Separability Behavior in Viscoelastic Properties of EPDM Gum Vulcanizate

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SYNOPSIS

Dynamic mechanical properties of EPDM gum vulcanizates were studied using the dynamic viscoelastometer, Rheovibron. A small sinusoidal strain was superimposed on a static strain and its effect on dynamic mechanical properties were analyzed. The results are discussed in terms of total strain which takes the static strain into account. Separability of time and strain effects for loss modulus and the nonseparability for storage modulus are discussed. A critical strain was identified after which the stress dissipation mechanism changes.

INTRODUCTION

Viscoelastic properties of elastomers are functions of frequency and dynamic strain amplitude. The effect of dynamic strain amplitude on storage modulus, loss modulus, and tan δ has been subjected to extensive study. Studies on gum vulcanizates have shown that the dynamic properties are influenced very little by the variation of dynamic strain.[1,2] In the case of filled vulcanizates, dynamic strain has a pronounced effect on the dynamic mechanical properties.[3-9] This effect depends on the type and amount of filler added. Many workers have studied the effect of small sinusoidal oscillations superimposed on large, statically relaxed strain.[10-15] Although initial studies using wave propagation techniques[16,17] were confined to low dynamic strain amplitude and high frequency domain (1000 Hz), the increased refinement of forced nonresonant servohydraulic testing machines has permitted the investigation of dynamic mechanical properties of prestrained elastomers in the frequency and amplitude ranges more typical of conditions encountered in many engineering applications of elastomers (strain amplitudes from 0.005 to 0.05 and frequencies from 0.05 to 1000 Hz). Rheovibron is an excellent development in the latter category. Despite the instrumental limitations,[18,19] simplicity associated with its operations has led to a host of experimental studies using this instrument.[20-27]

The dynamic viscoelastometer, Rheovibron DDV III EP, was used to study the effect of dynamic and static strains on dynamic mechanical properties. Work on the filled EPDM vulcanizates had shown that the measured properties were largely dependent on the dynamic displacement amplitude.[28] It had also been shown that for filled EPDM vulcanizate the storage modulus was a separable function of time and strain effects whereas, the loss modulus was not.[28] In this article, the effect of static strain on the dynamic mechanical properties of EPDM gum vulcanizate is reported. The separability behavior is also discussed.

EXPERIMENTAL

Materials

EPDM, Nordel 1660 was manufactured by Du Pont, (U.S.A.) and supplied by Andrew Yule, Kalyani, W. Bengal, India. Mooney viscosity ML 1 + 4 (100°C) = 60, specific gravity = 0.86. Sulfur: specific gravity = 1.92. All rubber accelerators were supplied by IEL, Rishra, India. The compound formulation used was: EPDM, 100; ZnO, 5; stearic acid, 1; *N*-cyclohexyl-

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benzothiazole 2-sulphenamide, 1.5; tetramethylthiuram disulfide, 1.

Mixing

Mixing was done in a laboratory type two roll mixing mill (Schwabenthan, roll size 33 × 15.25 cm). Temperature of the roll was controlled by circulating water through the rolls. The test pieces were molded in strip form of approximate dimensions 0.5 × 0.3 × 10 cm in an electrically heated hydraulic press at 160°C for 8 min.

Testing

Dynamic tests were carried out using the Rheovibron DDV III EP in the tension mode.[29] The test piece was first fixed in the clamps and the instrument was balanced.[29] The test piece was then stretched to a calculated length and clamped in that position. The instrument was set in manual mode. Displacement amplitudes were then changed in an increasing order. The test results at 3.5-Hz frequency are reported.

RESULTS AND DISCUSSION

Storage modulus is usually represented as a plot of E' against double strain amplitude. Double strain amplitude (DSA) is defined as

$$\text{DSA} = 2 \times \text{displacement amplitude} / \text{length of test piece.}$$

When the material under testing was not subjected to any static deformation, the response is simple and the plot of E' against DSA remains as a straight line parallel to the DSA axis. In the case of unfilled EPDM vulcanizate, a similar trend was reported.[9] In the above case the results may be satisfactorily interpreted on the basis of existing theories. As seen in Figure 1, application of a finite static strain changes the response pattern (different symbols represent different displacement amplitudes). After a certain value of dynamic strain, there was a sudden decrease in the dynamic modulus. This strain depended on the individual displacement amplitude. This pattern could not be satisfactorily interpreted. Hence DSA alone could not be taken as a measure of strain while analyzing the dynamic mechanical

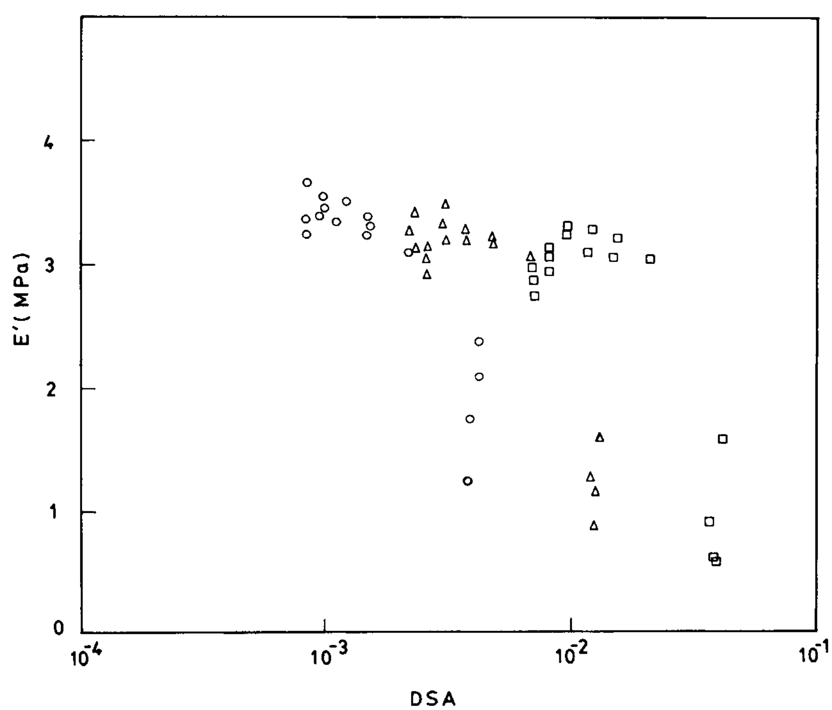

Figure 1 Semi-log plot of E against double strain amplitude (DSA) for EPDM gum vulcanizates. (⊙) Corresponds to displacement amplitude 0.0025 cm; (△) corresponds to 0.008 cm; (□) corresponds to 0.025 cm.

properties of strained vulcanizates. We therefore define total strain, ε as

$$\varepsilon = (L_2 - L_1 + A)/L1$$

where L_1 = initial length of test piece between clamps, L_2 = final length, and A = displacement amplitude, 0.0025 cm (L), 0.008 cm (M), 0.025 cm (H).

Representations on the basis of total strain (which differs from static strain by a small fraction when the strain is low) is given in Figure 2. This showed that up to a certain static strain the measured modulus remained constant (straight line portion) and thereafter decreased (after $\lambda = 1.2$, where λ, the extension ratio $= L_2/L_1$). Results were verified up to 90% static strain. Even though a drastic decrease of G' was shown to occur in the case of filled vulcanizate with an increase in static strain, there was only a minor decrease in the case of gum vulcanizates up to 40% static strain.[13] Calculating the engineering stress (based on the undeformed area of cross section) corresponding to the straight line range in Figure 2, it was found that the stress increased with increase in strain (Fig. 3). After the maximum, the incremental stress decreased drastically (not shown in Fig. 3) corresponding to the drop in modulus (Fig. 2). It was observed that the same test piece regained the original modulus when sufficient time was given for relaxation (24 h was found to be sufficient). From Figure 3 it was seen that if tangents were drawn to different regions of the curves, the points of intersection of these tangents lie on a vertical line. This showed a possible change in the molecular mechanisms of stress dissipation after a strain of 3.4%, irrespective of the displacement amplitude. It is also to be noted that at a particular static strain the stress almost doubles as the displacement amplitude increases. From this observation it may be presumed that the stress response at lower strains must be due to chemical cross-links, entanglements, and junction points; whereas, as the strain increases this becomes largely a contribution of chemical cross-links alone. A higher entanglement and junction slippage may be the reason for the sudden fall in the incremental stress.

Mechanical phase angle depends on the static strain and the displacement amplitude (and hence on the total strain) as shown in Figures 4 and 5. It was seen that (Fig. 4) phase angle also did not show any correlation with DSA. The scatter was also high. When plotted as a function of total strain (Fig. 5) the phase angles corresponding to individual dis-

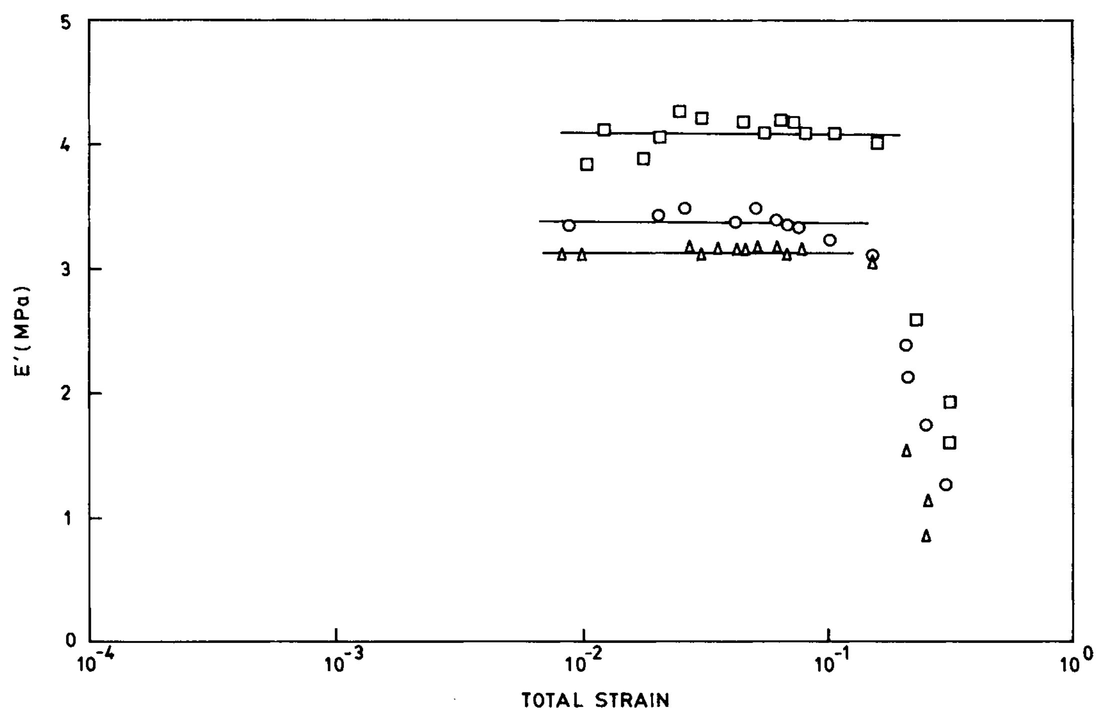

Figure 2 Semi-log plot of E' against total strain for EPDM gum vulcanizate. (-□-) Shifted by +1 MPa for the sake of clarity. See Figure 1 for other symbols.

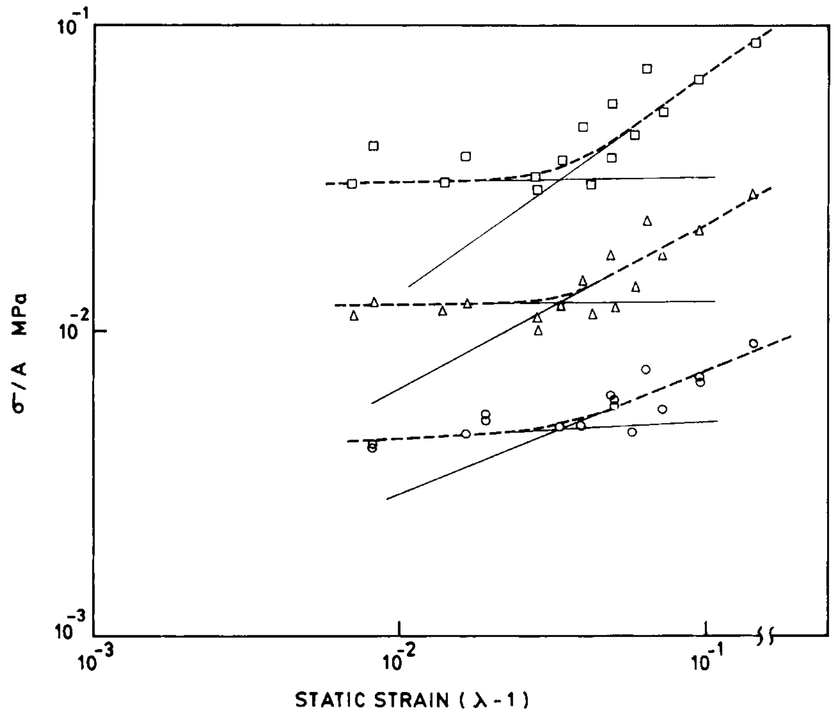

Figure 3 Log–log plot of σ/A against static strain ($\lambda - 1$). $A = 3.16$ is the instrument constant. See Figure 1 for other symbols.

placement amplitudes fell on separate curves. In Figure 5, points corresponding to a displacement amplitude of 0.008 cm were shifted by an arbitrary unit for the sake of clarity. As the strain increased, the mechanical phase angle decreased showing lower incremental energy loss. This again made the assumption stronger that at higher strains entanglements and junctions did not contribute to the vis-

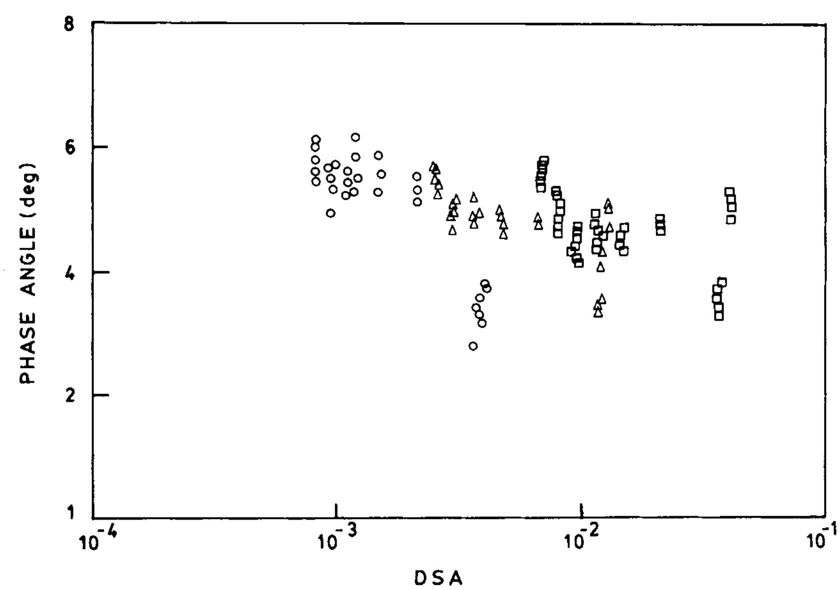

Figure 4 Semi-log plot of phase angle as a function of DSA. See Figure 1 for other symbols.

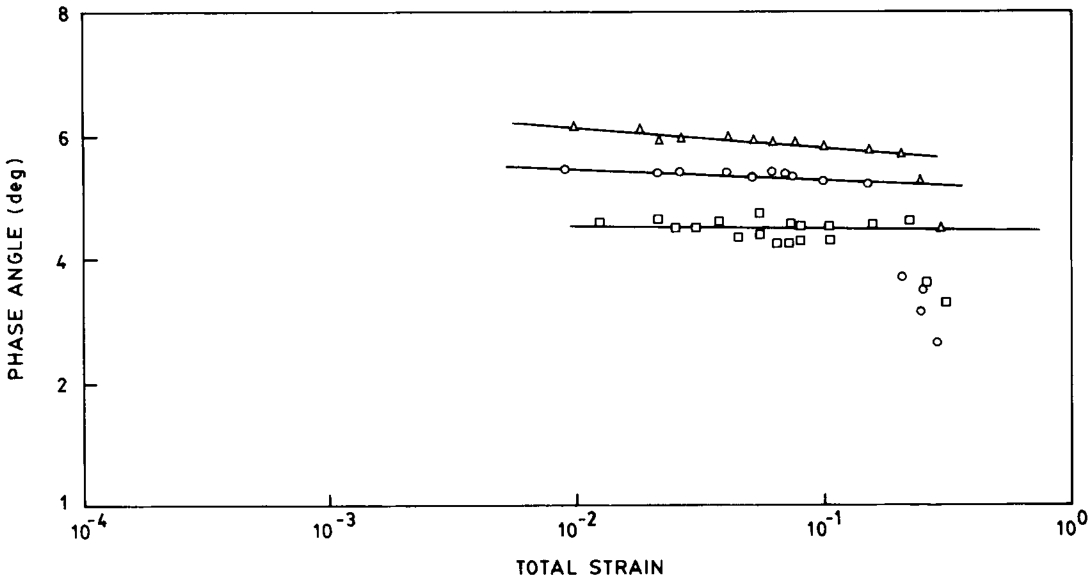

Figure 5 Semi-log plot of phase angle as a function of total strain. (- △ -) is shifted by +1. See Figure 1 for other symbols.

coelastic properties compared to the chemical crosslinks. Because the entanglements and junctions were associated with energy dissipation, their contribution would be higher toward tan δ.

From the above discussion it was logical that E'' should follow a trend as shown in Figures 6 and 7. Here also the displacement amplitude dependence of the test results was evident. All the above discussions show that when a small sinusoidal strain is superimposed on static strain, the viscoelastic functions become complex and hence proper care should be taken in selecting the strain measures.

In order to evaluate the theory of entanglement slippage and junction dislocation, the test up to 90% static strain was carried out on a test piece of 1-cm length. The test piece was stepwise strained from 40 to 90% (total test duration was 70 min). After the test, it was then brought back to a stress-free

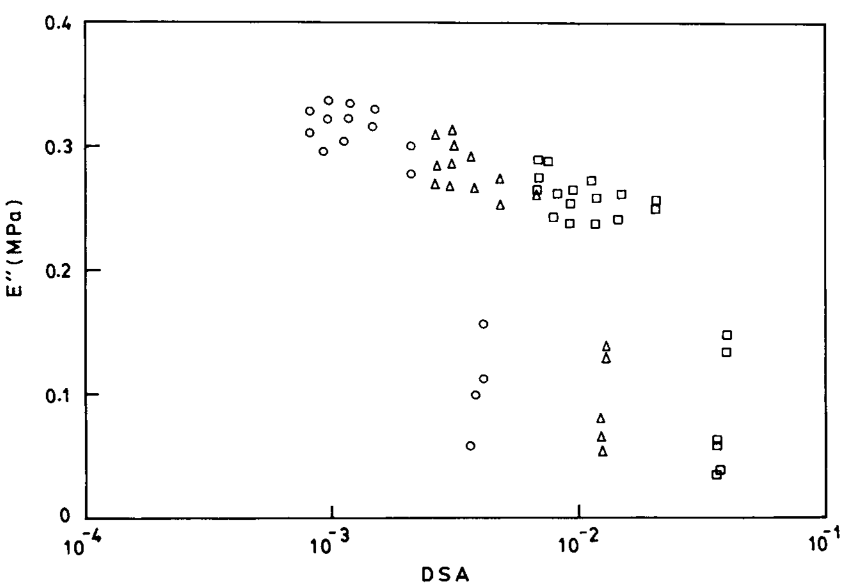

Figure 6 Semi-log plot of E'' as a function of DSA. See Figure 1 for other symbols.

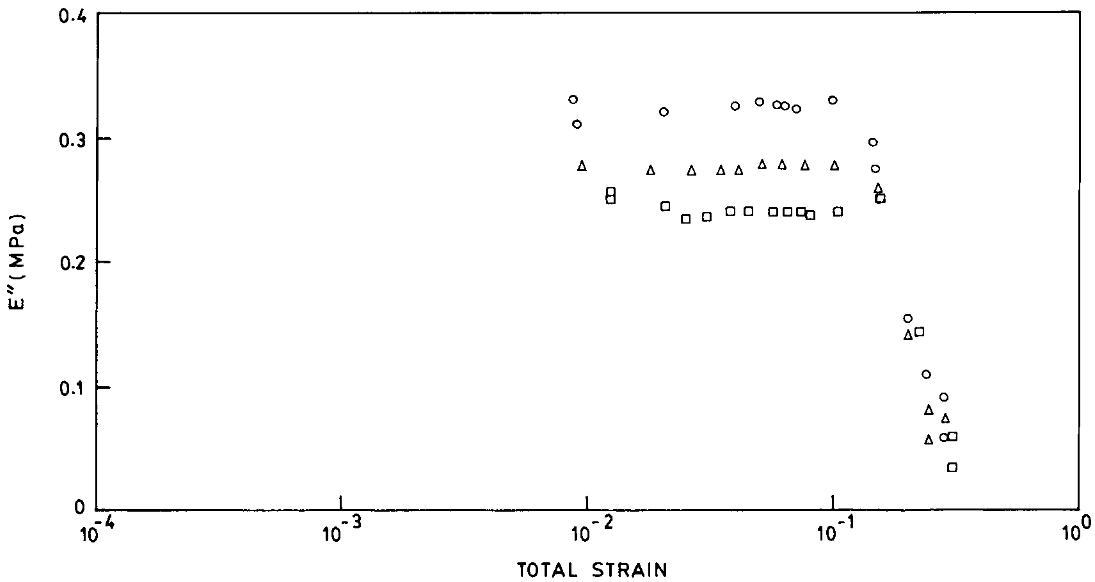

Figure 7 Semi-log plot of E'' as a function of total strain. See Figure 1 for other symbols.

state, making use of the instrument's stress dial to monitor the stress. A tension set of 9.4% was observed (calculated on the original length). This showed a complex modulus of 2.2 MPa and tan δ of 0.06 at 3.5 Hz and displacement amplitude 0.0025 cm. Under identical conditions of test piece dimensions, displacement amplitude, and frequency, an unstrained material showed a complex modulus 2.84 MPa and tan δ 0.095. The above drop in tan δ and E^* for a strained material might be explained as due

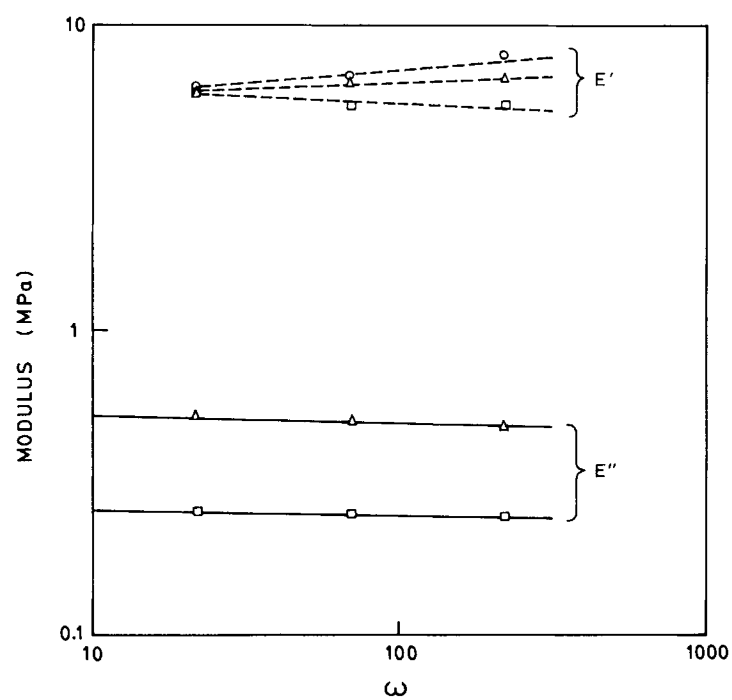

Figure 8 Log–log plot of E' and E'' as functions of angular frequency. In the case of E'', the lines are shifted by arbitrary units for the sake of clarity. See Figure 1 for other symbols.

to the presence of a lesser number of entanglements and junction points.

Storage modulus function for a filled vulcanizate of EPDM was shown to be a separable function of time and strain effects whereas the loss modulus was shown as a nonseparable function.[28] In this study we look into the separability aspect by plotting E' as a function of $\omega = 2\pi\nu$, where ω = the radial frequency and ν = the linear frequency. Straight line relation was observed in the tested range (Fig. 8) that is, $E' = A\nu + B$. This relation is similar to that given by Sullivan[30] except that the index m is equal to unity. The values of A and B were strain dependent and hence the straight line for different strains (shown by different symbols) were not parallel to each other. Thus the storage modulus function was not a separable function of time and strain effects and the elastic and relaxational components had different deformational dependence. Loss modulus as a function of frequency (Fig. 8) also showed a straight line relationship. The different lines corresponding to different deformational amplitudes (different strains) were parallel to each other. Hence, the loss modulus function was a separable function of time and strain effects.

CONCLUSIONS

Dynamic mechanical properties of EPDM gum vulcanizate were studied using the Rheovibron and the effect of superimposition of sinusoidal strain on static strain was analyzed. The properties showed a dependence on the displacement amplitude (under similar strain conditions) and the dependence became more prominent on the application of static strain. DSA was shown to be of little use in evaluating the results and a term total strain, which takes the static strain into account, was defined. The results showed that the storage modulus was a nonseparable function of time and strain effects whereas the loss modulus was shown to be a separable function. Results also showed that the molecular mechanisms responsible for stress dissipation changed after a critical strain of 3.4%, irrespective of the displacement amplitude.

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