

Dynamic Mechanical Properties of Silica-Filled Ethylene Vinyl Acetate Rubber

K. MUKHOPADHYAY, D. K. TRIPATHY, and S. K. DE*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

SYNOPSIS

Dynamic mechanical studies of ethylene vinyl acetate rubber indicated the presence of different transitions: the α -transition or glass-rubber transition temperature (T_g) at -17°C , the β -transition around -60 to -70°C observed as a shoulder, and the γ -transition in the temperature region of -127 to -135°C , apart from a high-temperature transition ($T_{1,1}$) at $+69^\circ\text{C}$. The α -transition temperature did not shift its position with incorporation of silica filler, but there was gradual sequential lowering of $\tan \delta$ peak values at T_g with increase in filler loading. Such sequential dependence of $\tan \delta$ values on filler incorporation was not observed in the cases of β - and γ -transitions. The $T_{1,1}$ transition was found to be less prominent in the presence of filler, particularly at high concentration. Treatment of the filler with a silane coupling agent caused a shift in the α -transition temperature to higher temperature by about 4°C . Studies on dynamic mechanical properties under isothermal conditions have shown that the coupling agent caused a breakdown of silica agglomerates during mixing. An increase in frequency caused a shift of $\tan \delta$ peak positions in the α - and γ -transition regions toward higher temperature. Although frequency did not have a significant effect on the $\tan \delta$ value at the α -transition, increase in frequency caused sequential lowering of $\tan \delta$ value at the γ -transition. In the high-temperature region, the $T_{1,1}$ peak exhibited by the gum compound gradually disappeared with increasing frequency.

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1. INTRODUCTION

Ethylene vinyl acetate rubber (45% vinyl acetate content), hereafter referred to as EVA, exhibits outstanding resistance to high temperature, weathering, and ozone. The material has been found to be suitable for use in the manufacture of mechanical rubber goods.¹

However, no systematic scientific investigations have been carried out to explore the potential application of this elastomer under cyclic deformation over a wide range of temperatures. The dynamic mechanical properties of elastomers are strongly dependent on temperature, frequency, type, and concentration of filler and the extent of deformation. Several investigators studied the dependence of dynamic mechanical properties of rubber vulcanizates

on the type and concentration of fillers²⁻⁷ under different test conditions.^{2,8-10}

The present paper reports the results of our studies on the dynamic mechanical properties of silica-filled EVA rubber over a wide range of temperatures (-150° to $+200^\circ\text{C}$), at different frequencies and strain amplitudes. Results on effects of the silane coupling agent on the dynamic mechanical properties of silica-filled EVA rubber are also included in this report.

2. EXPERIMENTAL

2.1. Materials

The EVA rubber used was levaprene 450 (45% vinyl acetate content), manufactured by Bayer, Germany. The filler used was precipitated silica (Vulcasil S), manufactured by Bayer, Germany. Its characteristics are as follows: specific gravity, 2.0; BET surface

* To whom correspondence should be addressed.

area 160–120 m²/g; and particle size 10–20 nm. The peroxide used for cross-linking of EVA rubber was dicumyl peroxide (96% pure), manufactured by Bayer, Germany. The coagent used for the peroxide cross-linking was triallyl cyanurate, manufactured by Degussa, Germany. The coupling agent used was vinyl silane A172, manufactured by Union Carbide.

2.2. Sample Preparation

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

The volume fraction of rubber in the swollen vulcanizate, V_r , which can be taken as a measure of cross-link density, was calculated using the following equation:

$$V_r = \frac{(D - FT) \int_r^{-1}}{(D - FT) \int_r^{-1} + A_0 \int_s^{-1}} \quad (1)$$

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

2.3. Test Method

The dynamic mechanical analysis of different vulcanizates was carried out in the tension mode using Rheovibron, DDV-III-EP of Orientec Corp., Japan. Experiments were carried out over a temperature range of –150 to +200°C at different frequencies and double-strain amplitudes (DSA). DSA is defined as

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

The rate of temperature rise was kept at 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%. Frequency-dependent properties were studied at four different frequencies: 3.5, 11, 35, and 110 Hz.

3. RESULTS AND DISCUSSION

3.1. Rheometric Properties

Results of the rheometric studies are given in Table I. It is evident that incorporation of silica filler lowers the optimum cure time of EVA rubber and the decrease is more in the presence of the silane coupling agent.

Table I Compounding Formulations^a: Composition in 100 Parts by Weight of Rubber

	Mix No.					
	E1	E2	E3	E4	E5	E5C
EVA ^b	100	100	100	100	100	100
Silica ^c	0	15	30	45	60	60
Vinyl silane A172	—	—	—	—	—	3
Optimum cure time at 100°C (min)	23	18	18	14	14	12
Volume fraction of rubber (V_r)	0.114	0.120	0.126	0.146	0.150	0.252

^a All mixes contain stearic acid; 1; antioxidant DN, 0.5; Rhenogran P-50, 3.0; dicumyl peroxide (96% pure), 1.2; triallyl cyanurate, 2.0.

^b Levaprene 450.

^c Vulcasil S.

3.2. Temperature-dependent Dynamic Mechanical Properties

3.2.1. Storage Modulus

Figure 1 illustrates the elastic modulus E' of EVA vulcanizates containing different loadings of silica

filler over a temperature range of -150 to $+200^\circ\text{C}$. This figure also demonstrates the effect of the coupling agent on the storage modulus of silica-filled EVA vulcanizate. The characteristic sigmoidal variation of the storage modulus with temperature was observed for all compositions. Both low- and high-

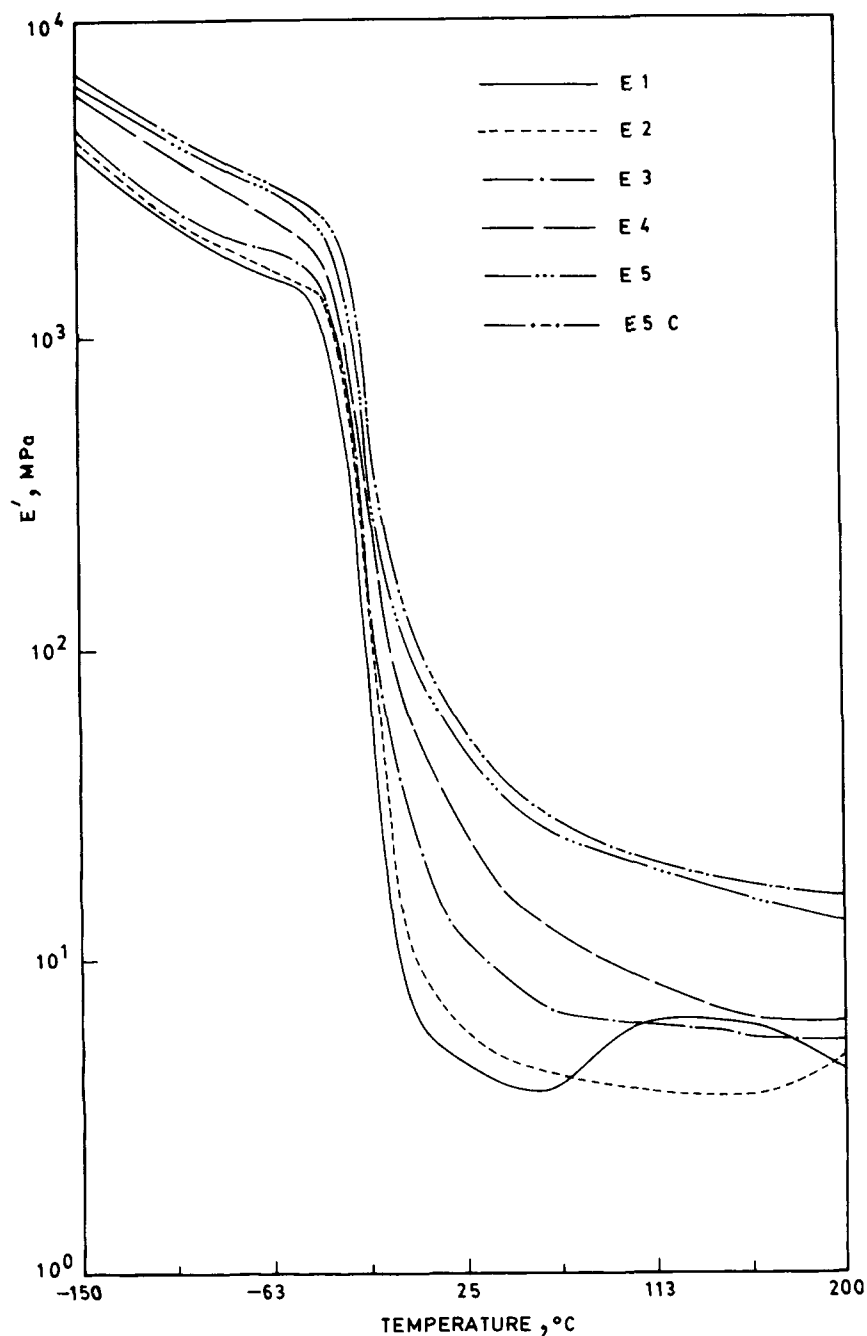


Figure 1 Effect of silica filler and silane coupling agent on the temperature-dependent elastic modulus of EVA vulcanizates (frequency, 11 Hz; DSA, 0.1%).

temperature moduli increased with increasing filler loading. This increase may be ascribed to the increase in apparent cross-link density due to polymer-filler interaction, as measured from V_r values (Table I). A similar effect has also been observed recently by other investigators.^{11,12} In contrast to the filled systems, the storage modulus of the gum EVA vulcanizate registered a broad peak around 110°C. This peak could be ascribed to the crystalline region of the polymer,^{13,14} which, however, gradually disappeared with incorporation of silica filler. Occurrence of a similar peak at high temperature due to the crystalline phase has been reported in the case of polyethylene¹⁵ and polybutadiene.¹⁶

Comparison of storage modulus values of E5 and E5C vulcanizates (Fig. 1) shows that the addition of the coupling agent increases the modulus at all temperatures. This can be attributed to enhanced

polymer-filler interaction in the presence of the coupling agent, which is supported by the fact that silane treatment increased the V_r of E5 vulcanizate from 0.150 to 0.252 (Table I).

In Figure 2, relative moduli, 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, have been plotted as a function of temperature. The relative moduli for the treated silica-filled vulcanizate (E5C) have also been plotted as a function of temperature. The nature of the plots for all compositions is identical. In the glassy region, all compositions showed near independence of the relative modulus on temperature. Relative moduli increased sharply in the transition zone. In the rubbery and high-temperature regions (up to about 125°C), the relative modulus decreased rather sharply, and above 125°C, the relative modulus again registered an increase. It

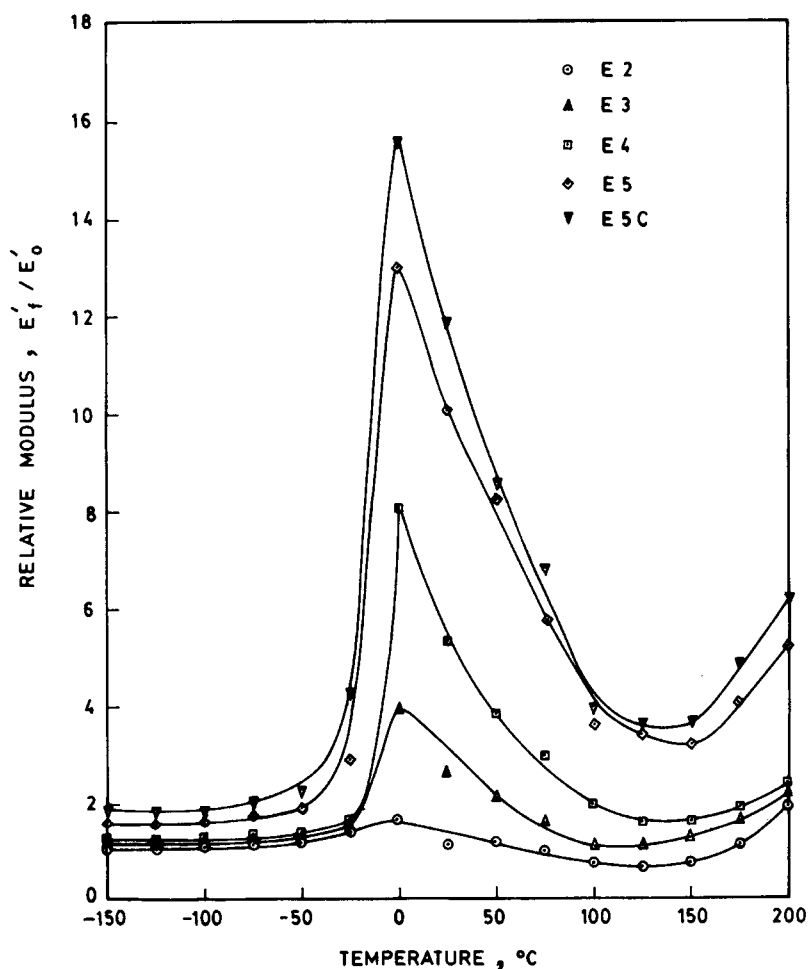


Figure 2 Relative modulus (E'_f/E'_m) of EVA vulcanizates as a function of temperature (frequency, 11 Hz; DSA, 0.1%).

is also evident from Figure 2 that, with an increase in filler concentration, the relative modulus increased throughout the range of experimental temperature. However, the increase was much higher in the rubbery and high-temperature regions than that in the glassy region. This suggests that the effect of filler in raising the storage modulus is more dominating in the rubbery and high-temperature regions than in the glassy state. A similar effect was also observed recently by Ding et al.¹¹ Figure 2 also shows that the coupling agent treatment of silica filler increased the relative moduli of the composite throughout the temperature range.

Figure 3 shows the manifestation of the dependence of storage modulus on silica concentration above the transition temperature (0°C). The experimental relationship is also compared with the modified Kerner equation.¹⁷ The complexity of the Kerner equation has been simplified by restricting its applicability to the rubbery state of filled compounds (i.e., above T_g) and assuming that the dynamic modulus of the filler greatly exceeds that of the polymer matrix. Now, assuming the Poisson ratio for the rubber as 0.5, at a given volume fraction of filler, ϕ , the Kerner equation can be written as¹⁷

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

where A is the filler-rubber interaction parameter.

The value of A can be obtained from the comparison of the loss moduli E'' of unfilled and filled specimens at the reference temperature. Figure 4 shows the plot of E''_m/E''_f (where E''_m and E''_f are the loss moduli of the gum and the filled matrices, respectively) vs. the volume fraction of filler at 0°C. A linear decrease in the E''_m/E''_f with volume fraction according to the following equation was observed:

$$E''_m/E''_f = 1 - A\phi \quad (4)$$

where A is same interaction parameter term used in eq. (3). The value of A has been found to be 3.7. Using $A = 3.7$ from eq. (4), it was found that the theoretical plot according to modified Kerner equation [eq. (3)] is close to the experimental plot (Fig. 3).

Flexibility at the desired temperature is one important property for a polymer in low-temperature

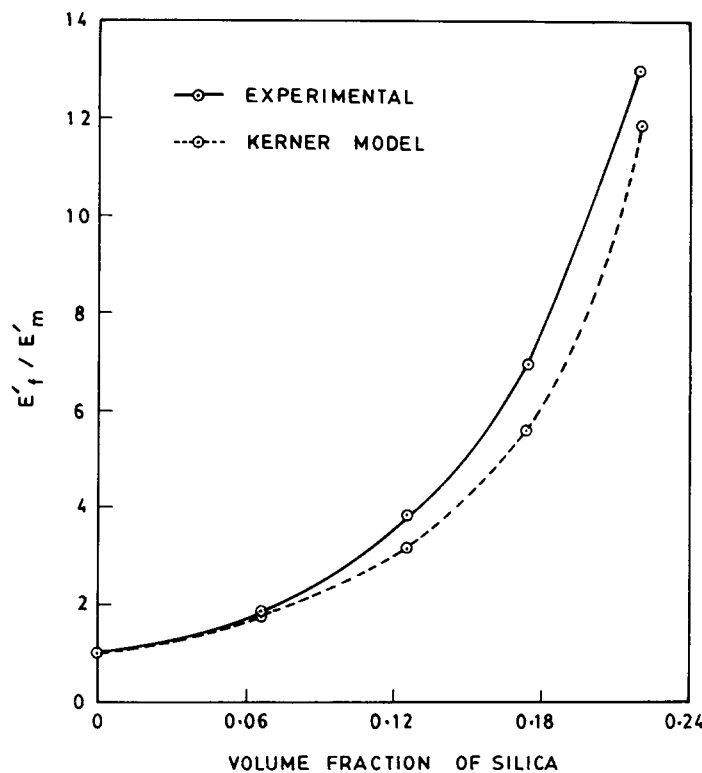


Figure 3 Relative modulus (E'_f/E'_m) as a function of silica concentration at 0°C (frequency, 11 Hz; DSA, 0.1%).

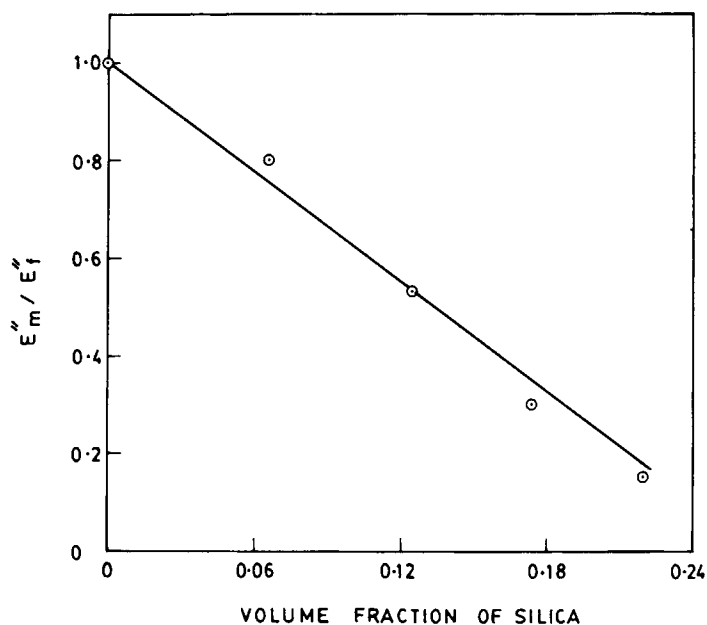


Figure 4 E''_m/E'_m as a function of silica concentration at 0°C (frequency, 11 Hz; DSA, 0.1%).

applications. The temperature at which the elastic modulus reaches 69 MPa is sometimes used as a measure of low-temperature stiffness.¹⁸ Figure 5

shows the low-temperature stiffness characteristics of EVA vulcanizates containing an increased volume fraction of silica filler. The effect of the coupling

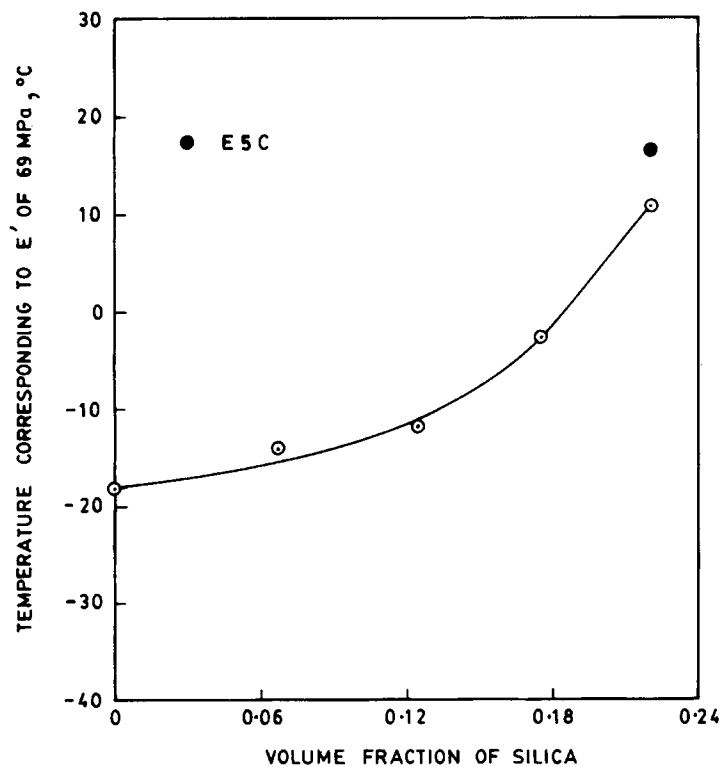


Figure 5 Effect of silica filler concentration on the low-temperature flexibility (i.e., temperature corresponding to E' of 69 MPa) of EVA rubber (frequency, 11 Hz; DSA, 0.1%).

agent on low-temperature characteristics of filled EVA vulcanizates (volume fraction of silica 0.22) has also been shown in the figure. It is apparent that the low-temperature flexibility decreased with increase in silica loading and incorporation of the coupling agent caused a further decrease. The effect of filler on low-temperature stiffness characteristics of EVA could be explained by the reduced polymer mobility due to adsorptive interaction between silica and rubber.¹⁹⁻²² The presence of the silane coupling agent in the filled vulcanizate caused significant reduction in the polymer mobility due to strong filler-coupler-rubber interaction, which is responsible for an additional decrease in the low-temperature flexibility in the case of E5C vulcanizate.

3.1.2. Damping

Figure 6 shows the influence of the silica filler and the coupling agent on the damping behavior of EVA

vulcanizates over the temperature range of -150 to $+200^{\circ}\text{C}$. All the compositions exhibit α - and γ -relaxations, which are characteristics of EVA copolymer as reported earlier.²³⁻²⁵ The primary transition, (i.e., the α -transition) occurred at -17°C . It is considered as the principal glass-rubber transition temperature of EVA copolymer and is attributed to the segmental motion of isolated $-\text{CH}_2-\text{CH}-\text{OCOCH}_3-\text{CH}_2-$ groups. A second transition typical of polyethylene was also observed in the temperature range of -127 to -135°C . This is the well-known γ -transition associated with motion of $-\text{CH}_2-$ groups in either the main or pendant chains. The motion occurs due to the presence of a limited number of $-\text{CH}_2-$ groups (maximum four $-\text{CH}_2-$ groups in sequence).²³ In the temperature region of -60 to -70°C , there also appeared a distinct "shoulder" exhibited by the gum and filled compositions. This is the β -relaxation peak due to

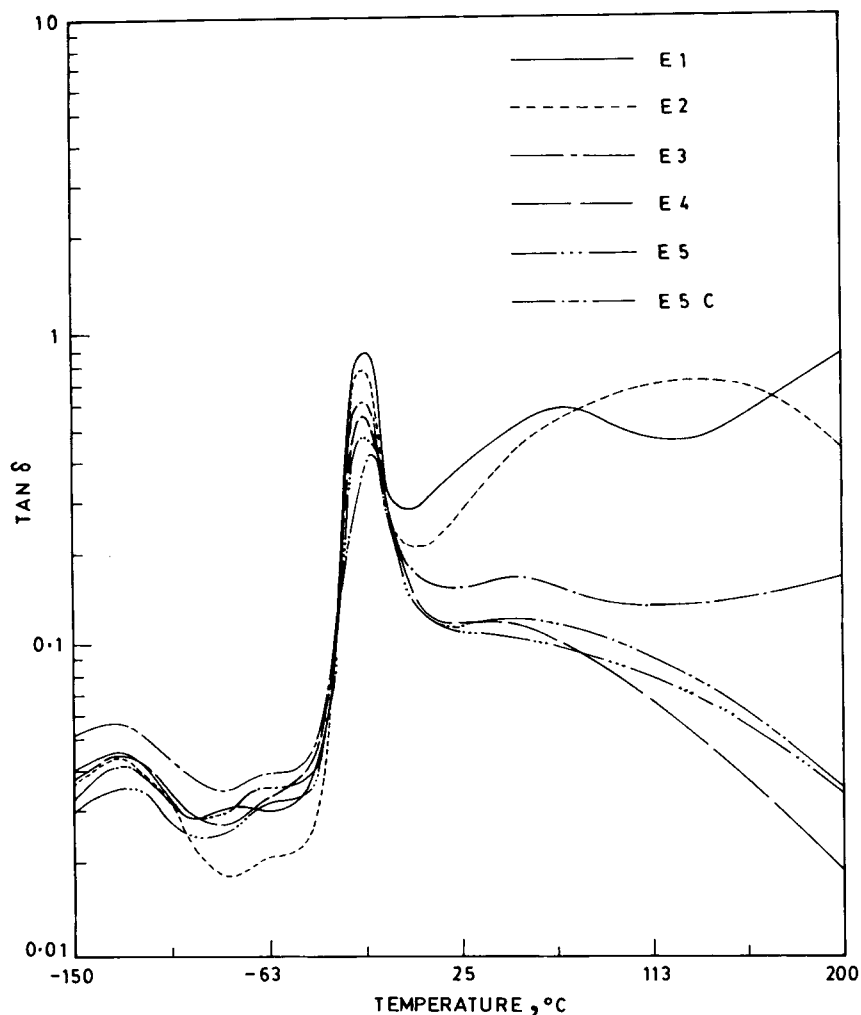


Figure 6 Loss tangent as a function of temperature for different EVA vulcanizates containing untreated and treated silica (frequency, 11 Hz; DSA, 0.1%).

the motion of acetoxy side groups. A similar peak due to the motion of side groups was also observed in other ethylene copolymers.^{23,24} It is important to note that there was no definite sequence in the variation of γ -relaxation with the variation of filler concentration. The β -relaxation also did not exhibit any sequential variation with filler concentration. The α -transition, on the other hand, exhibited a sharp peak corresponding to a temperature of -17°C . This is the major $\tan \delta$ peak temperature (dynamic glass transition temperature) and it did not shift its position with the variation of filler concentration. However, the magnitude of the $\tan \delta$ peak reduced systematically with increase in silica concentration.

Figure 7 shows the manifestation of the effect of silica concentration on $\tan \delta$ peak values. The relative damping values of filled EVA vulcanizates $\tan \delta_f / \tan \delta_m$ (the subscripts f and m referring to filled and matrix polymer, respectively) at the α -transition temperature have been plotted as a function of filler volume fraction: ϕ . As expected, a linear decrease in relative damping with an increase in silica concentration was observed according to the following equation²⁶:

$$\tan \delta_f = \tan \delta_m(1 - B\phi) \quad (5)$$

where B is the slope of the line. Figure 7 also depicts

the idealized plot of relative damping vs. the volume fraction of filler according to the Nielsen model²⁷:

$$\tan \delta_f = \tan \phi_m(1 - \phi) \quad (6)$$

The deviation of the experimental solid line from the idealized dotted line is the manifestation of the filler-rubber interaction, and the slope B of eq. (5) was introduced as the correction parameter for measuring filler-rubber interaction.²⁶ The correction parameter " B " is related to the effective thickness of the particle-matrix interphase through the relation²⁶

$$B = (1 + \Delta R/R)^3 \quad (7)$$

where R is the radius of dispersed particles and ΔR is the thickness of the immobilized polymer layer. The ΔR is 27 Å, taking an average particle diameter of 15 nm. This value is in good agreement with estimates of immobilized polymer layers reported in the literature.^{26,28}

In silica-filled EVA vulcanizates, there is significant interaction between rubber and filler (adsorptive interaction), which tends to immobilize a layer of rubber around each filler particle. This rubber-filler interaction, however, is not strong enough to bring about any change in glass transition temper-

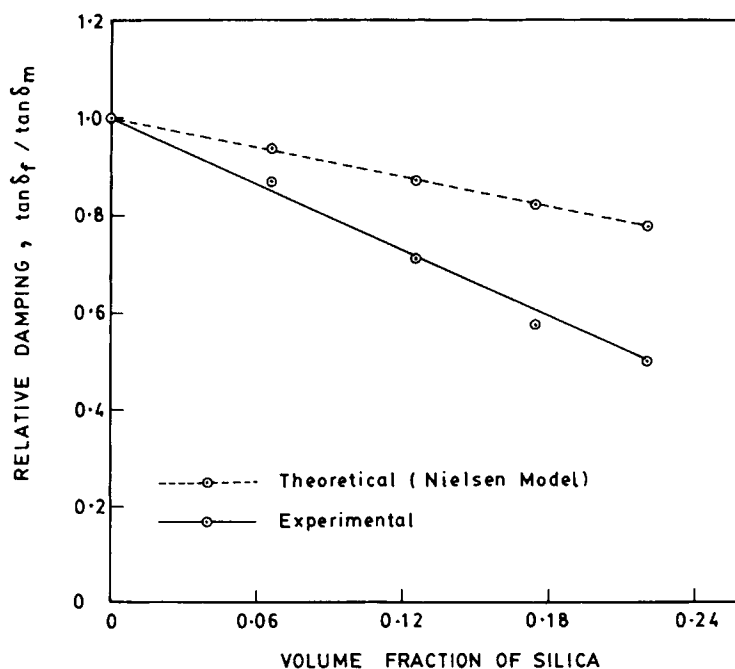


Figure 7 Effect of silica filler concentration on relative damping at the α -transition temperature (frequency, 11 Hz; DSA, 0.1%).

ature. In cases where strong polymer-filler interactions are coupled with high surface area solids as in the case of polyethylene glycol filled with high surface area silica,²⁹ it may be expected that the T_g will shift to higher temperature. This phenomenon was demonstrated by the silane-treated silica-filled vulcanizate (E5C) where the T_g shifted toward higher temperature by about 4°C compared to the T_g of the matrix rubber. The peak magnitude was also reduced with a narrow spread with the silane-treated system. It was studied earlier,³⁰ that under the silane treatment of silica filler both chemisorbed and physisorbed silane on the silica surface are produced. The physisorbed layer does not become dispersed into the matrix. Therefore, most of the physisorbed silane stays near the interface. The increase in T_g and decrease in peak magnitude are thus caused by the increase in cross-link density in the interfacial regions between the silane-treated silica and the polymer matrix. The increase in cross-link density

is attributed to the bonding between the silica filler and the matrix through the physisorbed silane.³⁰ The V_r values reported in Table I also support this phenomenon. The V_r value increased slowly with increasing silica concentration, and with the E5C vulcanizate, the V_r value was much higher than that of E5 vulcanizate.

The damping behavior in the rubbery and high-temperature regions of different silica-filled composites also reveals some interesting phenomena. For gum vulcanizate, a broad peak was observed around 69°C, which may be attributed to the mobility of amorphous phase of EVA rubber. This is referred to as the $T_{1,1}$ transition (liquid-to-liquid transition), as has been observed in other polymers.^{13,25} This peak became broadened as silica filler was incorporated (as in the case of E2 vulcanizate), and with a further increase in filler loading, the peak gradually disappeared because of the reduced mobility of the amorphous chain by the filler-rubber

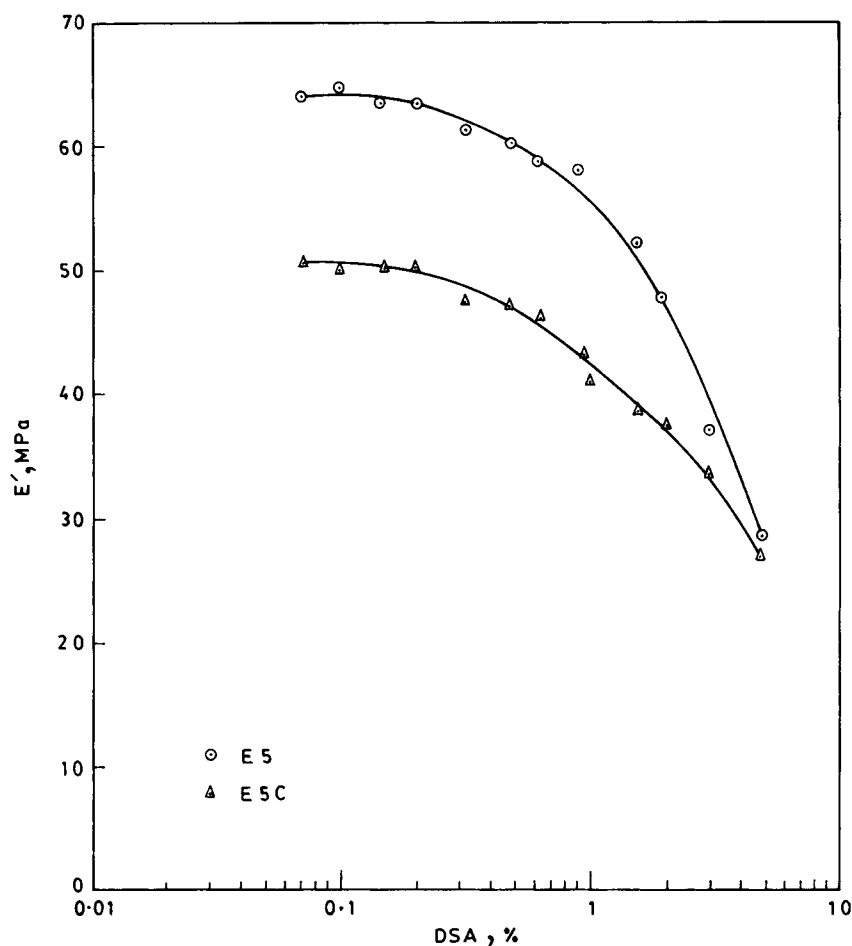


Figure 8 Storage modulus as a function of double-strain amplitude for untreated and treated filled EVA vulcanizates (frequency, 11 Hz; temperature, 27°C).

interaction. A similar suppression of the $T_{1,1}$ peak was observed by cross-linking in the case of EPDM rubber.¹³

3.2. Effect of Strain Amplitude on the Dynamic Mechanical Properties

Figure 8 demonstrates the variation of storage modulus as a function of double-strain amplitude (DSA, 0.07–5%) at room temperature for untreated and silane-treated silica-filled EVA vulcanizates (volume fraction of silica, 0.22). Elastic moduli of all compositions decreased with increasing double-strain amplitude.

The quantity $\Delta E'$ is defined as

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

where E'_0 is the elastic modulus at very 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 highly filled rubber

vulcanizates³¹ and is attributed to properties of the filler particle. The augmentation of $\Delta E'$ has been emphasized by the breakdown of secondary or physical forces destroying the filler interaggregates under straining.² In the present study, $\Delta E'$ can be taken as a measure of agglomeration breakdown of silica filler. The untreated silica-filled vulcanizate E5 showed a very high $\Delta E'$ value (35.7 MPa) as compared to that of silane-treated vulcanizate E5C (23.5 MPa).

The agglomeration breakdown of silica filler also takes place during mixing under the shearing force. The greater the dispersibility of silica filler in the rubber, the more effective is the breakdown process during mixing.³² The silane coupling agent improves the dispersibility of silica through strong filler–coupler–rubber interactions.^{33,34} Thus, most of the silica agglomerates are destroyed during mixing in the silane-treated composition. In the case of untreated filled vulcanizate, E5, a greater number of silica agglomerates remained intact after mixing because of less dispersibility of silica in the rubber. Also, this

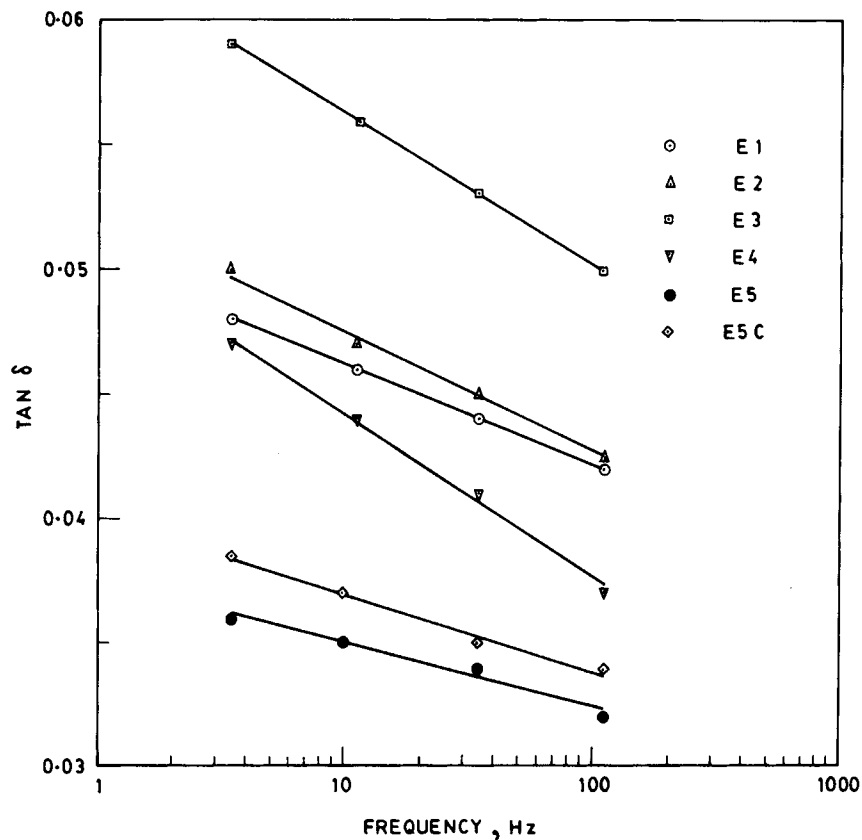


Figure 9 Effect of frequency on $\tan \delta$ peak magnitudes at γ -relaxation temperatures (DSA, 0.1%).

is why under the effect of strain amplitude the untreated vulcanizate E5 exhibited a reasonably higher $\Delta E'$ value (i.e., higher degree of agglomeration breakdown under straining) than did the corresponding treated vulcanizate E5C. A similar feature was observed in promoter-treated carbon black-filled natural rubber vulcanizate.⁶

3.3. Effect of Frequency on Dynamic Mechanical Properties

Figure 9 shows the effect of frequency on the $\tan \delta$ magnitude in the γ -relaxation region. It is interesting to note here that although silica filler did not cause any sequential variation of $\tan \delta$ values at the α -transition (Fig. 6), increased frequency caused a sequential lowering of $\tan \delta$ values in the γ -transi-

tion. The β -transition also exhibited similar behavior. A linear decrease in the $\tan \delta$ value with increasing frequency was observed for all EVA vulcanizates. This indicates that the γ -relaxation, caused by a restricted number of methylene groups in the side chain, is unaffected by the filler, but is a frequency-dependent phenomenon.

Figures 10–13 show the changes in $\tan \delta$ with temperature at different frequencies (3.5, 11, 35, and 110 Hz) for E1, E2, E3, and E4 vulcanizates, corresponding to silica concentrations of 0, 6.6, 12.5, and 17.4 vol %, respectively. In all cases, the α -, β -, and γ -relaxation peak positions shifted toward higher temperature with increasing frequency. The E5 and E5C vulcanizates (figures not shown) also exhibited a similar shift of α -, β -, and γ -relaxation peaks with increasing frequency. The nature of $\tan \delta$ vs. temperature plots at different frequencies for

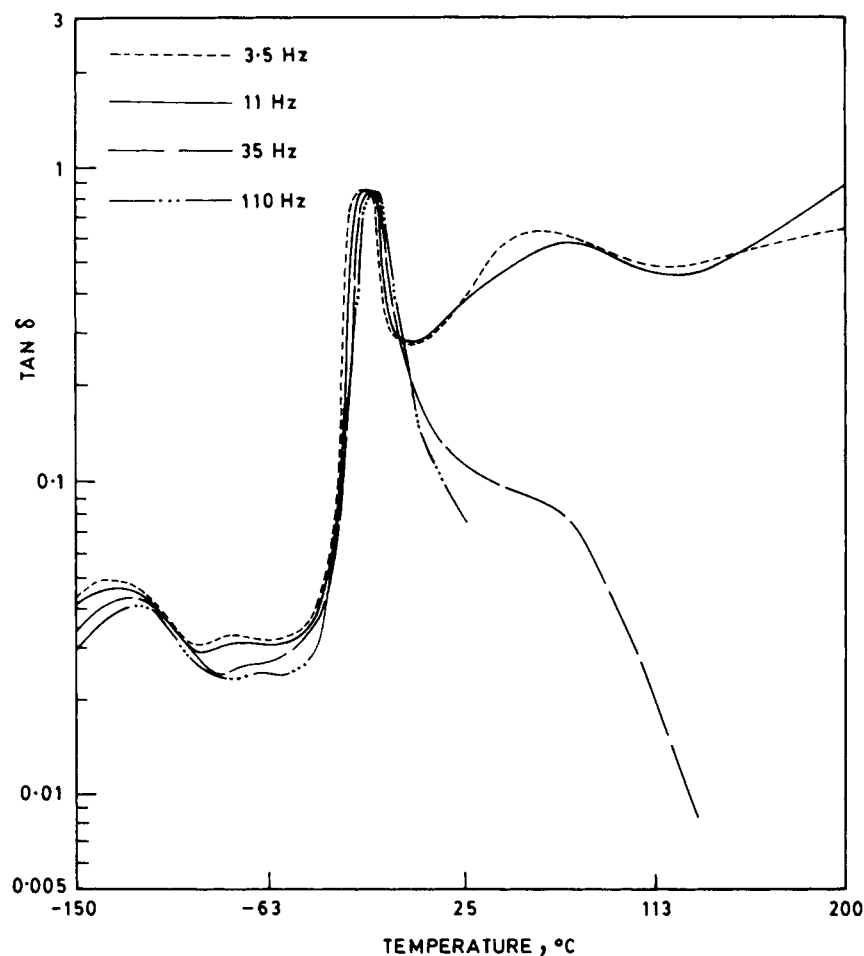


Figure 10 $\tan \delta$ as a function of temperature for gum EVA vulcanizate E1 at different frequencies (DSA, 0.1%).

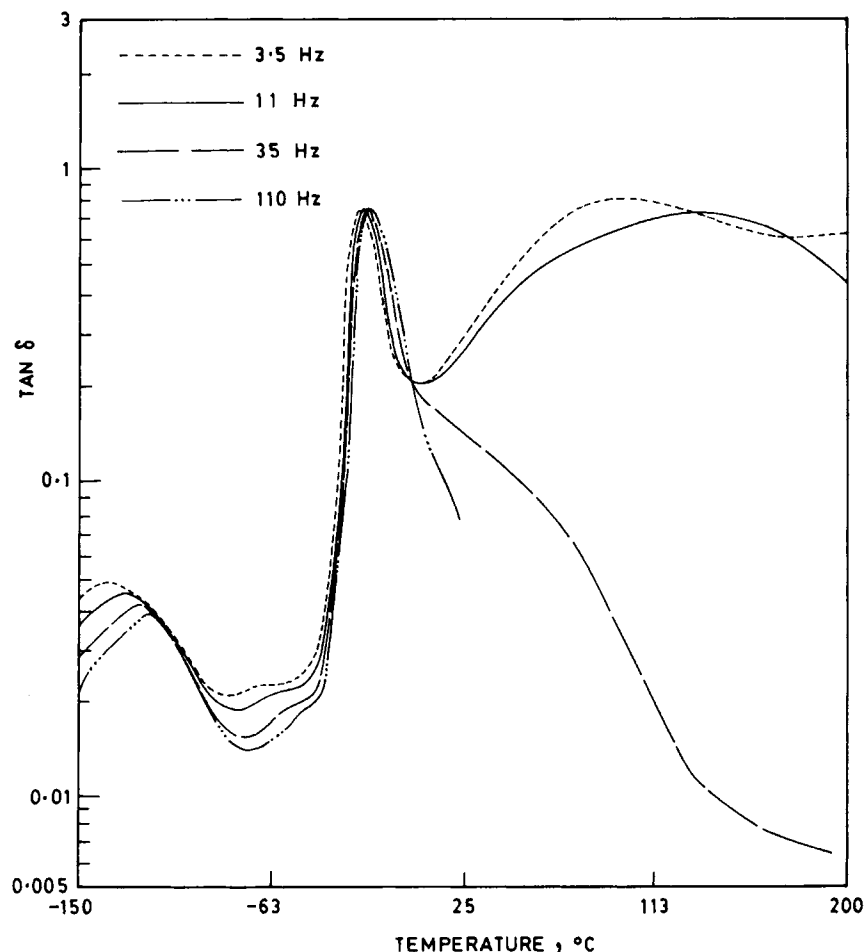


Figure 11 Tan δ as a function of temperature for E2 vulcanizate at different frequencies (DSA, 0.1%).

E5 and E5C vulcanizates is similar to that of E4 vulcanizate (Fig. 13). The α -peak magnitudes, unlike γ -peak values, were found to be almost independent of frequency.

Furthermore, the variation of tan δ with temperature at the $T_{1,1}$ transition for E1, E2, and E3 vulcanizates at different frequencies is very interesting. It was observed in Figure 10 that the $T_{1,1}$ peak exhibited by the gum compound was sharp and distinct at low frequency (3.5 Hz) and it became broader and shifted its position toward higher temperature with rising frequency (11 Hz), and at high frequency (35 Hz), the peak rendered to a small "shoulder" only. Similar also is the case with E2 vulcanizate (Fig. 11). For E3 vulcanizate (Fig. 12), the $T_{1,1}$ peak was observable only at 3.5 Hz, and at 11 Hz, a small "shoulder" was visible that disappeared and the damping curve in this region became a broad plateau

at high frequency (35 Hz). The values of tan δ also lowered drastically at high frequency (35 Hz) for E1 and E2 vulcanizates. Similar "suppression" of the $T_{1,1}$ peak with rising frequency has also been reported earlier.³⁵ This phenomenon may be explained by the "pseudorigidity" effect of the frequency. In this effect, the "relaxation time" (which may be considered as the inverse of frequency) responsible for chain mobility reduces drastically with increasing frequency, which results in temporary "freezing" of the amorphous chain.

For highly filled vulcanizates (E4, E5, and E5C), the $T_{1,1}$ peak was not observed even at low frequency (3.5 Hz), because of the filler interruption to the "chain mobility." Accordingly, it can be argued that increased frequency and high filler loading has a similar effect on the $T_{1,1}$ transition of EVA vulcanizates.

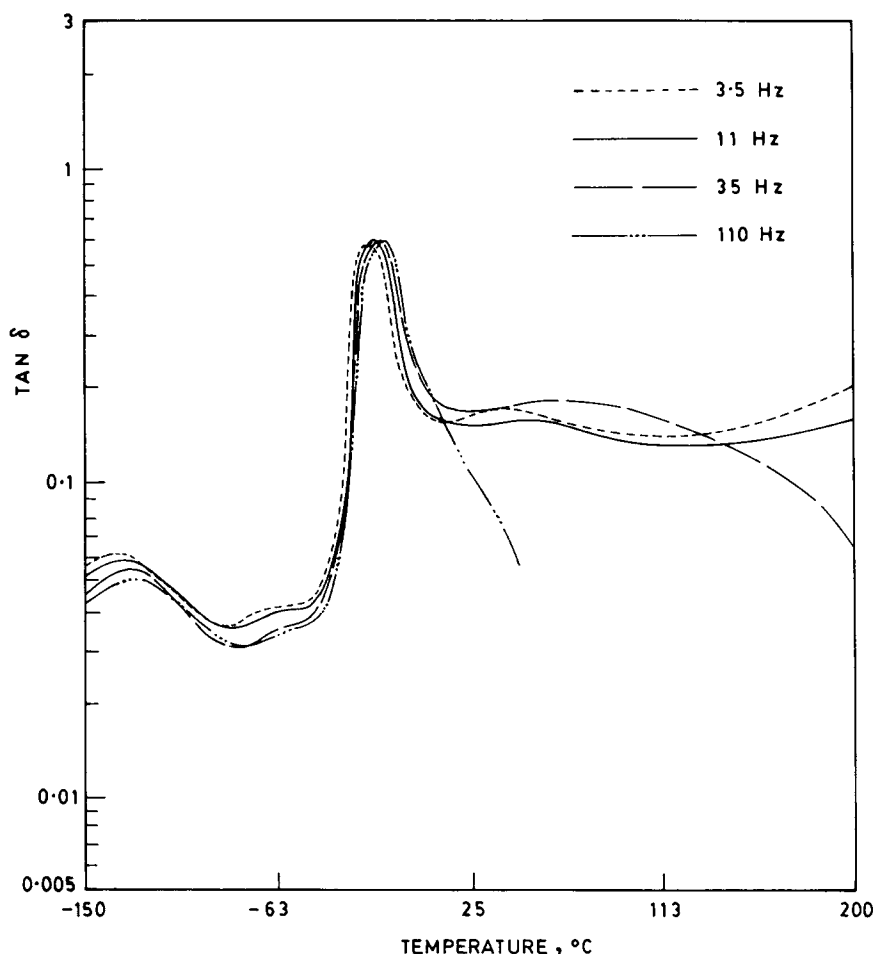


Figure 12 Tan δ as a function of temperature for E3 vulcanizate at different frequencies (DSA, 0.1%).

CONCLUSIONS

1. EVA vulcanizates exhibit different transitions, namely, the α -transition at -17°C (glass transition temperature, T_g), β -transition around -60 to -70°C , and the γ -transition in the temperature region of -127 to -135°C . The gum EVA vulcanizate also shows a first-order transition ($T_{1,1}$) corresponding to a temperature around $+69^{\circ}\text{C}$.
2. Silica filler causes an increase in elastic modulus throughout the temperature range. The filler effect on the elastic modulus is more prominent in the rubbery and high-temperature regions than in the glassy state.
3. The glass transition temperature is found to be unaffected by the silica filler. However, treatment of the silica filler with the silane coupling agent causes a shift in T_g toward higher temperature.
4. The study of isothermal strain-dependent dynamic mechanical properties reveals that silica agglomerations in highly filled EVA vulcanizates are greatly reduced by the silane treatment of silica during mixing.
5. Frequency causes sequential lowering of tan δ peak values in the γ -relaxation region apart from shifting the peak positions toward higher temperature. Frequency also causes "suppression" of $T_{1,1}$ peak in the high-temperature region in the case of gum vulcanizate. Fillers, particularly at high concentration, also cause suppression of the $T_{1,1}$ peak, as is observed in case of high frequencies. Accordingly, the effect of frequency on the $T_{1,1}$ transition is less marked in filled vulcanizates.

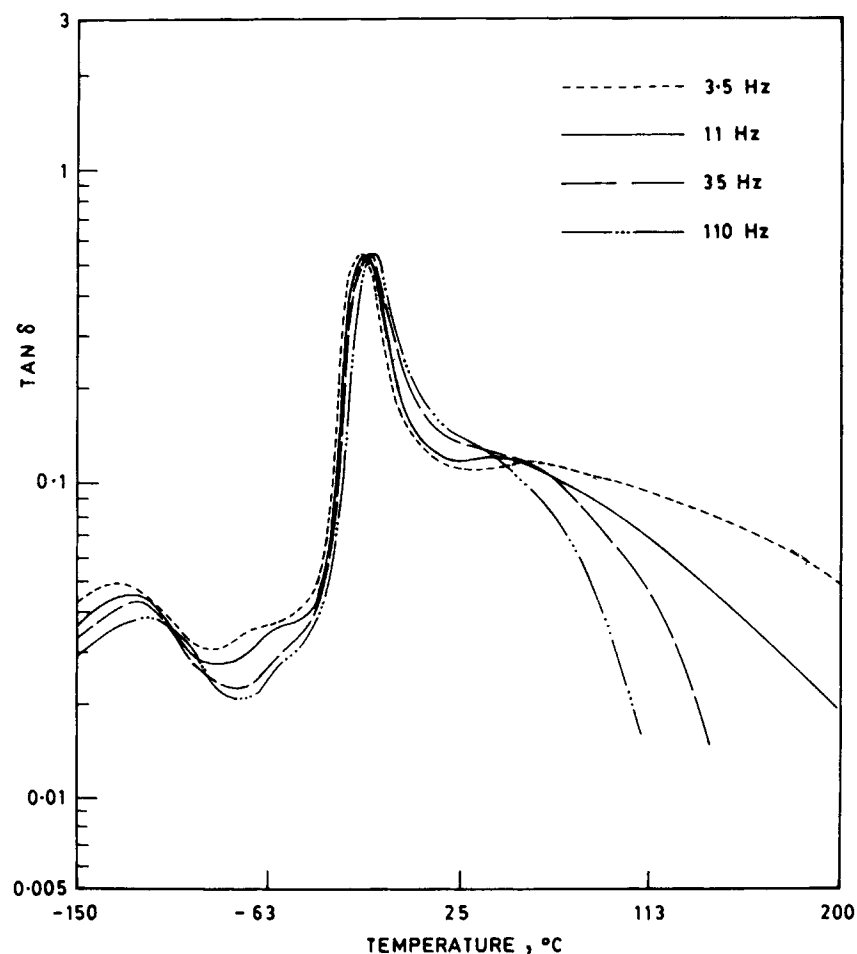


Figure 13 Tan δ as a function of temperature for E4 vulcanizate at different frequencies (DSA, 0.1%).

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