Effect of Plasticizer Type and Concentration on the Dynamic Mechanical Properties of Epoxidized Natural Rubber Vulcanizates

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ABSTRACT: The low temperature and isothermal dynamic mechanical properties for different plasticizers like aromatic oil, paraffinic oil, and di-octyl phthalate (DOP) in epoxidized natural rubber (ENR) vulcanizates were studied. 10, 20, and 40 phr of aromatic oil were used for studying the effect of plasticizer concentration on the above mentioned properties. Though the low temperature flexibility was equally improved by all the three types of plasticizers, the addition of paraffinic oil was found to be more effective in ENR. Increasing concentration of aromatic oil in ENR showed that the T_g values are decreased and the low temperature flexibility increased.

1. INTRODUCTION

THE RIGIDITY OF an unplasticized polymeric mass is caused by an internal three-dimensional honeycomb or gel structure formed by contacts between polymer molecules at various points along the chains. Plasticization reduces the relative number of polymer-polymer contacts thereby decreasing the rigidity of the three-dimensional structure and allowing deformation without rupture. Efficiency of the plasticizer depends on the strength of the intermolecular attractions between the

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polymer molecules and the mobility of the plasticizer [1]. There are many pioneering works in the field of plasticization of polymers–especially plastics–due to its wide importance in the processing of plastics. In the rubber industry too, plasticizers are important, as far as processing and low temperature applications are concerned. The effect of incorporation of plasticizers into elastomers on the physical and dynamic mechanical properties has been studied by a number of researchers [2–6]. However, the effect of plasticizer-polymer interaction varies from polymer to polymer and plasticizer to plasticizer. Therefore, great emphasis is placed on the analysis and selection of a suitable plasticizer system for each polymer. Since dynamic mechanical analysis and the behavior of the polymer in the glass transition region can provide a lot of information regarding the efficiency of a plasticizer, our present work puts emphasis on the dynamic mechanical aspects of the effect of different types of plasticizers such as aromatic and paraffinic oil and dioctyl phthalate (DOP). The effect of varying concentrations of aromatic oil in epoxidized natural rubber vulcanizates is also studied.

2. EXPERIMENTAL

50 mol % epoxidized natural rubber was used as the base polymer. Details of materials used in the study are given in Table 1. Formulations followed for studying the effects of different types of plasticizers are given in Table 2 and those used for studying plasticizer concentration effects are given in Table 3. In each case 60 phr of high reinforcing type carbon black (ISAF, N-220) was used. Mixing was done on a laboratory-size, two-roll mill (32.5 × 15.0 mm). Plasticizer addition was done carefully to avoid adsorption of the plasticizer to the filler surface. The mill temperature was kept about 60–70°C by cold water circulation. Rheometric characteristics were studied using a Monsanto Rheometer, R–100, and Mooney viscosity determinations were made on a Mooney Viscometer (Negretti Automation, UK). Samples were vulcanized at 150°C for their respective optimum cure times and conditioned for a minimum period of 48 hours before tests were done.

Samples for dynamic mechanical analysis were prepared to the dimensions 7 cm × 1 cm × 0.5 cm. Dynamic mechanical analysis was carried out on a dynamic viscoelastometer, Rheovibron model DDV-III-EP (Orientec Corporation, Japan). Low temperature tests were carried out from −100 to +250°C in a liquid nitrogen atmosphere at a heating rate of 2°C/min and at 35 Hz. Isothermal tests were carried out for different dynamic strains varying from 0.7×10^{-3} DSA (0.07% dynamic strain) to 50×10^{-3} DSA (5% dynamic strain) at 35 Hz. Double strain

Table 1. Details of materials used.

Material	Specifications/Details	Source
Epoxidised Natural Rubber (ENR)	50 mol % epoxidised Sp. gravity—1.03, glass—transition temperature— −20 ± 2°C, Mooney viscosity $ML_{(1+4)}$ 100°C − 96	Malaysian Rubber Producer's Research Association, Brickendonbary, U.K.
Carbon black	Intermediate super abrasion furnace black (ISAF), N-220 High structure density—1.83 g/cc	Phillips Carbon Black Limited, Durgapur
Aromatic oil	ASTM No. 3 grade density—0.8	Bharat Petroleum Corporation Ltd. Calcutta, India
Paraffinic oil	Density—0.83 g/cc	S. D. Fine Chemicals Ltd., Boisar, India
Di-octyl phthalate (DOP)	Denisty—0.985 g/cc	Ranbaxy Laboratories Limited, Punjab India

Table 2. Formulations followed for type of plasticizer studies.

Compound/Design	Type of Plasticizer	Amount in phr
PLZO	—	—
10 ARO	Aromatic oil	10.0
10 PAR	Paraffinic oil	10.0
10 DOP	Di-octyl phthalate	10.0

All formulatons contain:
ENR-50—100.0 phr; Na_2CO_3—0.3 phr; ZnO—5.0 phr; Stearic acid—2.0 phr; ISAF (N-220)—60.0 phr; IPPD—2.0 phr; CBS—1.5 phr and Sulfur—1.5 phr.

Table 3. Formulations followed for plasticizer concentration effect studies.

	PLZO	10 ARO	20 ARO	40 ARO
ENR-50	100.0	100.0	100.0	100.0
Na_2CO_3	0.3	0.3	0.3	0.3
ZnO	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
Carbon black ISAF (N-220)	60.0	60.0	60.0	60.0
Aromatic oil	—	10.0	20.0	40.0
IPPD	2.0	2.0	2.0	2.0
CBS	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5

amplitude (DSA) refers to the ratio of displacement amplitude (ΔL) of the sample to the length of the sample (L) :– ($2\Delta L/L$). Tests were carried out first at the lowest available strain and later the strain was increased stepwise to the maximum [7]. Tests for each sample were carried out in triplicate to ensure consistency in the results.

3. RESULTS AND DISCUSSIONS

3.1 Effect of Type of Plasticizer

3.1.1 EFFECT OF TEMPERATURE ON STORAGE MODULUS AND THE LOSS TANGENT

Figure 1a depicts the effect of type of plasticizer on the storage modulus, E' values as a function of temperature. A mix without any plasticizer is also shown for comparison. From the tests, it is clear that the addition of all three types of plasticizers has more or less the same effect on the E' values. The addition of 10 phr of paraffinic or aromatic oils or DOP shifted the E' curve to a lower temperature range irrespective of the nature of the oil. The temperature at which the E' values reach 69 MPa is generally considered as the mark of low temperature flexibility for polymers [4,8]. In this case the addition of any of these three plasticizers shifted the low temperature flexibility values by about 37 °C, indicating a high effectiveness of the plasticizer in the ENR matrix. The slight variations observed in the E' values depending on the type of plasticizer are not considerable. Figure 1b shows the effect of different types of plasticizers on the loss tangent or the damping peak, tanδ, as a function of temperature. From Figure 1b, it can be seen that the addition of plasticizers shifts the glass-transition temperature, T_g, to lower temperatures, and the effect is more pronounced with

10 phr paraffinic oil (Table 4). Efficiency of a plasticizer can be partially accounted for in the efficiency with which it shifts the T_g to a lower temperature and increases the tanδ peak height value. This effect was attributed to the free volume increase on the incorporation of a light molecular component to the polymer phase [9,10]. From the curves of Figure 1b, it is observed at the glass-transition temperature that there is a small increase in the $\tan\delta_{max}$ in the case of 10 DOP. All three compounds showed a decrease in the tanδ values at higher temperatures compared to OPLZ. This may be indicating that just after the commencement of the rubbery plateau, the chain flexibility of the macromolecules is enhanced by the presence of plasticizers. At still higher

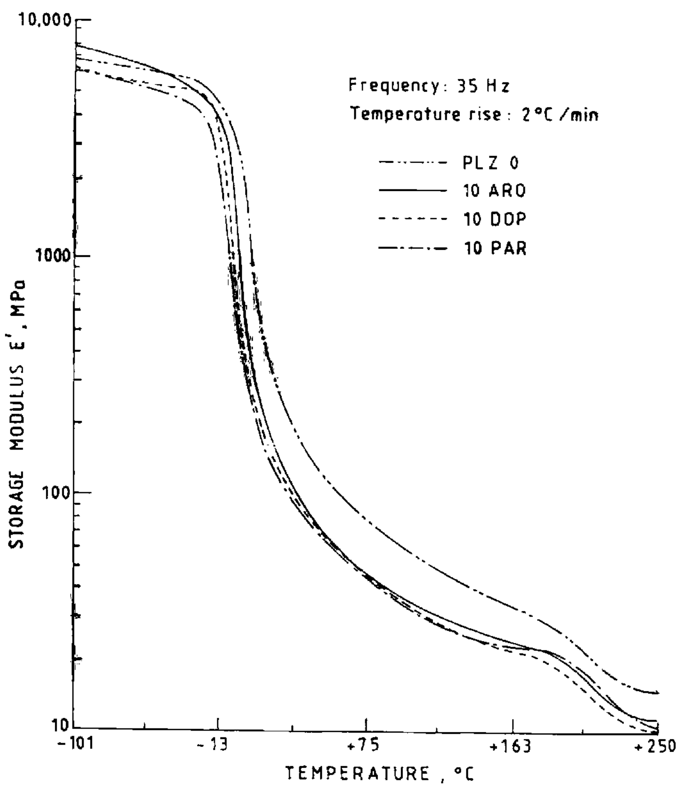

FIGURE 1a. Elastic modulus, E', vs. temperature plots–effect of different types of plasticizers in ENR vulcanizates.

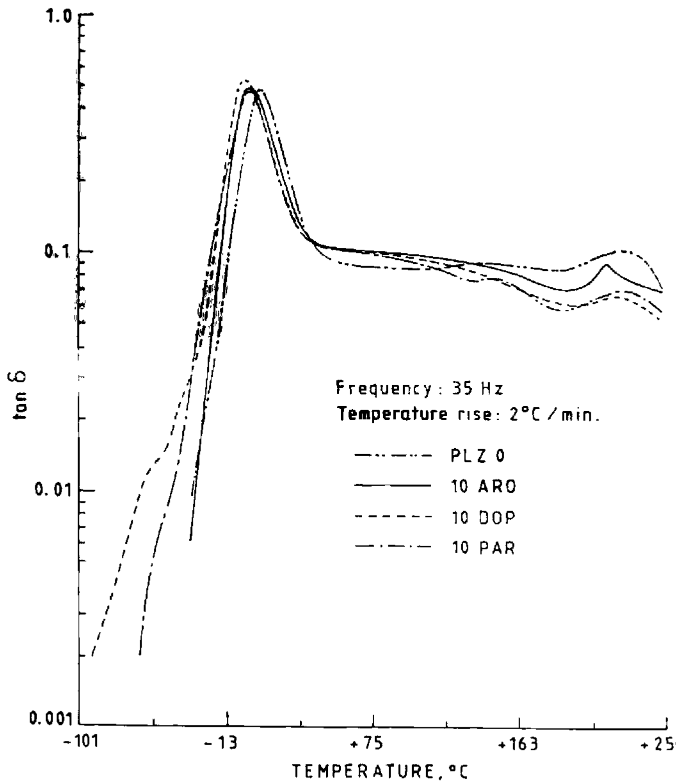

FIGURE 1b. Loss tangent, tanδ, vs. temperature plots–effect of different plasticizers in ENR vulcanizates.

temperatures, the tendency for plasticizers to vaporize increases and will result in a higher rigidity in the polymer matrix, thus reducing the tanδ to lower values compared to the unplasticized system. The heat stability of these systems at higher temperatures is decreased by the presence of plasticizer.

3.1.2 EFFECT ON ISOTHERMAL DYNAMIC MECHANICAL PROPERTIES

Figures 2 and 3 depict the effect of varying strain on the storage modulus, E'; loss modulus, E'' and the phase angle; respectively, for the three different plasticizer systems. Compared to the temperature dependent tests, the variable strain tests show a marked influence of the effect of type of plasticizer on the dynamic mechanical properties. Considering Figure 2, it can be seen that all the three plasticizers fol-

Table 4. Effect of plasticizer type on the glass-transition temperature, T_g and the tan δ_{max} values.

Mix Designation	T_g (°C)	tan δ_{max}
PLZO	+ 7	0.503
10 ARO	+ 2	0.497
10 PAR	− 3	0.486
10 DOP	− 2	0.550

low the characteristic sigmoidal shape of the E' curve. In addition, compared to the unplasticized system, the E' values are lower throughout the test strains range for all three plasticized systems. In the case of vulcanizate 10 ARO, the E' values were higher than the DOP and paraffinic oil mixes, which followed very similar trends in the case of the E' curve. This result may indicate that a higher strain energy is required to break down the agglomerate structure when aromatic oil is used. Figure 3a indicates the carbon black structure breakdown and reformation taking place at low and intermediate strain ranges [14]. The E'' curves show that the agglomerate structure which breaks down on the application of small sinusoidal strains are considerably reduced

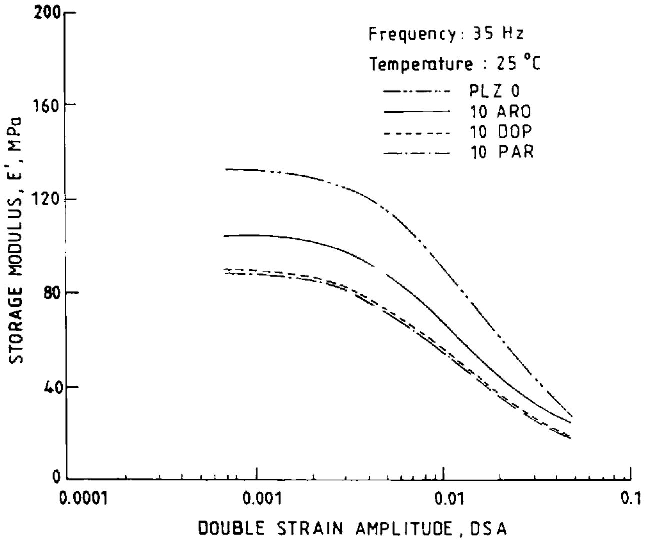

FIGURE 2. Elastic modulus, E', vs. strain amplitude plots of ENR vulcanizates–effect of type of plasticizer.

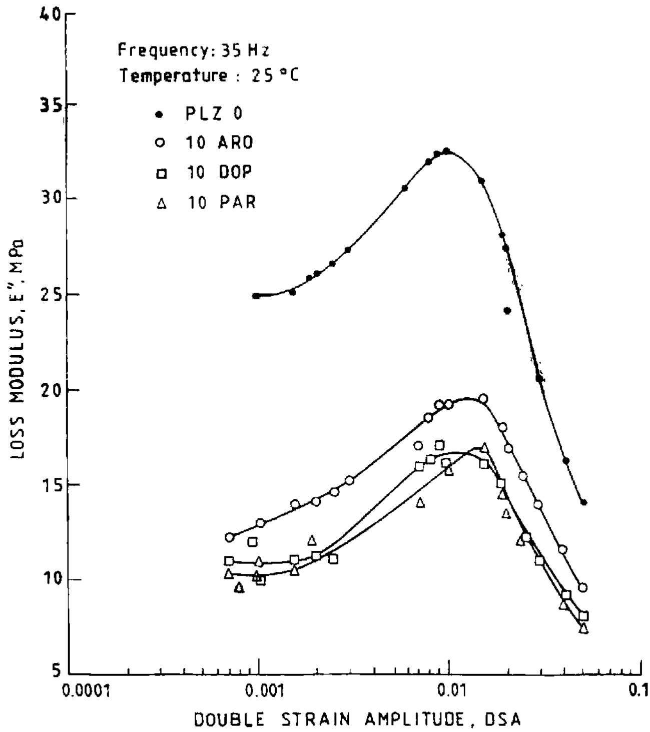

FIGURE 3a. Loss modulus, E'', vs. strain amplitude plots of ENR vulcanizates—effect of type of plasticizer.

on the addition of plasticizers. The difference among the plasticizers is observed in the medium strain application range, where considerable structure breakdown and reformation are taking place. Here, it may be noted that the maximum of agglomerate structure breakdown and reformations are taking place at a lower strain value in the case of unplasticized vulcanizate. Compounds 10 DOP, 10 PAR and 10 ARO required increasing strain energies to reach this peak E'' value. This variation observed among different plasticizer systems may be attributed to the specific interaction of each plasticizer with the filler. The phase angle value, δ, is shown as a function of DSA in Figure 3b. The polymer-filler friction, which contributes to the loss tangent values, can be observed in these curves. 10 DOP forms the lower bottom line and 10 ARO the top line of the phase angle vs. DSA spectra. However, 10 DOP changes this trend at higher strain. This indicates a higher plasticizer efficiency through a reduction in the interchain and filler-rubber friction in the case of the 10 DOP system than 10 ARO and 10 PAR until the DSA reaches 2%.

3.2 Effect of Plasticizer Concentration

3.2.1 EFFECT OF TEMPERATURE ON THE ELASTIC MODULUS AND THE LOSS TANGENT VALUES

Plasticizer concentration effects were studied using 10, 20 and 40 phr of aromatic oil for the 60 phr of ISAF black loaded vulcanizates. Figure 4 shows the effect of different loadings of aromatic oil on the elastic modulus, E', and loss tangent, $\tan\delta$, of the ENR vulcanizates as a function of temperature at 35 Hz. For comparison, an unplasticized system is also given. Previous studies on the plasticizer concentration effect on the bromobutyl rubber vulcanizates showed that at concentrations up to 10 phr of plasticizer the effect on the low temperature properties was negligible [4]. However, in the case of ENR, we have observed that the addition of plasticizer affects the low temperature dynamic mechanical

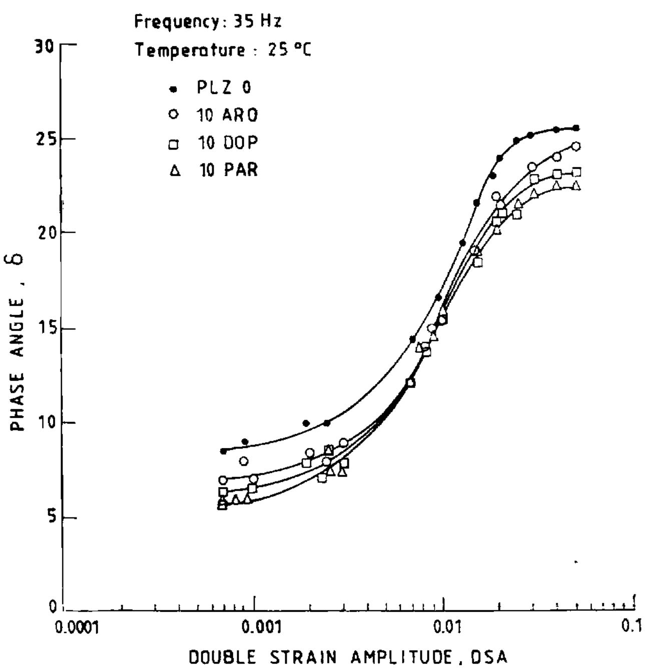

FIGURE 3b. Loss angle, δ, vs. strain amplitude plots of ENR vulcanizates–effect of type of plasticizer.

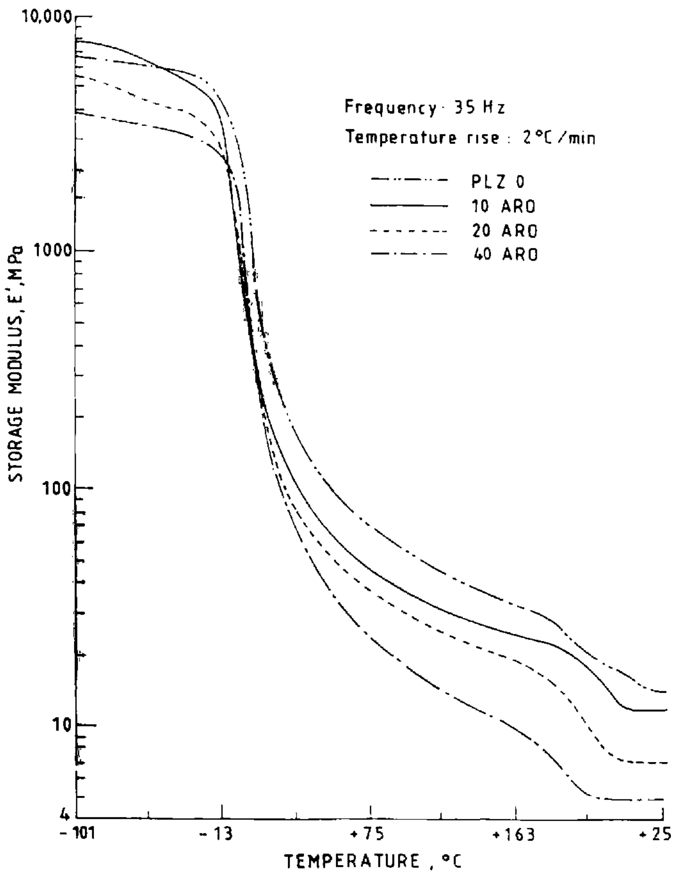

FIGURE 4a. Elastic modulus, E', vs. temperature plots of ENR—effect of plasticizer concentration.

properties irrespective of the type of plasticizer. With increasing concentration of aromatic oil an improvement in the low temperature flexibility of the vulcanizate is observed (Table 5). Loss tangent peak height increased with increasing plasticizer concentration (Figure 4b) substantiating the fact that low molecular weight plasticizers increase the total free volume of the system [4]. In the rubbery region, the effect of plasticizer concentration becomes more prominent. The heat stability of the compound is considerably reduced at higher plasticizer concentrations as can be seen from the E' and $\tan\delta$ curves. The $\tan\delta$ and E' values show a sudden drop in the high temperature range.

3.2.2 ISOTHERMAL DYNAMIC MECHANICAL PROPERTIES

Figure 5 shows the effect of application of sinusoidal strain on the dynamic mechanical properties, E', E'' and phase angle, respectively, of the ENR vulcanizates with varying plasticizer concentration. Like plasticizer type, plasticizer concentration also has a profound influence on the isothermal dynamic mechanical properties. Figure 5a shows that with increasing plasticizer concentration, there is a considerable reduction in the E' values throughout the test strain range. The typical sigmoidal shape of the curve in the case of carbon black filled vulcanizates is retained irrespective of the plasticizer concentration. This may indicate that increased plasticizer concentration prevents the carbon black particles from forming on agglomerate structure of high

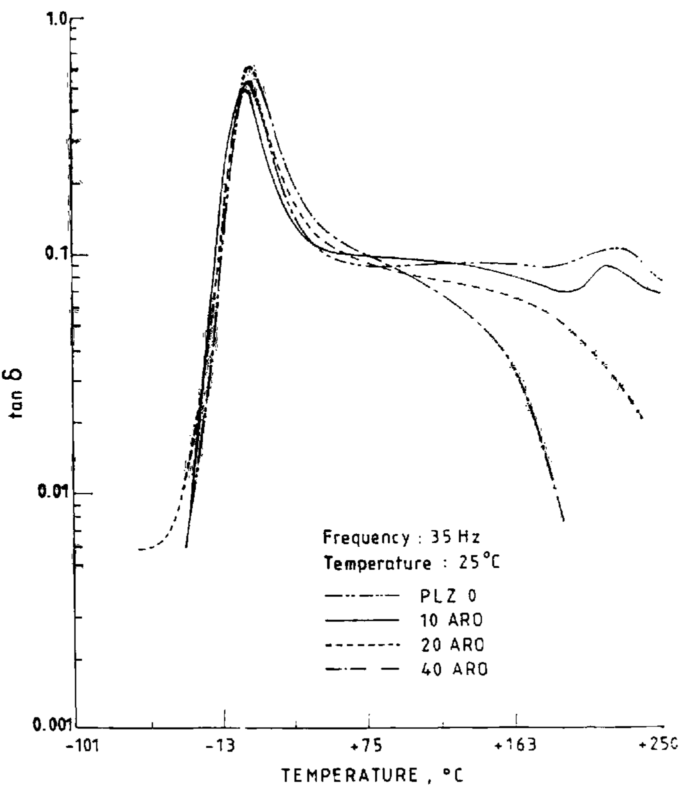

FIGURE 4b. Loss tangent, tanδ, vs. temperature plots of ENR–effect of plasticizer concentration.

Table 5. Effect of aromatic oil concentration on the low temperature flexibility of ENR vulcanizates.

Compound Designation	Temperature at which E' = 69 MPa, °C
PLZO	77
10 ARO	51
20 ARO	40
40 ARO	33

order which would have resulted in higher E' values at the lower strain ranges [11–13]. Figure 5b shows the effect of varying strain application on the loss modulus, E' values. Plasticizer concentration is found to be significant only in the intermediate strain region. At low and high strain values the addition of 10, 20 and 40 phr of aromatic oil does not influence the E'' values significantly. Hysteresis which results from the breakdown and reformation of the black agglomerates is maximum in the intermediate strain range [14]. This hysteresis results in a peak value in the E'' curve. The E'' values decrease with increasing plasticizer concentration. The E'' peak position shifted to a higher strain range with increasing oil concentration. At higher plasticizer concentrations the agglomerating tendency of the carbon black is considerably reduced and hence, it may require a higher span of time for the structure to break down and then reforms in the plasticized state. Figure 5c shows the effect of strain on the phase angle values. Unlike the earlier researcher's reports [5], we have observed changes in the values at the lower strain ranges also. The phase angle values did not show any particular trend with increasing plasticizer concentration. Though the unplasticized vulcanizate reaches a plateau region at the highest applied strain ranges, the plasticized systems showed a continuous increase in the phase angle values with increasing strain. The anomaly showed by the PLZO vulcanizate in Figure 5c may be due to the inhomogeneous mixing of the filler in the absence of any plasticizer. The higher values of δ observed in the case of highly plasticized systems may be due to higher agglomerate structure breakdown that results from loose structure formations of carbon black in the presence of higher plasticizer concentrations. On the other hand, high concentrations of plasticizer may be resulting in feeble inter-aggregate contacts. As observed in the case of the E'' values, the compounds 20 ARO and 40 ARO require a higher strain for maximum filler agglomerate structure breakdown-reformation process, as it registers a higher δ value at higher DSA.

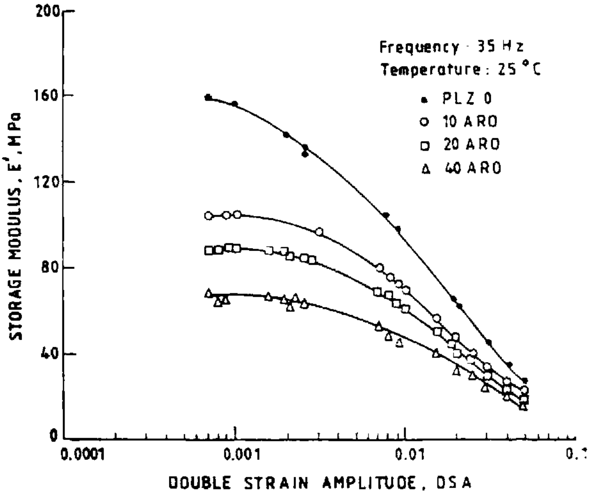

FIGURE 5a. Elastic modulus, E', of ENR vulcanizates—effect of plasticizer concentration.

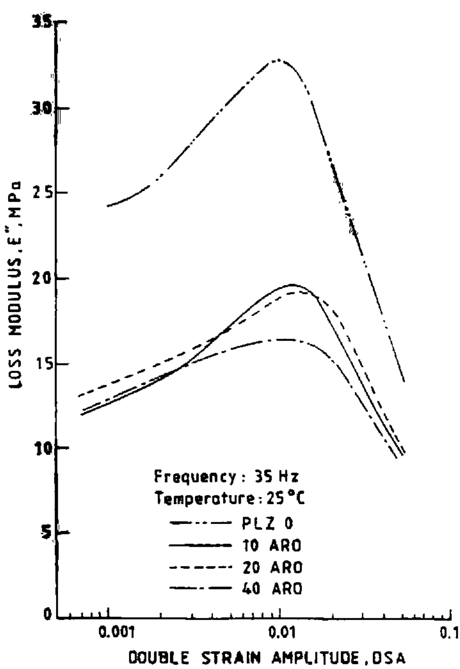

FIGURE 5b. Loss modulus, E'', of ENR vulcanizates—effect of plasticizer concentration.

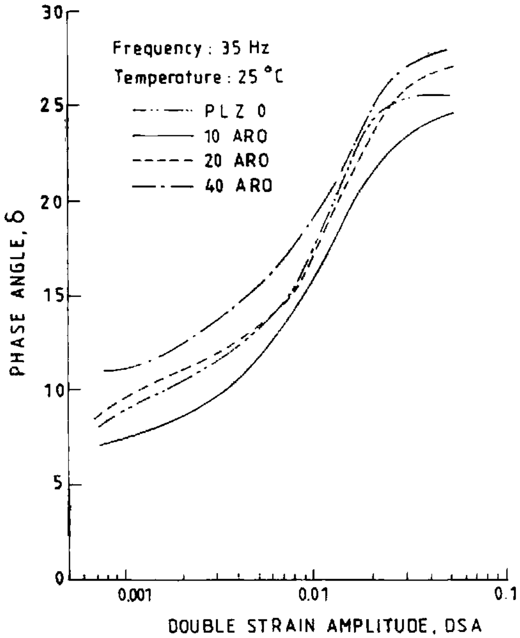

FIGURE 5c. Loss angle, δ, of ENR vulcanizates–effect of plasticizer concentration.

4. SUMMARY AND CONCLUSIONS

Studies carried out using three types of plasticizers (DOP, paraffinic oil and aromatic oil) showed that the temperature dependent and low strain dependent dynamic mechanical properties are affected by the type of plasticizer used. Low temperature flexibility was equally improved by all the three types of plasticizers, whereas the T_g values were shifted to a slightly lower temperature, particularly with the paraffinic oil. Isothermal studies also showed that the addition of paraffinic oil and DOP could be more effective than aromatic oil in the ENR vulcanizates.

T_g values were decreased and the loss tangent peak height increased with increase in aromatic oil concentration. Low temperature flexibility increased with increasing aromatic oil concentration. In the case of the unplasticized system, the non-homogeneity of the compound resulted in fluctuations in E'' and tanδ values. However, isothermal dynamic mechanical properties showed that higher time is required for the three-dimensional agglomerate structure breakdown-reformation process with increasing plasticizer concentration.

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