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# The effect of carbon black concentration on the dynamic mechanical properties of bromobutyl rubber

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The effect of carbon black concentration on the dynamic mechanical properties of bromobutyl rubber vulcanizates has been studied over a wide range of temperature ( − 150 to + 250 °C), frequency (3.5 to 110 Hz) and dynamic strain amplitude (0.07 to 5%). The influence of carbon black concentration on the glass–rubber transition has also been investigated with respect to the isochronal variation in dynamic properties. The influence of carbon black concentration consists mainly of the change in the levels of the moduli values in the glassy and rubbery state. In the glassy region; the increase in stiffness with carbon black loading may be fully explained by the hydrodynamic effect of the carbon black particles embedded in the polymer continuum. With increased carbon black concentration the glass–rubber transition temperature (tan δ peak temperature) does not show a shift in its location but peak shoulder broadening and decrease in peak height are observed. At a particular temperature, the effect of carbon black concentration on dynamic properties of bromobutyl rubber is dependent on the combined effects of applied strain amplitude and frequency. With increase in filler concentration the thermal stability of the vulcanizate increases.

## 1. Introduction

The performance of most rubber products is related to their dynamic properties which is a very important consideration when rubber compounds are designed for components to be used in dynamic applications (where rubber products are employed under conditions of rapidly repeated deformation of relatively small amplitude compared to ultimate breaking value of elongation). Rubber–carbon black composites have a complicated dependence on composition and conditional variables and the viscoelastic response of such composites cannot be fully explained by any of the available theories. Only qualitative explanations and logical arguments have been given for certain phenomena [1–4]. The effects of different variables such as the type of carbon black [1, 5–9], volume fraction of carbon black [9–11], plasticizer loading [12, 13], processing conditions [14–16], strain amplitude, strain rate, frequency, temperature [4, 8, 16, 17], static strain [18] and strain history [19], on dynamic mechanical properties of rubber–carbon black composites have been extensively studied by many investigators. Most of these investigations were, however, carried out at room temperature using low amplitude and covering a narrow range of frequency. To achieve complete understanding of the viscoelastic nature of the filled elastomer composites it is essential to carry out a detailed investigation on dynamic mechanical properties over a wide range of temperature, frequency and strain amplitude. Dynamic mechanical properties become more relevant to practical importance when carried out at an amplitude, frequency and temperature corresponding to the working conditions [20].

The object of this study is to investigate the effect of carbon black concentration on the dynamic mechanical properties of bromobutyl rubber vulcanizates over a wide range of temperature, dynamic strain amplitude and frequency.

## 2. Experimental details

### 2.1. Materials used and sample preparation

All the samples were prepared from commercial grade bromobutyl rubber; Polysar bromobutyl $X_2$ (Polysar, Canada). The studies were made with both gum and filled stocks; having the basic composition in parts by weight of 100 polymer/5 zinc oxide/1 stearic acid–2 N–(1,3-dimethyl butyl) N phenyl–P–phenylene diamine (vulcanox 4020)/1 sulphur/0.7 tetramethyl thiuram disulphide (Accicure TMT)/1.2 dibenzthiazyl disulphide (Accicure MBTS)/10 highly saturated paraffinic plasticizer. For this study a wide range of black loading (N-220, manufactured by Phillips carbon black, INDIA) such as 0, 15, 30, 40, 50, 60, 70, 100, phr was chosen. A model filled compound was also prepared using 70 phr untreated soda-lime glass beads of 80 to 220 μm diameter. The mixing was carried out in a laboratory size two-roll mixing mill (13″ × 6″). Cure properties were determined on a Monsanto Rheometer (R-100). All the compositions have long plateau cure characteristics. A standard 20 minutes cure, at 150 °C was given to all the samples. Specimens for dynamic testing were cut from the cured sheet.

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## 2.2. Test method

Rheovibron (DDV–III–EP) was used for dynamic mechanical analysis. The equipment has computerization and automation facilities both in operation and data processing, which provides a programmed heating rate, high measurement accuracy and sensitivity. Details about the equipment is discussed elsewhere [21, 22].

Dynamic mechanical properties were measured from $-150$ to $+250\,^{\circ}C$. Temperature control of the sample was restricted to a programmed increase of $1\,^{\circ}C\,min^{-1}$ from the lowest to the highest temperature, whenever results were scanned isochronally over a wide range of temperature. The dynamic strain amplitude (in tension mode) was varied between $0.7 \times 10^{-3}$ DSA (0.07% dynamic strain) to $50 \times 10^{-3}$ DSA (5% dynamic strain). Double strain amplitude (DSA) refers to the ratio of peak-to-peak deformation (total excursion path) of the sample to the length of the sample ($2\Delta L/L$). The frequency range was 3.5 to 110 Hz. For a particular sample, tests were carried out first at the lowest available strain and later the strain was increased stepwise to the maximum. This is very important because dynamic mechanical properties of filled vulcanizates are affected by prior deformation.

## 3. Results and discussion

### 3.1. Elastic modulus

Fig. 1 shows the storage modulus, $E'$ for bromobutyl compounds, containing increasing volume percentage (volume fraction, $\phi \times 100$) of carbon black, over a wide range of temperature ($-150$ to $+250\,^{\circ}C$). The applied dynamic strain amplitude and frequency test conditions were 0.1% DSA and 11 Hz, respectively. The characteristic sigmoidal variation of the storage modulus with temperature is clearly apparent from the figure. The nature of the curve for all the compositions is similar. From the nature of the curve characteristic regions may be easily seen. They are, respectively, A glassy region, B transition region, C rubbery region and D the high temperature region where degradation of the polymer chain takes place. Increased filler loading increases $E'$ for all experimental temperatures. Even in the glassy region with increasing filler loading $E'$ is enhanced considerably above that of the unloaded pure gum vulcanizate. In Fig. 2, storage modulus $E'$ measured at very low temperature ($-130\,^{\circ}C$), where the polymer is essentially in the glassy state, is plotted against the volume fraction ($\phi$) of filler loading. It is observed that $E'$ increases linearly with $\phi$. Theoretically calculated value based on the Smallwood equation [23, 24] $E' = E'E_0(1 + 2.5\phi)$ is also plotted. The agreement of the theoretically calculated value with experimentally observed value is excellent, even at very high filler concentration. Thus, in the glassy region the increase in $E'$ (stiffness) with filler loading may be attributed to the hydrodynamic effects [25, 26] of the carbon black particles embedded in the polymer continuum. All other factors such as elastomer–carbon black bonds [27–29], three-dimensional carbon black aggregate structure [1, 2, 30–32], and the rubber hard shell surrounding the filler aggregate which effects the value of $E'$ in the rubbery elastic region of a polymer have no influence in the glassy region.

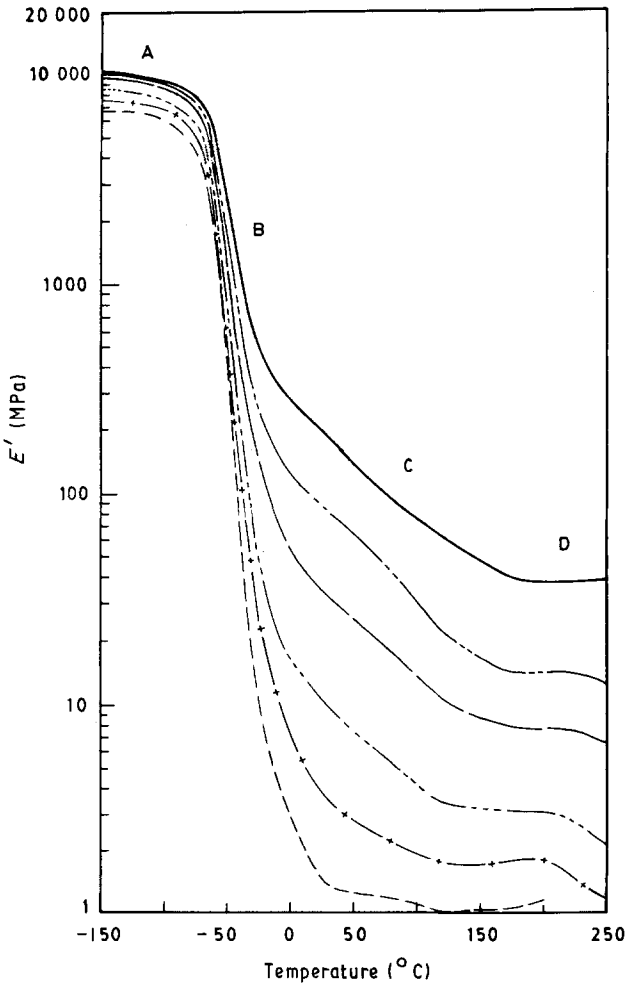


*Figure 1* Dynamic mechanical spectra of carbon black-loaded BIIR vulcanizates, effect of carbon black concentration on $E'$. (--- 0 phr, —+—15 phr, ——·—— 30 phr, ———— 50 phr, —— ·· —— 70 phr, —— 100 phr) Frequency 11 Hz, strain 0.1% DSA.

In many applications, low temperature flexibility is

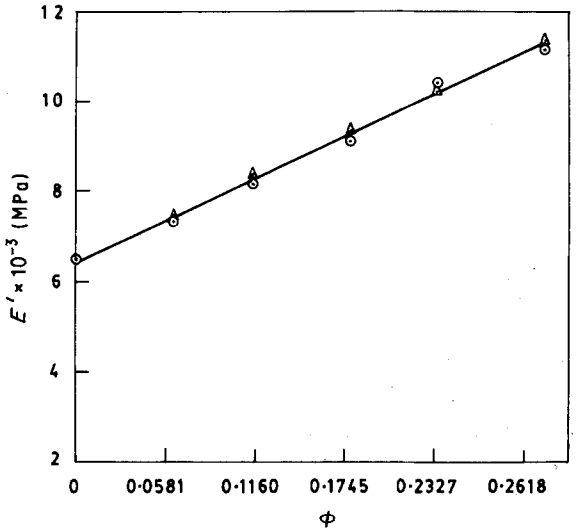


*Figure 2* Effect of filler concentration on elastic modulus $E'$ in the glassy state. Temperature $-130\,^{\circ}C$, frequency 11 Hz, strain 0.1% DSA. (⊙ experimental result, △ calculated from Smallwood's equation).

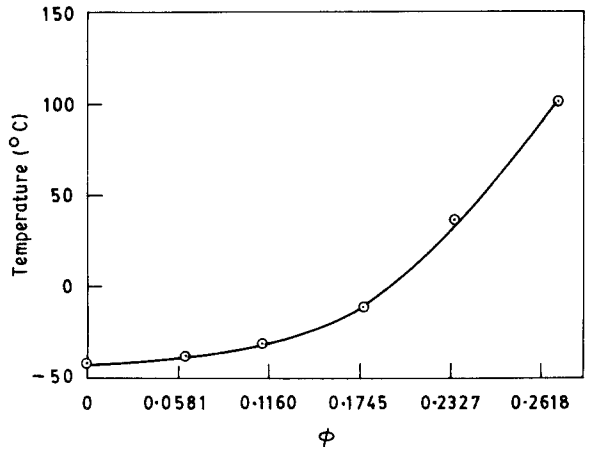


*Figure 3* Effect of carbon black concentration on low temperature flexibility. Temperature at which $E'$ value reaches 69 MPa (10 000 psi). Frequency 11 Hz, strain 0.1% DSA.

very important. The temperature at which the elastic modulus, $E'$ reaches 69 MPa (10 000 psi) is used to show a measure of low temperature stiffening [33]. Fig. 3 depicts the effect of filler concentration on low temperature stiffening characteristics of BIIR vulcanizate. The slope of the curve increases with a gradual increase in the filler loading and indicates the strong influence of carbon black loading on flexibility at higher filler levels.

## 3.2. Loss modulus

Fig. 4 illustrates the change of loss modulus, $E''$, with temperature for the vulcanizates. It is apparent from the figure that the temperature corresponding to the major loss modulus peak (α) does not shift its position with filler concentration. Increased carbon black concentration, however, causes broadening of the peak and increases the $E''$ peak magnitude appreciably. Far below the major $E''$ peak, in the glassy region, a minor $E''$ peak (β) is also observed. The peak position and the peak magnitude are not affected by filler loading. This peak observed in the glassy state may be ascribed to the rotation of methyl groups, directly attached to

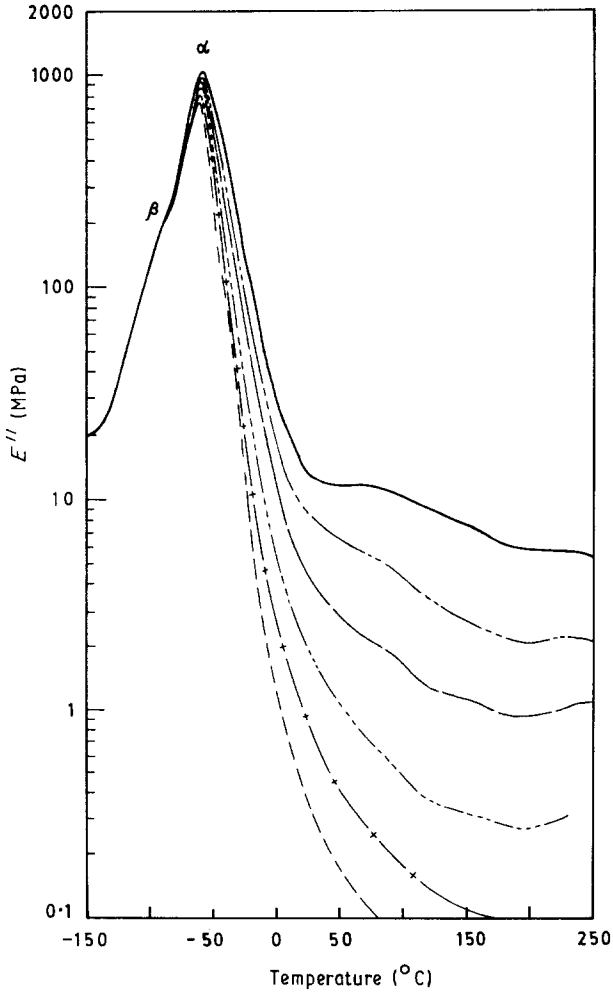


*Figure 4* Dynamic mechanical spectra of carbon black-loaded BIIR vulcanizates, effect of carbon black concentration on $E''$. Symbols as in Fig. 1.

the backbone in BIIR vulcanizates. The value of $E''$ in the glassy state does not vary significantly with varying carbon black concentration. Near and above transition (major $E''$ peak) the value of $E''$ increases with increasing filler concentration for all the experimental temperatures. Fig. 5 indicates the effect of filler concentration on the dynamic viscosity, in transition

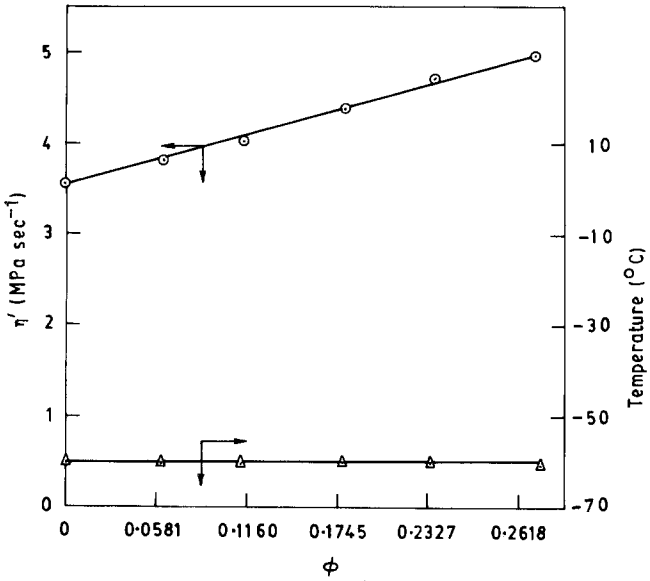


*Figure 5* Effect of filler concentration on dynamic viscosity and $E''$ peak temperature. Frequency 11 Hz, strain 0.1% DSA.

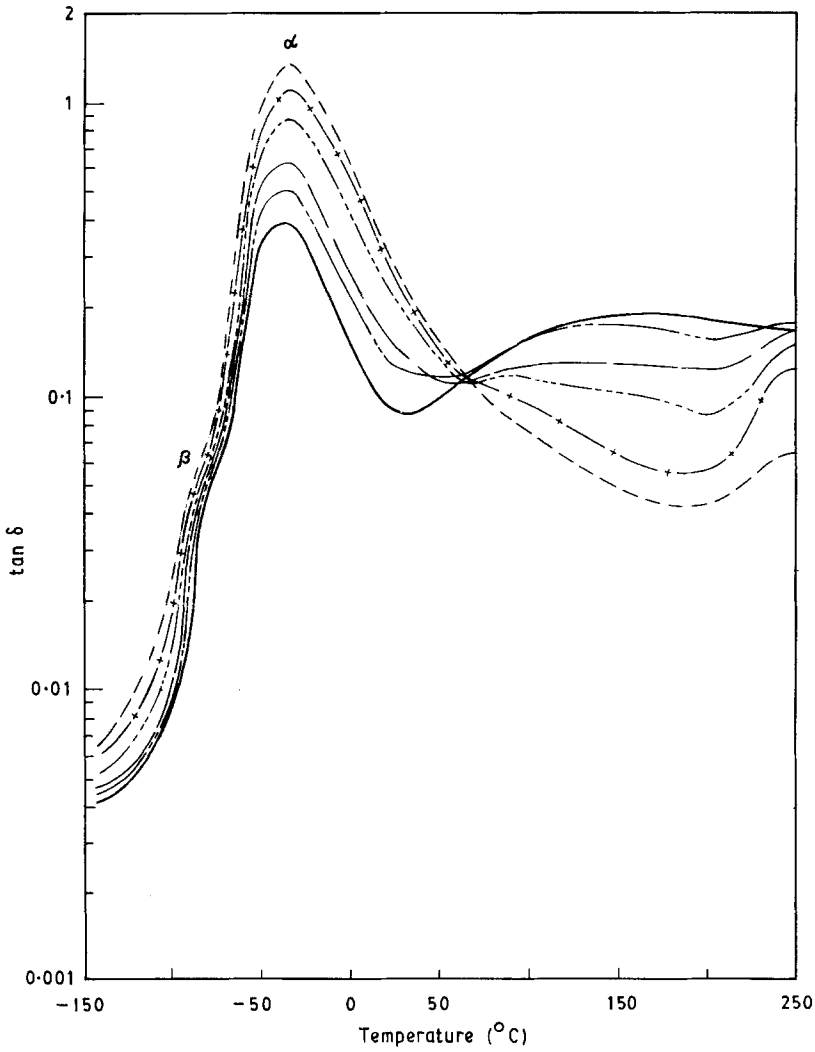


*Figure 6* Dynamic mechanical spectra of carbon black-loaded BIIR vulcanizates, affect of carbon black concentration on tan δ. Symbols as in Fig. 1.

region. Dynamic viscosity is defined as $\eta = G''/w$, where $G'' = E''/3$ and $w$ is the frequency of vibration expressed in radians per second ($w = 2\pi\nu$), [8]. The max value of $E''$ for all the compositions was taken to calculate the dynamic viscosity. The dynamic viscosity increases with increasing carbon black concentration and follows a linear relationship with carbon black concentration.

## 3.3. Damping

Fig. 6 shows the loss tangent spectra of the vulcanizates. It is apparent from the figure that in the glassy region tan δ decreases with filler concentration. β relaxation is also reflected in the tan δ curve as it is observed in the loss modulus curve. The tan δ peak temperature is not significantly affected by the filler concentration whereas the tan δ peak magnitude decreases with an increase in carbon black concentration (Fig. 7). It is also observed from the figure that above the glass–rubber transition temperature (tan δ peak temperature) the curves for different vulcanizates intersect at about a temperature of 57 to 62 °C as reported by Smit for SBR carbon black composites [34]. It is evident from the figure that at higher temperatures (far above the glass–rubber transition) highly filled vulcanizates (70 and 100 phr carbon black loaded systems) show a broad maximum. Filled polymer constitutes a system with complex structure leading to a new relaxation phenomenon which is absent in the gum vulcanizate [35, 36]. BIIR filled with active fillers exhibits relaxation phenomena in the highly elastic region (above the glass–rubber transition) which may be ascribed to the segmental mobility in the interphasic layers of the polymer absorbed between and within the active filler aggregates (hard shell) [36]. Fig. 8 shows the effect of frequency on the glass–rubber transition temperature. As expected, with increasing frequency, the glass–rubber transition temperature shifts towards the higher temperature for all the compositions.

## 3.4. Effect of dynamic strain amplitude

Fig. 9 shows the storage modulus; $E'$ for vulcanizates containing an increasing concentration of carbon black as a function of dynamic strain amplitude at 25 °C and 3.5 Hz, respectively. This is a familiar effect [11, 14, 16] and is explained by the fact that an increasing amplitude of oscillation causes the gradual breakdown of the secondary filler aggregate network structure and results in dynamic modulus reduction. As expected, the effect is small at a low degree of loading and very pronounced at a higher degree of loading. Pure gum vulcanizate does not show this effect. This non-linearity in viscoelastic behaviour in

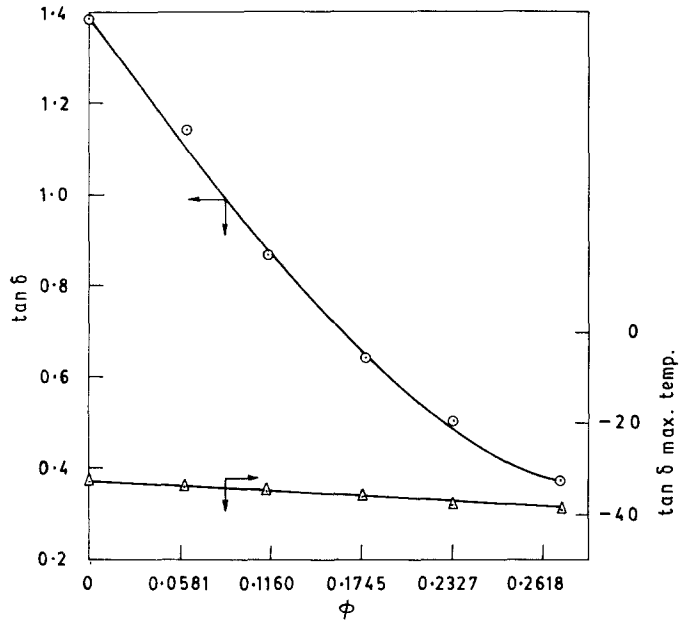


*Figure 7* Effect of carbon black concentration on tan δ peak value and dynamic transition temperature (tan δ peak temperature). Frequency 11 Hz, strain 0.1% DSA.

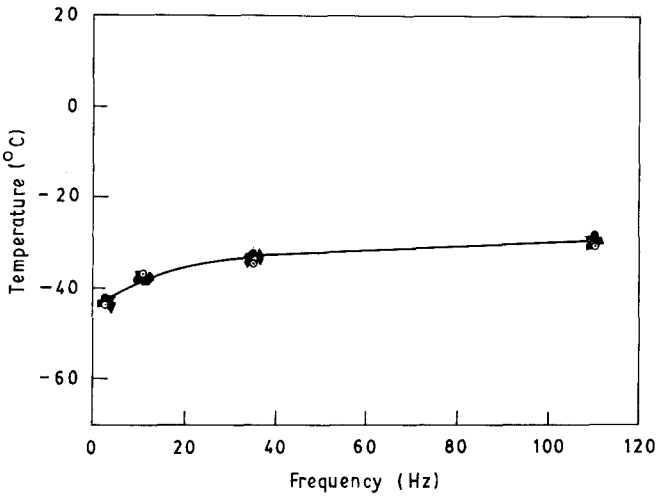


*Figure 8* Effect of frequency on glass–rubber transition temperature. Strain 0.1% DSA. (● 0 phr, ⊙ 15 phr, ▲ 30 phr, ■ 50 phr, ▼ 70 phr, ▽ 100 phr).

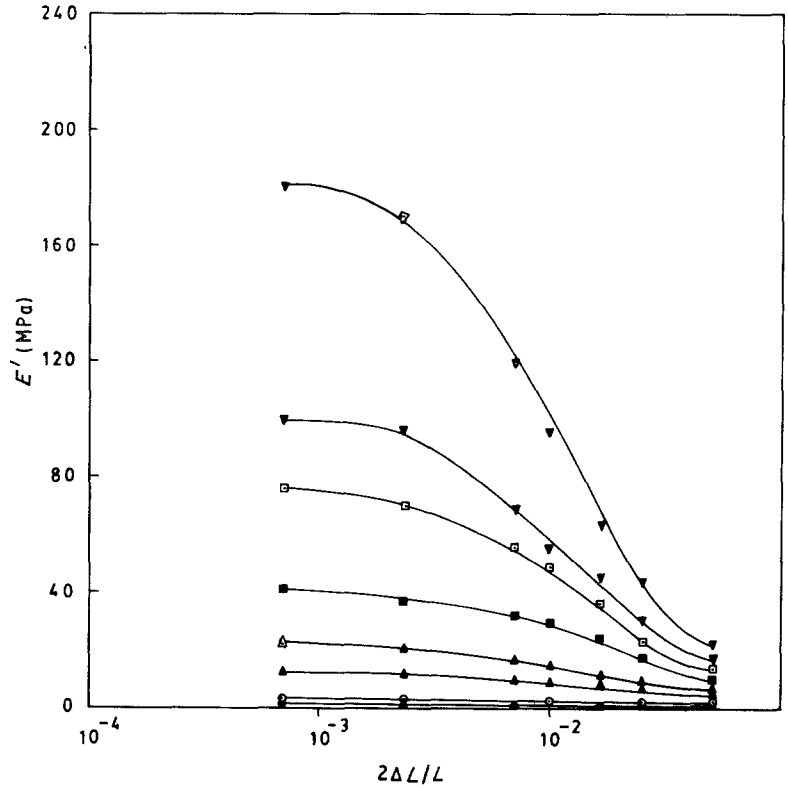


*Figure 9* Storage modulus as function of dynamic strain. Frequency 3.5 Hz, temperature 25 °C. (▽ 100 phr, ▼ 70 phr, ⊡ 60 phr, ■ 50 phr, △ 40 phr, ▲ 30 phr, ⊙ 15 phr, ● 0 phr).

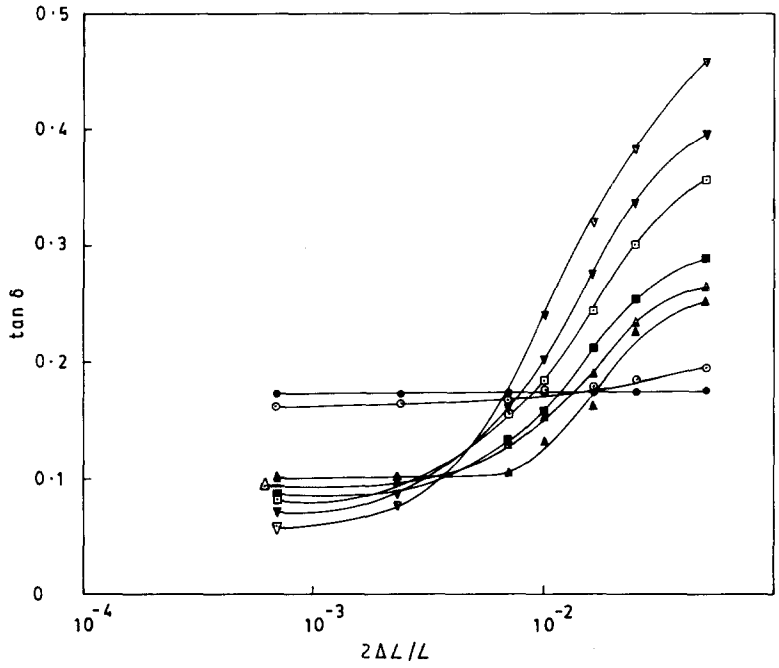


*Figure 10* Tan δ as a function of dynamic strain. Symbols as in Fig. 9.

the case of BIIR–carbon black composites is, however, not only due to the temporary rupture of weak cohesive bonds of the filler aggregate structure but desorption of the absorbed hard shell by the increasing amount of disruptive stress also has an affect [36].

Fig. 10 shows tan δ plotted against double strain amplitude, for the same vulcanizates. It is apparent from the figure that at very low dynamic strain test condition for a particular vulcanizate the tan δ value remains apparently constant with increasing dynamic strain. The range of strain over which tan δ remains constant is very limited and depends on filler concentration in the sample. Above this limiting value, tan δ increases with dynamic strain for filled systems. The higher the concentration of black in the sample, the steeper the rise in tan δ value. The low strain tan δ value for gum vulcanizate is, however, higher than the filled system and dynamic strain has no significant effect on the magnitude of tan δ. At relatively higher amplitude tan δ of filled vulcanizates surpasses the tan δ of gum vulcanizate. At intermediate amplitudes of oscillation considerable breakdown–reformation of black aggregate structure [2, 8, 16, 22] and desorption–reabsorption of hard shell (healing) [34, 36] take place. This, being an energy dissipative process, causes hysteresis (tan δ) to be higher in the intermediate region of amplitude. The junction point of the tan δ value between the gum and the filled system depends on filler loading and frequency.

## 3.5. Effect of frequency and strain

Fig. 11 shows the interrelation between carbon black loading, frequency and strain amplitude for $E'$. The effect of increasing frequency is to increase $E'$ for all the carbon black concentration and at all amplitudes. Fig. 12 shows the effects of frequency and dynamic strain on tan δ. It is apparent from the figure that the effect of frequency becomes progressively less pronounced as the carbon black loading increases. For a particular vulcanizate at any particular frequency over a limited range of strain (below junction point) the value of tan δ decreases with an increase in filler loading and within this range of amplitude the difference in the value of tan δ between different filler loaded vulcanizates increases with frequency. It is also clear from the figure that a highly glass bead loaded vulcanizate also behaves in a linear fashion like a gum system. In more quantitative detail, e.g. Fig. 13, it is found that $E'$ follows a linear relationship with frequency. (Breakdown and healing process is well pronounced at 1% dynamic strain (Figs 9 and 10) and thus has been chosen for detailed study.) With increasing frequency the healing process which is presumably responsible for the increase of hysteresis (tan δ) in the intermediate strain becomes less pronounced, thus, it is expected that the rate of rise in tan δ with frequency, will decrease with filler loading as is evident from Fig. 14. For highly loaded system (60, 70 and 100 phr) tan δ decreases as frequency increases from 35 to 110 Hz, which may be accounted for by the excessive internal heat generation at higher frequency.

## 3.6. Effect of temperature and dynamic strain

Fig. 15 reflects the variation of $E'$ with carbon black concentration, temperature and dynamic strain amplitude at 11 Hz. $E'$ decreases with an increase in temperature at all amplitudes but the absolute magnitude depends on dynamic strain and carbon black concentration. As the temperature increases the hard shell surrounding the filler particle tends to behave like a matrix [36] and the vulcanizates attain a particular energy required to break down the filler aggregate structure appreciably [16]. The dynamic modulus thus decreases with temperature. The higher the loading and lower the strain more will be the absorbed hard shell and filler aggregate available to be mobilized and broken down by heat energy. Thus the effect of rising temperature is more pronounced at higher

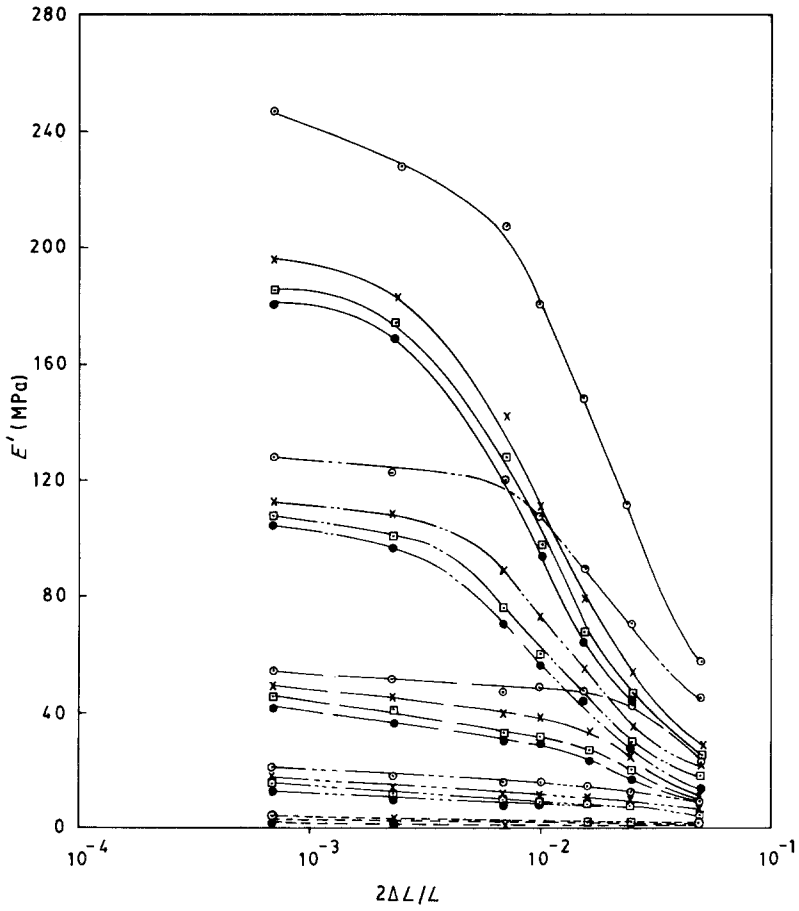


*Figure 11* Storage modulus as function of frequency and dynamic strain. Temperature 25 °C. (—— 100 phr, ——- -—— 70 phr, ——— —— 50 phr, ——--—— 30 phr, ----- 0 phr, ⊙ 110 Hz, × 35 Hz, ⊡ 11 Hz, ● 3.5 Hz).

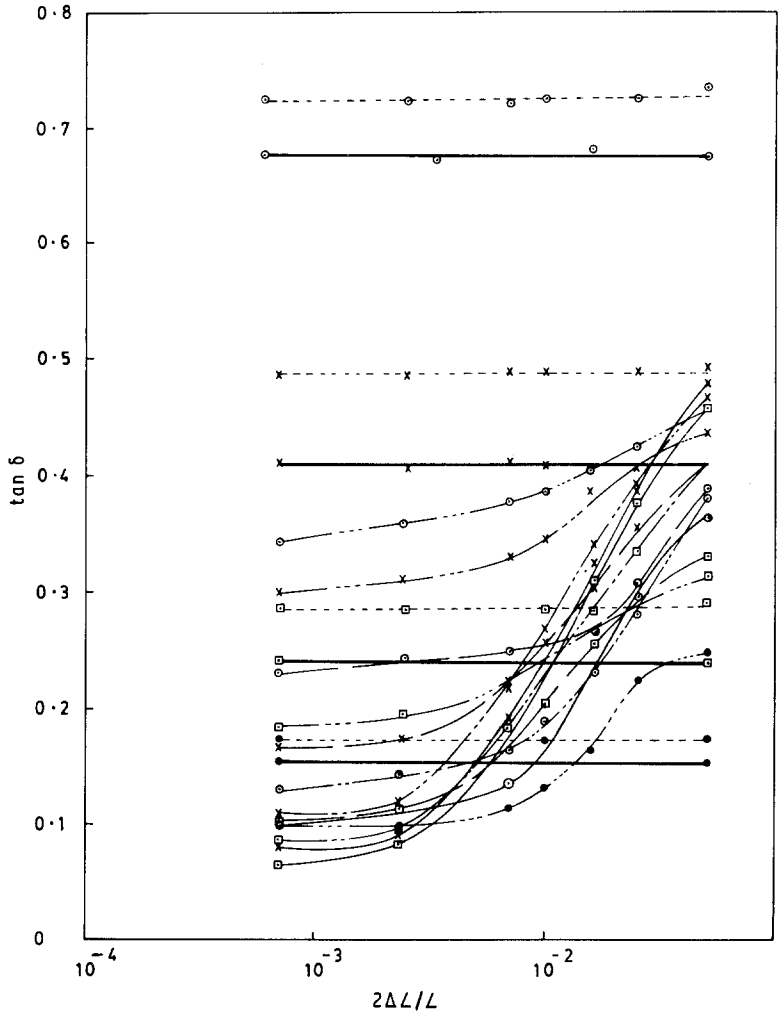


*Figure 12* Tan δ as a function of frequency and dynamic strain. Symbols as in Fig. 11 (——glass).

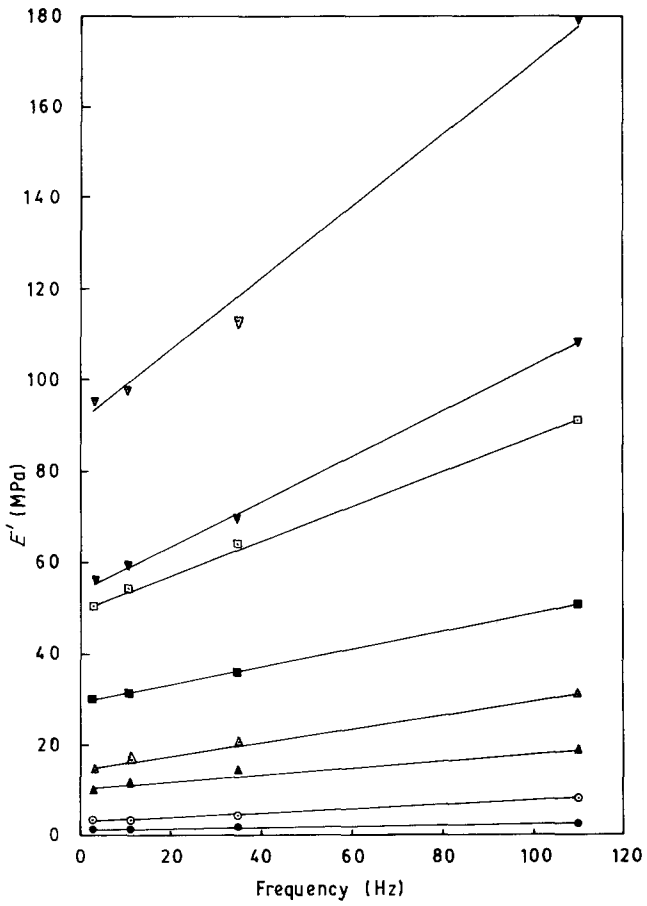


*Figure 13* Storage modulus as a function of frequency. Temperature 25%, 1% dynamic strain. Symbols as in Fig. 9.

loading and low amplitude than at low loading and higher amplitude. Fig. 16 shows the temperature and strain effects on tan δ for various loading of the vulcanizates. Tan δ for highly filled systems (60 phr and above) increases with temperature. The magnitude of increase depends on strain, temperature and filler loading, however, tan δ decreases with temperature for low filled (15, 30 phr) and gum systems. This increase in tan δ (damping) for highly loaded system may be attributed to the progressive increasing amount of hard-shell mobilization with temperature. At 5% strain for a highly loaded system (above 60 phr) temperature has no significant effect on tan δ. Fig. 17 depicts the dependence of $E'$ on frequency (1%

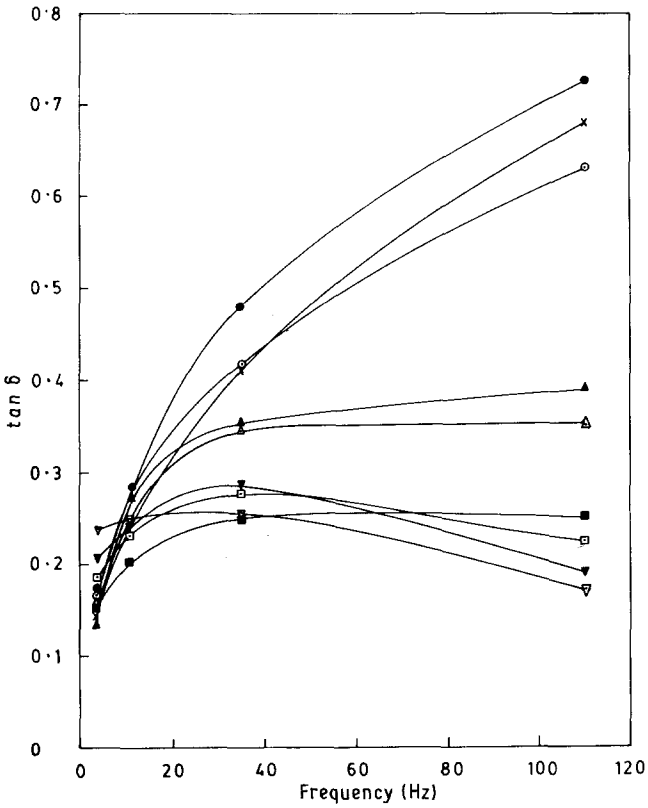


*Figure 14* Tan δ as a function of frequency. Symbols as in Fig. 9 ( × glass).

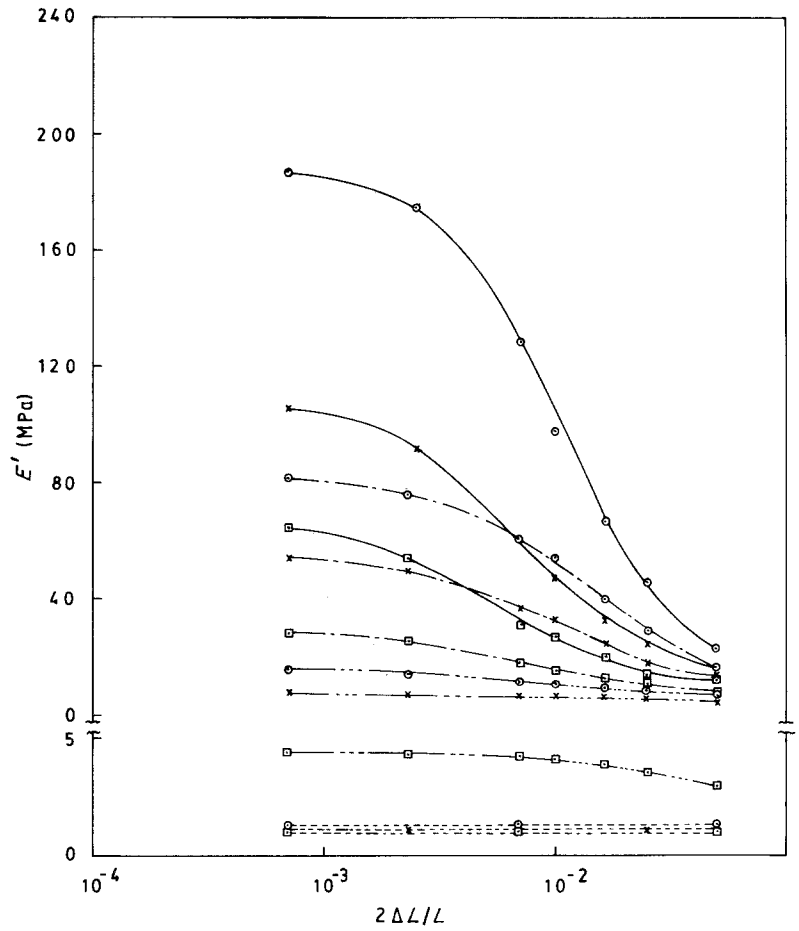


*Figure 15* Storage modulus as a function of temperature and dynamic strain. Frequency 11 Hz. (—— 100 phr, ———— 60 phr, ——·—— 30 phr, ——— 0 phr, ⊙ 25 °C, × 50 °C, ⊡ 100 °C).

dynamic strain) at three different temperatures. $E'$ follows a straight line relationship with frequency at all temperature. Fig. 18 shows the sensitivity of tan δ on temperature and frequency at 1% dynamic strain. For highly loaded systems (60 phr and above) tan δ increases with temperature at all frequencies, however, the magnitude of increase in the tan δ value decreases with increase in frequency. For gum and low loaded systems tan δ value decreases with temperature and the temperature sensitivity increases with frequency.

Figs 19 and 20 show the effect of temperature on $E'$, and tan δ over a wide range of temperature, at 5% dynamic strain and a frequency of 11 Hz. This is very important so far as practical utility of the composites

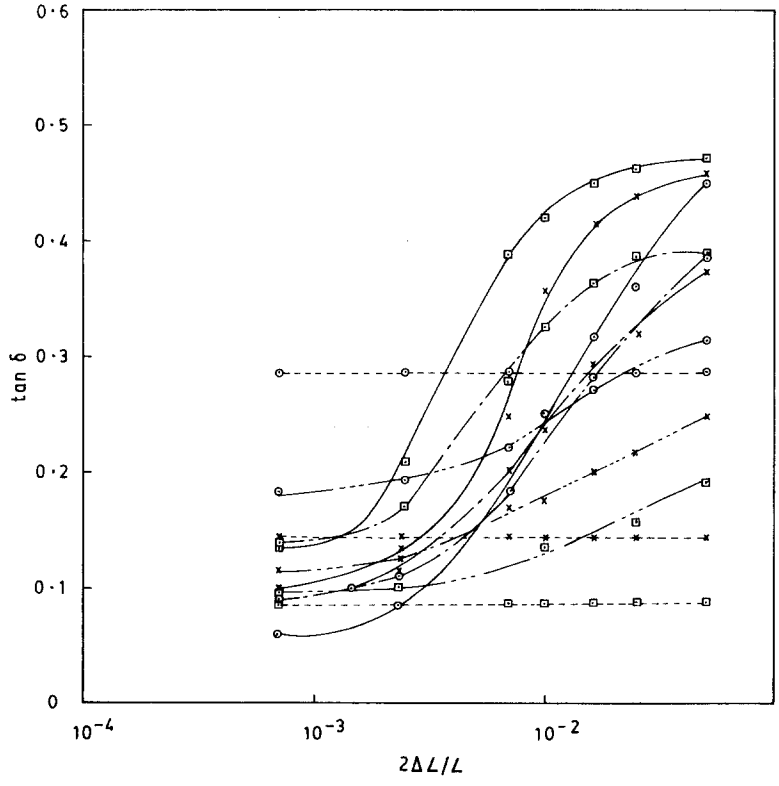


*Figure 16* Tan δ as a function of temperature and dynamic strain. Symbols as in Fig. 15.

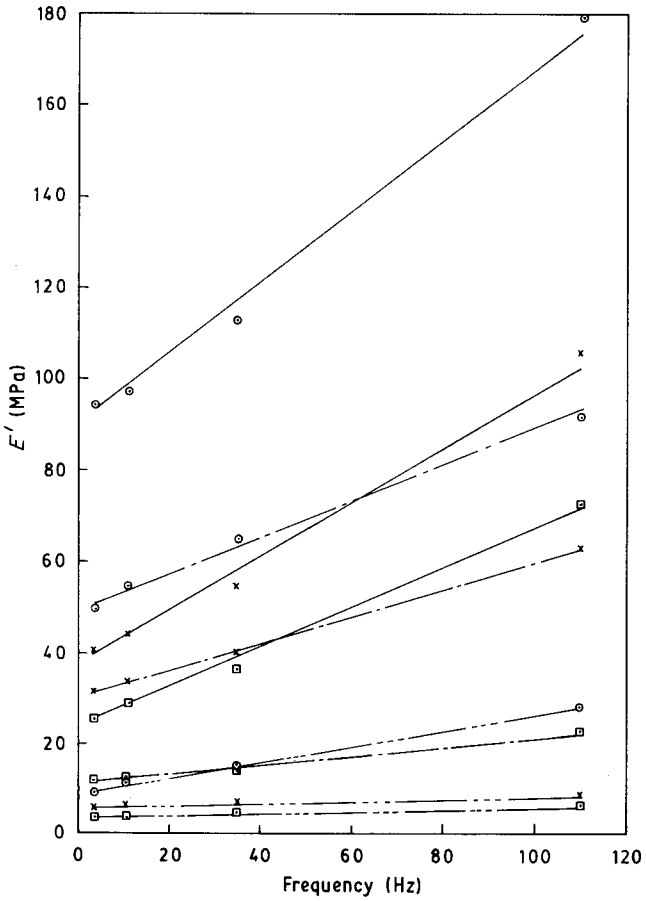


*Figure 17* Storage modulus as a function of frequency and temperature. 1% dynamic strain. Symbols as in Fig. 15.

are concerned. The effect of temperature on $E'$ becomes more pronounced as the filler loading increases. For gum compound $E'$ does not change appreciably. The value of tan δ is more sensitive to temperature for gum and low loaded vulcanizates. Vulcanizates filled with 100 phr black have practically no effect on tan δ as temperature increases from 25 to 150 °C. Above 200 °C tan δ increases for all the vulcanizates except 100 phr loaded system. This is due to the thermal degradation of the polymer chain. It is clear that this effect decreases as black loading increases. Thus, an increase in concentration of black in the vulcanizate increases the thermal stability of the composites.

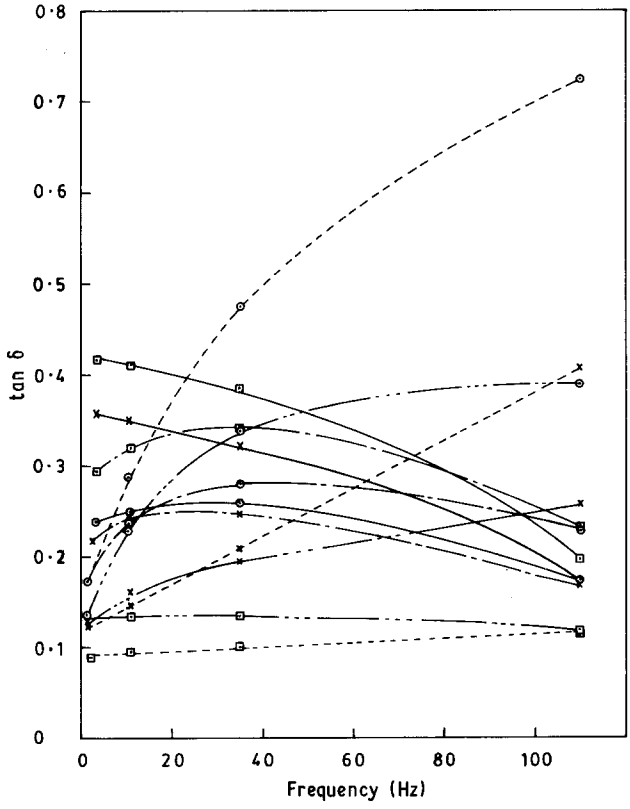


*Figure 18* Tan δ as a function of frequency and temperature. Symbols as in Fig. 15.

## 4. Conclusion

The influence of reinforcing carbon black concentration on the dynamic mechanical properties of bromobutyl rubber has been examined. The basic conclusions that may be drawn from the above investigation are as follows.

(1) Increased carbon black concentration increases the storage modulus over the entire experimental temperature range. The augmentation in storage modulus in glassy region may be fully explained by hydrodynamic effect of the carbon black particles embedded in the polymer continuum. Other factors namely carbon black aggregate structure, adhesion between carbon black and rubber which affect the dynamic properties of rubber–carbon black systems in the rubbery elastic region do not, at all, effectively influence the same in the glassy region. With gradual increase in black loading low temperature flexibility decreases.

(2) Loss modulus, $E''$ peak temperature is not affected by filler loading, but $E''$ peak magnitude and dynamic viscosity linearly increase with filler concentration.

(3) The glass–rubber transition temperature (tan δ

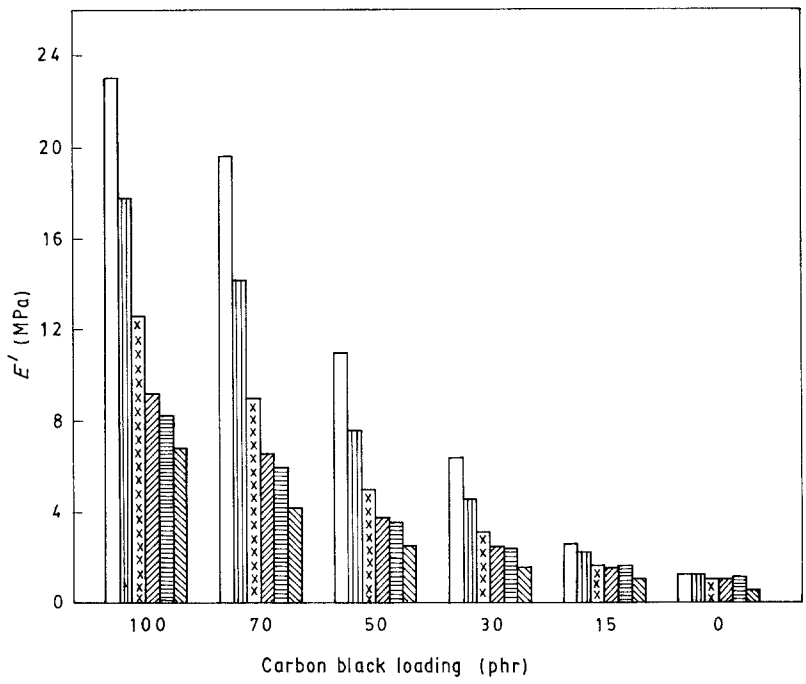


*Figure 19* Elastic modulus and temperature. Frequency 11 Hz, 5% dynamic strain. (□ 25 °C, ▥ 50 °C, ▩ 100 °C, ▨ 150 °C, ▤ 200 °C, ▧ 250 °C).

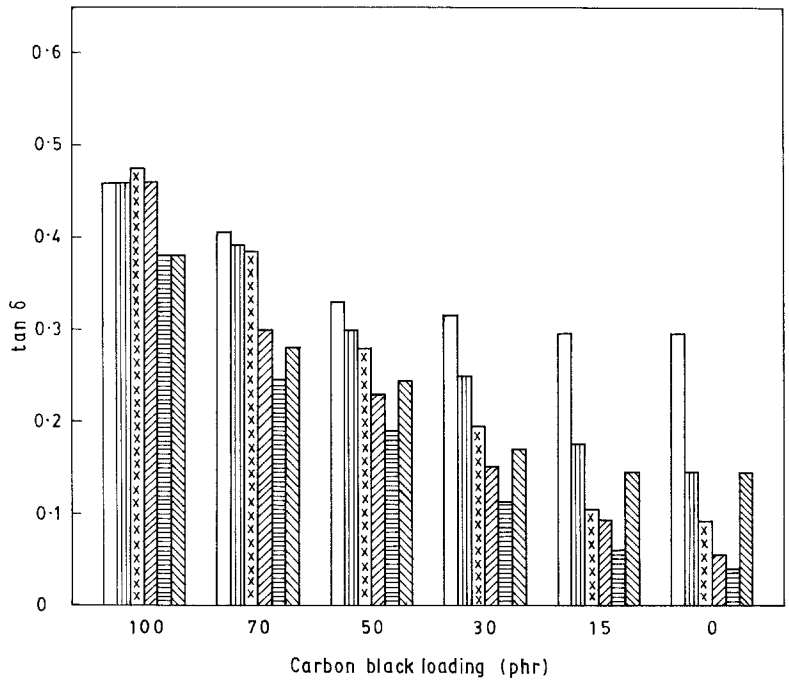


*Figure 20* Tan δ and temperature. Symbols as in Fig. 19.

peak temperatures) is not significantly affected by filler loading. An increase in filler loading shows tan δ peak broadening and a decrease in peak height.

(4) At a particular temperature, the effect of carbon black concentration on dynamic properties is dependent on the combined affects of applied strain amplitude and frequency.

(5) The healing process (gradual reformation of previously destroyed secondary filler aggregate structure and absorbed hard-shell) is a time dependent phenomenon and frequency has a decisive effect on this process.

(6) An increased filler concentration increases the thermal stability of the vulcanizates.

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