showed very high $\Delta E'$ value (25.4 MPa). The $\Delta E'$ value gradually decreased with decreasing filler loading. In the unfilled vulcanizate (EBO) the $\Delta E'$ factor became virtually insignificant. The secondary structure breakdown of carbon black filler takes place during mixing. However, the breakdown of the secondary structure of carbon black is not complete during mixing and a significant amount of agglomerates remain intact. The higher the carbon black loading, the greater is the extent of intact agglomerates left in the vulcanizates. Thus during the experiment of isothermal dynamic mechanical properties under the effect of strain amplitude, the highly filled vulcanizates exhibited higher degree of secondary structure breakdown of carbon black. This observation is in line with the findings of earlier studies.[1,5,7,33,34]

Figure 11 demonstrates the effect of degree of cross-linking on the agglomerate breakdown of carbon black filler under the effect of double strain amplitude. The storage modulus at any DSA decreased with increase in degree of crosslinking. Moreover, it is evident from Figure 11 that in contrast to highly and moderately crosslinked vulcanizates (that is, the EB4H and EB4, respectively), the lightly crosslinked system, EB4L exhibited low value of $\Delta E'$. The $\Delta E'$ value of EB4L vulcanizate was 14.6 MPa which is significantly less than those of EB4H (26.6 MPa) and EB4 (25 MPa) vulcanizates. This does not agree with the findings of an earlier study[35] in which $\Delta E'$ was found to be almost independent of the state of cure. It could be emphasised that in the lightly crosslinked EVA vulcanizate along with

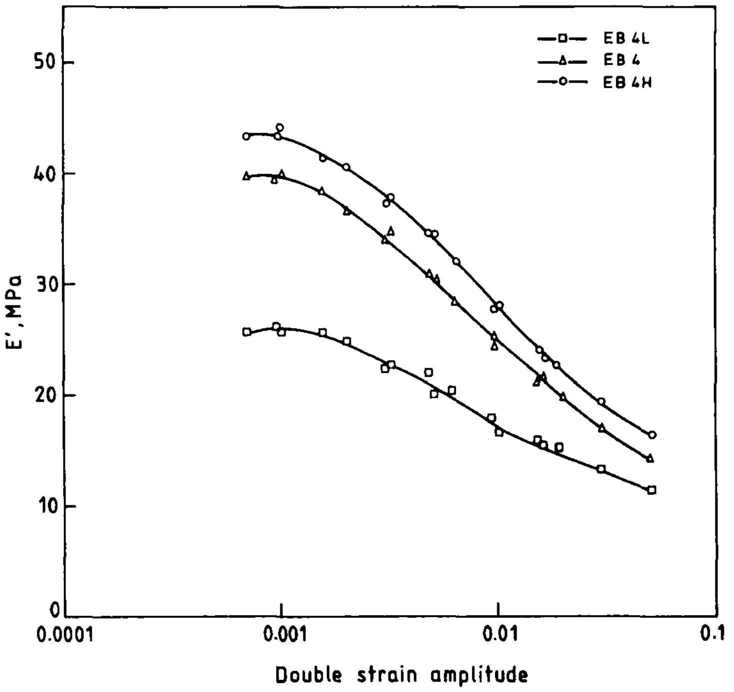

FIGURE 11 Plot of storage modulus versus double strain amplitude at 27°C at different degrees of crosslinking and at fixed carbon black volume fraction of 0.23.

the breakdown of secondary structure of carbon black filler, there also occurs the phenomenon of molecular chain slippages under the effect of strain amplitude and this causes the reduction in $\Delta E'$.

CONCLUSIONS

Unfilled and carbon black filled EVA vulcanizates exhibit different transitions namely the α-transition (or the principal glass transition temperature, T_g) at −17°C, the γ-relaxation in the temperature region of −125° to −135°C and the β-relaxation around −65° to −75°C. Furthermore, there is also a high temperature transition at +62°C exhibited by the unfilled composition. This transition disappears at high carbon black loading.

Increase in carbon black concentration causes increase in storage modulus at any given temperature. The effect of filler on the storage modulus is more pronounced in the rubbery and high temperature regions than in the glassy state. Enhanced degree of crosslinking causes decrease in storage modulus in the glassy state and increase in the rubbery and high temperature regions.

Incorporation of carbon black filler does not cause any shift in the glass transition temperature which remains also unaffected by the variation in the degree of crosslinking.

The study of isothermal dynamic mechanical properties indicates the breakdown of carbon black agglomeration (secondary structure) under the effect of strain amplitude in highly filled vulcanizates. The secondary structure breakdown under strain amplitude effect is less significant in the lightly crosslinked system.

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