Strain Dependent Dynamic Mechanical Properties of Carbon Black and Clay Filled Epoxidised Natural Rubber Vulcanizates

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ABSTRACT: Dynamic mechanical properties of carbon black and clay filled epoxidised natural rubber have been studied over a wide range of temperature and varying dynamic strain conditions. Low temperature studies indicated the absence of an adsorbed layer of elastomer around the clay particles for the various loadings studied. Low strain properties under room temperature conditions were found to be dependent on the transient aggregate structure existing in the case of carbon black filled vulcanizates whereas for clay, except the hydrodynamic effect, no other profound effect could be observed under the low loading conditions studied. From the physical property studies also it may be concluded that there is no profound reinforcing mechanism operating in the case of clay and ENR.

KEY WORDS: Epoxidised natural rubber, carbon black and clay fillers, agglomerate structure, strain dependent dynamic mechanical properties.

1.0 INTRODUCTION

CARBON BLACK FILLED rubber vulcanizates under sinusoidal strain application conditions were the interest of study of many workers [1–6]. Payne and Whittaker [3] have studied the effect of clay in natural rubber and water; they established the presence of a three dimensional

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structure similar to that of carbon-black-rubber systems. However their studies were confined to the application of a sinusoidal strain under isothermal conditions. The lack of an investigation into the effects of a non-reinforcing filler in the glassy region of rubber justify the necessity of such a study. The presence of an adsorbed layer of rubber around the carbon black particles were found to shift the glass transition temperature of carbon-black-loaded rubber vulcanizates [5,25]. In the case of clay it is still to be investigated whether such an adsorption-desorption mechanism operates on the surface of clay particles, which may give an indication of the reinforcing behaviour of a filler through its interaction parameters with the elastomeric phase.

In our present investigation, we report the results of our studies on the dynamic mechanical properties of carbon black and clay filled epoxidised natural rubber (ENR) under low strain conditions. A systematic investigation of the mechanical and dynamic mechanical properties of this elastomer is undertaken in order to evaluate its potential in the application of vibration isolation and damping.

2.0 EXPERIMENTAL

2.1 Materials

The elastomer used in this study was epoxidised natural rubber (ENR), 50 mol% epoxidised, supplied by Malaysian Rubber Producers Research Association, Brickendonbury, U.K. The reinforcing filler, carbon black (ISAF, N-220), was manufactured by Philips Carbon Black Ltd., India and the clay used in this study was a non-reinforcing type supplied by Andrew Yule and Co. Ltd., India.

2.2 Preparation of the Samples

Formulations of the mixes used are given in Table 1. Mixes of A, B, C, D and E contains 0, 20, 30, 40 and 50 phr of ISAF black (N-220) and mixes F, G and H 20, 30 and 40 phr of china clay respectively. Compounds were prepared on a laboratory size two roll mill (39 cm × 15 cm) after masticating with sodium carbonate according to ASTM D3182. Curing characteristics were determined on a Mooney viscometer (Negretti Automation, U.K.) and Monsanto rheometer (R-100). Details are given in Table 2. At 150°C all mixes showed a long plateau cure. Specimens for dynamic mechanical tests were prepared in dimensions 7.0 cm × 0.5 cm × 0.3 cm. Samples were conditioned at room temperature before testing.

Table 1.

	A EN_{gum}	B EC20	C EC30	D EC40	E EC50	F EL20	G EL30	H EL40
ENR-50	100	100	100	100	100	100	100	100
Na_2CO_3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
C-black ISAF (N220)	—	20	30	40	50	—	—	—
China clay	—	—	—	—	—	20	30	40
Aromatic oil	—	2	3	4	5	—	—	—
IPPD[a]	2	2	2	2	2	2	2	2
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CBS[b]	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Optimum cure time at 150 °C, (min)	8	7	7	7	7	7	7	7

[a]N-isopropyl N′phenyl para-phenylene diamine.
[b]N-cyclohexyl benzothiazyl sulfenamide.

Table 2.

	A EN_{gum}	B EC20	C EC30	D EC40	E EC50	F EL20	G EL30	H EL40
Tensile properties								
a) M100, MPa	1.2	3.6	4.7	6.0	7.0	1.2	1.5	1.7
b) M300, MPa	3.9	16.5	18.8	20.6	21.6	3.2	4.1	4.9
c) Tensile strength, MPa	14.1	19.9	25.5	26.5	22.7	17.3	19.7	20.2
d) Elongation at break, %	876	714	686	657	618	760	754	712
Tear strength, N/mm	23	37	44	46	53	29	30	33
Resilience, % at 45°C	44	37	31	26	30	17	17	20
Heat build-up, ΔT°C	11	15	21	26	30	17	17	20
Compression set at constant strain, %	63	62	41	40	40	79	85	100
Abrasion loss, cc/1000 rev	3.24	1.48	1.41	1.77	1.28	2.49	2.65	1.96
Hardness, shore A	38	51	58	65	68	45	50	52
Flexibility, Demattia, Kcs to break	260	270	325	>325	>325	>300	>300	>300
Vro/Vrf	1.00	1.00	0.75	0.83	0.71	1.67	1.21	1.25

2.3 Test Procedure

Physical properties of the vulcanizates were determined according to the following ASTM and BS standards. The following physical properties were determined: tensile and tear properties (Universal Testing Machine, Zwick model 1445, ASTM D412-87), hardness (shore A, ASTM 2240-86), resilience (Dunlop Tripsometer, BS:903: Part A8 1963, method C), compression set (ASTM D623-78, method B), abrasion resistance (Cryodon Akron DuPont Abrader, BS:903: Part A9, method C) and heat build-up (Goodrich Flexometer, ASTM D623-1978, method A). Volume fraction of the rubber in solvent swollen vulcanizate in both unfilled and filled rubber vulcanizates were determined according to the method suggested by Kraus [7].

Dynamic mechanical properties of the samples were studied on a dynamic viscoelastometer, Rheovibron (model DDV-III-EP). Details of the equipment are given elsewhere [8]. Tests were carried out for a temperature range of $-130°C$ to $+50°C$ and in a special case up to $+200°C$ at a heating rate of 2°C/min at a frequency of 35 Hz. Frequency is selected so as to simulate the test conditions to practical application conditions such as tire treads. All of the sample tests were carried out from the lowest strain [as low as 0.7% double strain amplitude (DSA)] to the highest strain (5% double strain amplitude). Three specimens from each formulation were tested under the same conditions. Dynamic strain was increased stepwise from a lower value to the highest value.

3.0 RESULTS AND DISCUSSION

3.1 Physical Properties of the Vulcanizates

3.1.1 EFFECT OF CARBON BLACK AND CLAY LOADING

Effect of carbon black loading on the physical properties of ENR-50 are given in Table 2. Tensile properties like modulus at 100% and 300% elongation and tensile strength are showing the reported trends as observed in the case of strain crystallizing rubbers [9–12] while resilience and abrasion loss values decrease with increased loading of ISAF. Unlike the earlier worker's reports [13], we have found that the tear strength of filled ENR-50 is very high. As anticipated this may be due to the strain induced crystallization property as well as the knotty tearing characteristics of ENR [14]. Heat build-up characteristics of the vulcanizates are shown in Figure 1. Increased filler loading which increases the rubber-filler interaction area resulted in an increased molecular friction and hence higher heat build-up. Mullins and Tobin [15]

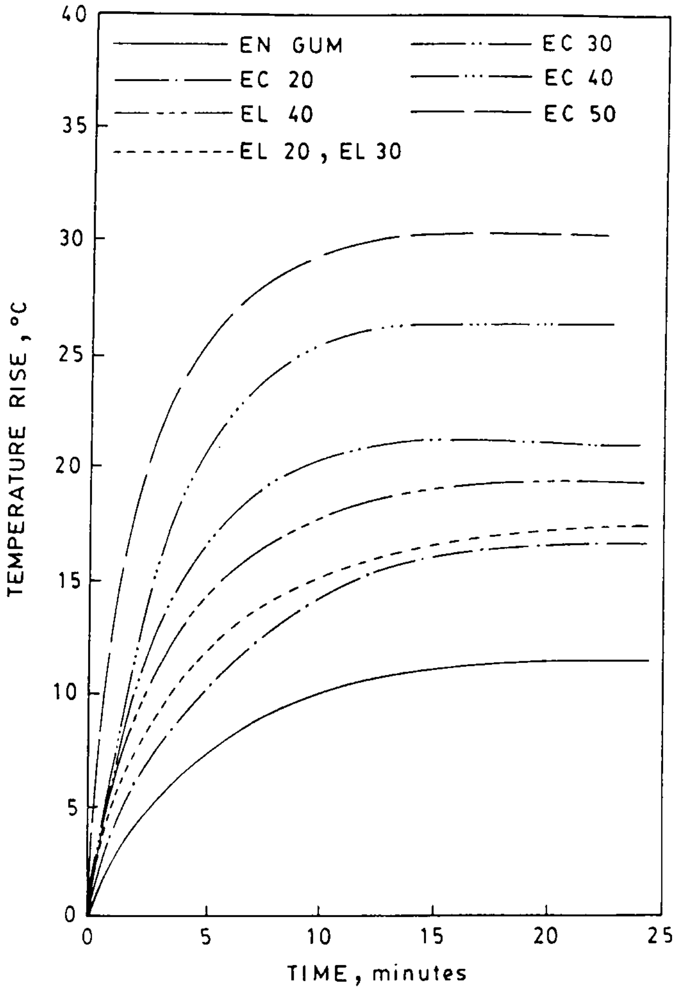

FIGURE 1. Heat build-up characteristics of filled ENR-50 vulcanizates.

suggested this reinforcement mechanism as the strain amplification by the filler incorporated in the rubber matrix. This leads to a shift from the ideal network behaviour of the gum elastomer and non-linearity. Hardness as expected, increases with increased loading. Flex resistance values showed improvement with carbon black loading up to 30 phr, beyond which the flex resistance remained almost constant. Kraus plot (Figure 2) showed that there is a high degree of reinforcement in the case of carbon black loaded vulcanizates. This is similar to that observed earlier by other workers in rubbers like NR. Figure 2 shows the Kraus plot for clay-filled vulcanizates. The Vro/Vrf values were found to increase beyond 1.0 indicating the formation of more vacuoles and filler-rubber detachments at the filler-rubber interface in the case of clay filled vulcanizates [16]. It may be concluded that clay is not imparting a reinforcement to the ENR matrix as may be expected through the interaction mechanism operating between the hydroxy groups and epoxy groups. This is also evident from the physical properties as summarized in Table 2. The changes in properties on the addition of filler is much less marked in this case as compared to the carbon black filled vulcanizates.

3.2 Dynamic Mechanical Properties

3.2.1 EFFECT OF TEMPERATURE ON STORAGE MODULUS, LOSS MODULUS AND TAN δ

Effect of variation of temperature on the dynamic mechanical parameters like storage modulus, E', loss modulus, E'' and loss angle, tan δ are shown in Figures 3–5. Variation of glass transition temperature (T_g) and tan δ values with filler loading and type of filler are shown in Table 3. The glass transition temperature appears as a result of the reduction in molecular mobility at lower temperatures and a collapse of the free volume. The mobility of the polymer at any temperature de-

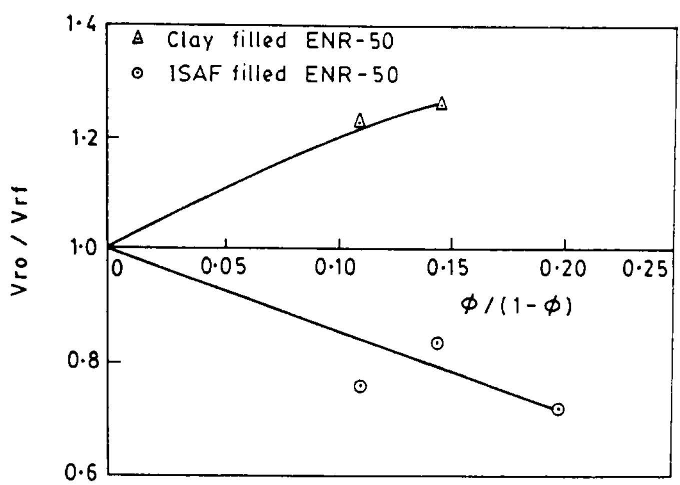

FIGURE 2. Kraus plot for ISAF and clay filled ENR-50.

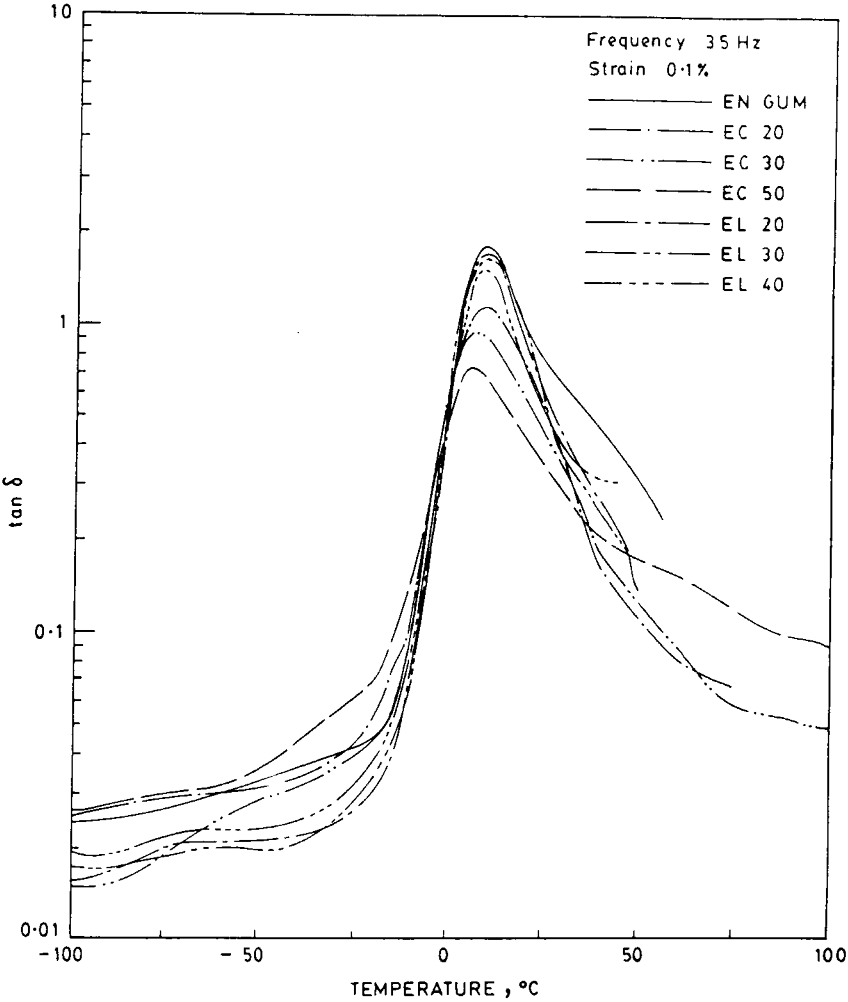

FIGURE 3. Temperature dependence of loss tangent tan δ.

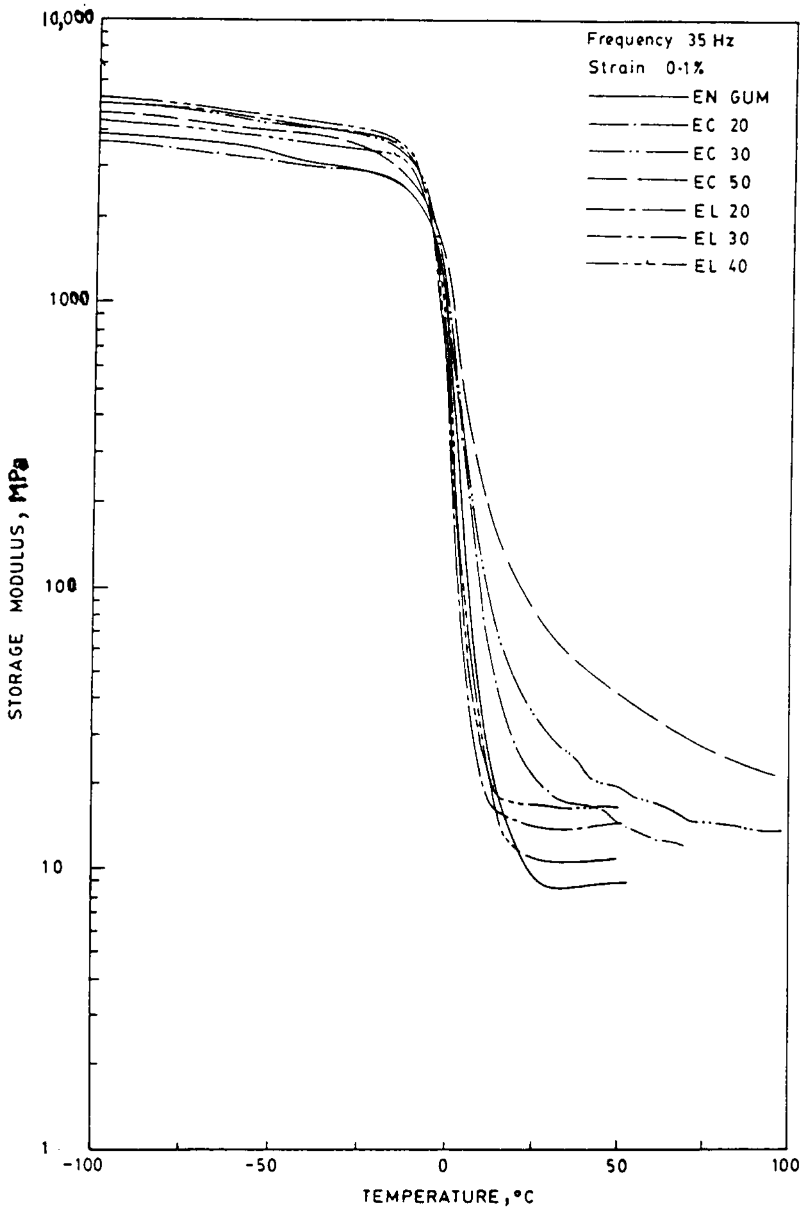

FIGURE 4. Temperature dependence of storage modulus, E' values.

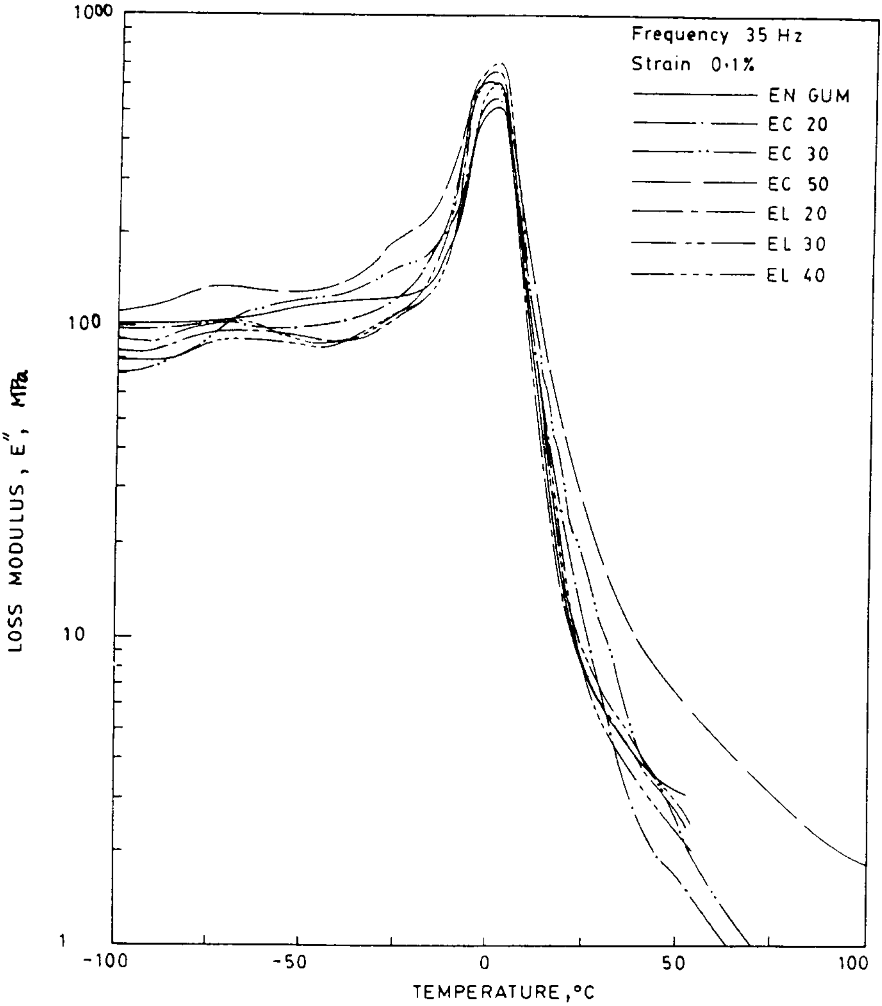

FIGURE 5. Temperature dependence of loss modulus, E'' values.

Table 3.

	A EN_{gum}	B EC20	C EC30	D EC40	E EC50	F EL20	G EL30	H EL40
Maximum tan δ	1.86	1.17	0.95	0.85	0.71	1.75	1.73	1.56
Glass transition Temperature, °C	9	9	8	7	6	9	9	9

pends on the free volume remaining [17]. Kraus [18] and Payne [19,20] showed that the free volume of the vulcanizate is not altered considerably by the presence of filler in the rubbery state but expands with decreasing temperatures below T_g. It was observed that T_g shifted by a maximum of 3°C to a lower temperature in the case of 50 phr ISAF loaded vulcanizates. In the case of clay filled vulcanizates hardly any shift towards lower temperature was noticed. Increasing the amount of plasticizer has the profound effect of lowering the T_g regardless of the increase in filler concentration. In the case of clay filled vulcanizates, since there is no plasticizer, no shift in T_g values is observed. In the case of carbon-black-loaded vulcanizates tan δ peak values showed a decrease with increasing loading, whereas in the case of clay filled vulcanizates, the change is not so marked as shown in Figure 3. Filled elastomers exhibit a complex structure consisting of an absorbed hard immobilized layer of rubber within and between the filler aggregates and surrounding it and the bulk rubber. As reported by earlier workers [21] the absorbed hard layer would result in a perturbed relaxation response and the property of these layers shift towards the glassy state. The low temperature tan δ (max). values observed can be ascribed to the relaxation due to the bulk rubber. With an increase in carbon black loading, the amount of bulk rubber decreases and hence a decrease was noticed in tan δ (max) values. Results are shown in Table 3. Lowering of tan δ (max) values was much less in the case of clay filled vulcanizates. This smaller decrease may be due to the fact that agglomerate structures do not exist in the case of clay filled vulcanizates and hence a higher amount of bulk rubber that can result in a higher tan δ (max).

3.2.2 EFFECT OF STRAIN ON STORAGE MODULUS, E′

Figure 6 shows the effect of variation of storage modulus with increasing volume percentage of carbon black as a function of strain amplitude, at 26°C and 35 Hz frequency. At other experimental frequencies also we have observed the same trend; the results are not reported here. E' values showed a decrease with a progressive increase in strain, though it was constant at very low strains. The drop in E' values was slow at the lower strain and it was rapid at higher strain. The characteristic sigmoidal shape was observed when plotted against the logarithm of double strain amplitude. The drop in E' values at intermediate range of strain is more prominent in the case of higher loading of filler rather than in the case of gum or low loaded samples. In the clay filled vulcanizates, modulus values were seen to increase slightly with the addition of filler. Radok and Tai [22] showed that an inclusion

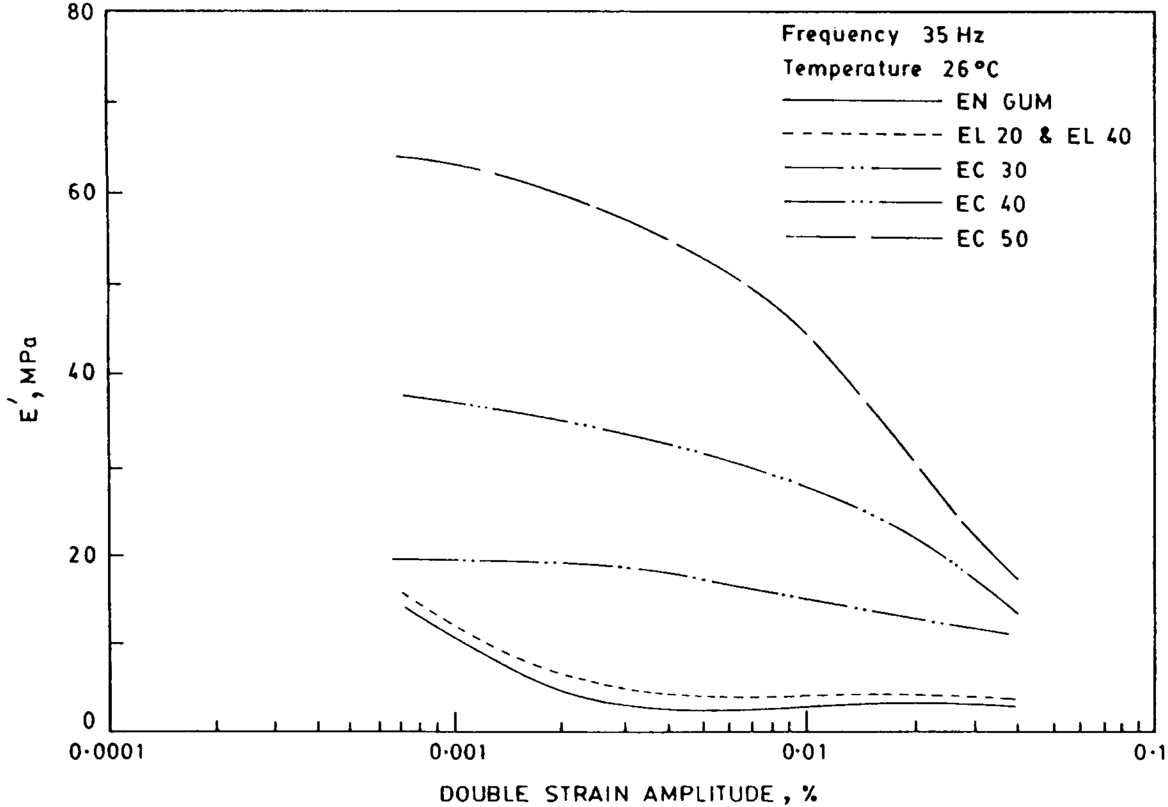

FIGURE 6. Strain amplitude dependence of storage modulus, E'.

in a viscoelastic material plays the role of a stress raiser and it changes the time dependent behaviour of the viscoelastic medium. In the case of clay due to the lack of an aggregate structure and the dewetting characteristics with the rubber matrix the observed E' values were comparable to that of the gum throughout the strain range studied. However, the small increase in modulus value with the addition of clay may be due to the stress raising behaviour of the inert inclusion in the rubber matrix and its hydrodynamic effects. In the case of gum vulcanizates a very small dependence of modulus on amplitude is observed. Payne and Whittaker [23] suggested that this dependence may be due to the slippage of entanglements and motion of chains with free ends. The Eo' (up to 0.1% strain, where E' value is linear) values of 50 phr ISAF filled vulcanizates is approximately eight times larger than that of the gum vulcanizates. Although, the modulus of the filled vulcanizates decreases markedly with an increase in strain amplitude, it is still much higher than that of the gum rubber at the lower limit of modulus and at higher strains for carbon black filled vulcanizates. Some of these differences are due to the hydrodynamic effects of the filler particles embedded in the viscous medium.

As the relaxation or retardation response of most rubbers covers a wide range of relaxation or retardation times, the measured response must reflect the perturbed relaxation behaviour of the rubber matrix. Investigation by swelling, electron microscopy, glass transition temperature [21,24], modulus and tensile measurements [25,26] have shown the presence of a shell of immobilized rubber around black particles in a filled rubber vulcanizate. This immobilized rubber can be identified as bound rubber [27,28] or the occluded rubber [29,30] within the carbon black agglomerates. This immobilized rubber will cause a perturbed relaxation response of the rubber matrix, as found out quantitatively by Radok and Tai [22]. Therefore, this mechanism could account for the increase in $E\infty'$ when carbon black is added. The present study gives additional evidence of the same mechanism. Clay filled vulcanizates have not shown such an improvement. This lack of improvement may be due to the lack of formation of bound rubber, occluded or absorbed layers around the clay particles due to the less adhering nature of filler to rubber and the absence of a structure in the case of clay.

3.2.3 EFFECT OF STRAIN ON TAN δ

Figure 7 illustrates the effect of strain on tan δ values for the black filled and clay filled vulcanizates respectively. Typically the loss tangent values pass through a maximum as a function of the applied

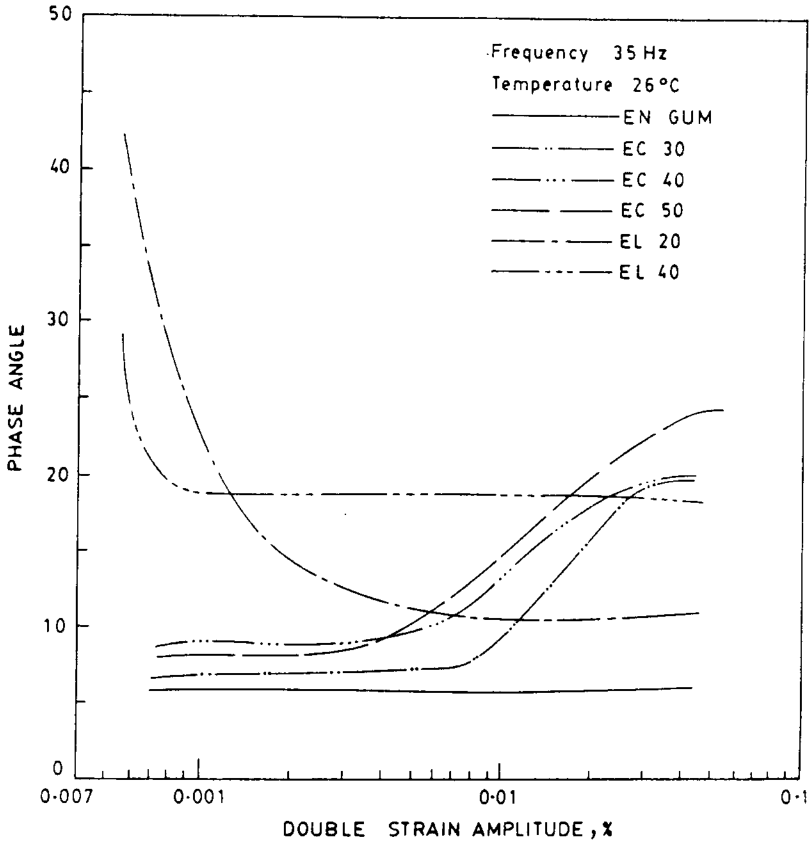

FIGURE 7. Strain amplitude dependence of phase angle δ.

strain. The amplitude dependence of tan δ has been interpreted qualitatively on the basis of the inter-aggregate interaction mechanism used for the amplitude dependence of the elastic modulus. Hysteresis is assumed to result from breakdown and reformation of inter-aggregate bonds [31]. At intermediate strains considerable breakdown and reformation of bonds takes place. Thus, hysteresis is high. At higher amplitudes E' and tan δ continue to decrease, thus their product E'' can become quite low. As reported by Payne [31], we have also observed an increase in tan δ values due to the aforesaid phenomenon. Clay filled vulcanizates showed similar behaviour to that of gum vulcanizates. However the tan δ values were higher than that of the gum vulcanizates. Studies by Payne et al. [32] on clay filled water and rubber systems have shown that these systems behave in the same way as the carbon black loaded systems at low strain values. In the present system we have observed that at intermediate and high strain values tan δ values did not show any difference in trend from that of the gum except that it gave a higher value at these strains. This trend also can be attributed to the hydrodynamic effects of the clay particles in the system. Because our study was confined to a maximum loading of 40 phr of clay, highly loaded systems were not analyzed.

3.2.4 EFFECT OF STRAIN ON LOSS MODULUS, E''

The effect of strain on loss modulus, E'', values for carbon black and clay filled vulcanizates is shown in Figure 8. As observed the E'' values pass through a maximum at intermediate values of strain where there is a sharp drop in E' values. The maxima in E'' values increased with an increase in filler loading. However, this phenomenon is not observed in the case of clay filled vulcanizates, which emphasizes the fact that in clay filled vulcanizates there is no secondary structure that undergoes breakdown and reformation on the application of small strain, which—on the other hand—can result in a higher hysteresis at intermediate strain amplitudes.

3.2.5 EFFECT OF HIGH TEMPERATURE AND STRAIN ON STORAGE MODULUS, LOSS MODULUS AND THE LOSS ANGLE TAN δ

Room temperature to high temperature studies on the vulcanizate containing 50 phr ISAF for 0.7% strain and 5% strain are shown in Figure 9. At 0.7% strain a sharp drop in tan δ and loss modulus values above 100°C is observed. Whereas, at 5% strain tan δ and E'' values showed a gradual but slow decrease in values. At a lower strain the already existing three dimensional structure of carbon black causes the structure breakdown. As observed in the case of isothermal studies carbon black structure breakdown is almost complete and at the higher temperatures the application of a further higher strain results in molecular chain breakdown. The broken chain ends result in a higher hysteresis and hence a higher value for tan δ and E''. At 0.7% strain since there is no significant molecular chain breakdown higher temperature results in a higher chain mobility and a lower friction between the molecular chains. The sharp drop in the value tan δ is due to the structure breakdown of carbon black agglomerates under temperature and strain.

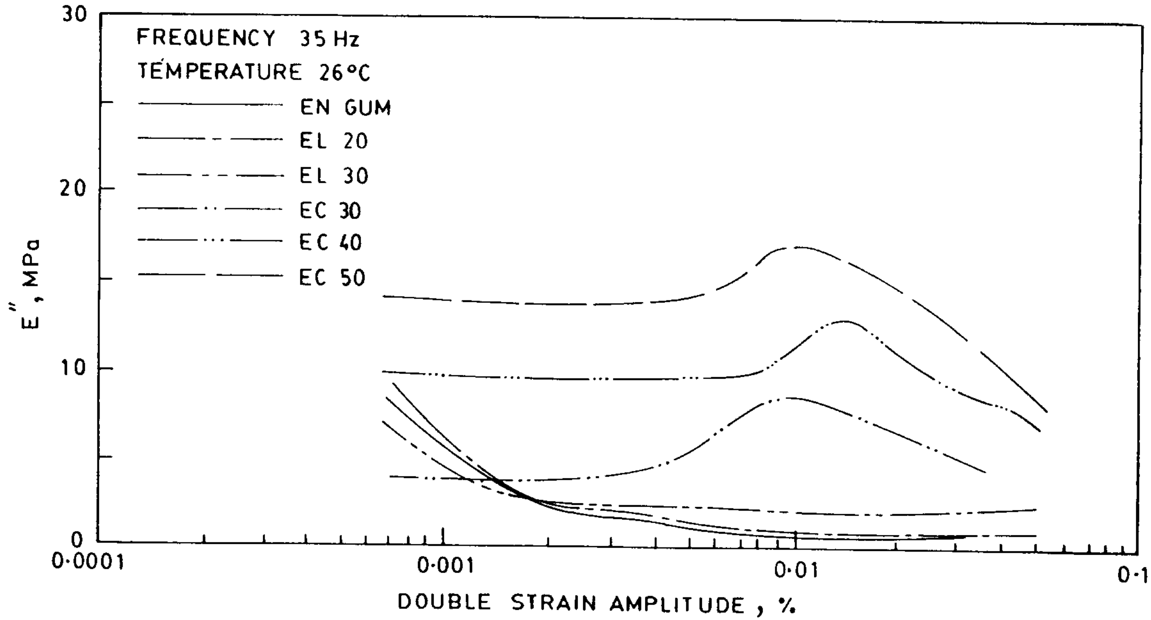

FIGURE 8. Strain amplitude dependence of loss modulus, E''.

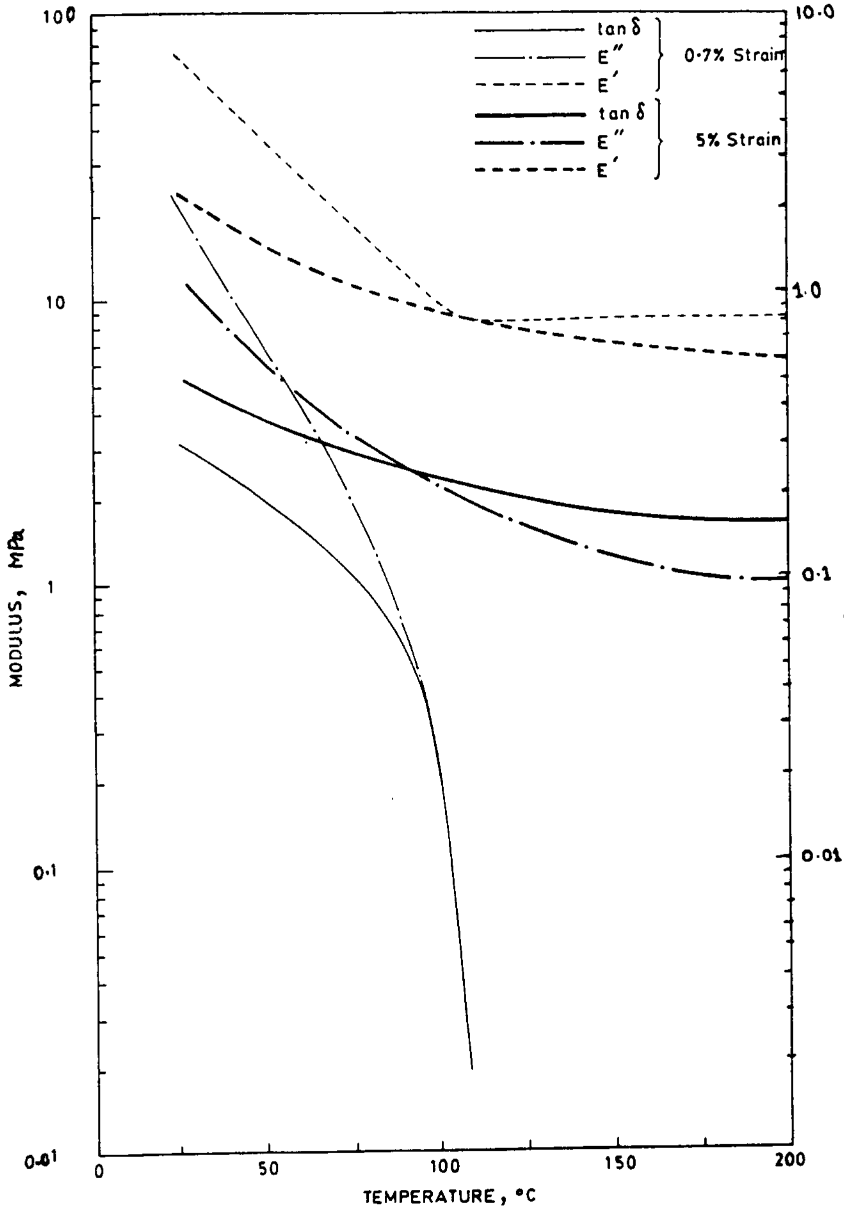

FIGURE 9. Effect of high temperature and strain on storage modulus, E', loss modulus, E'' and loss tangent, tan δ of vulcanizate EC50.

4.0 CONCLUSIONS

From the foregoing investigation it is found that clay filled vulcanizates have not shown any shift in the glass transition temperature, indicating the absence of an adsorption-desorption mechanism operating on the clay surface as existing in the case of carbon black filled vulcanizates. Isothermal studies further indicated the absence of a three-dimensional agglomerate structure in the case of clay. The dewetting and non-reinforcing nature of clay in ENR may also be determined from the physical property studies.

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