

Static and Dynamic Strain-Dependent Viscoelastic Behavior of Black-Filled EPDM Vulcanizates

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SYNOPSIS

The strain dependence of the dynamic mechanical properties of HAF-N330-filled EPDM vulcanizate was studied using a Rheovibron DDV III EP. It is shown that when a dynamic strain is superposed on a static strain, the viscoelastic response of filled rubbers becomes more complex. Under these conditions, dynamic mechanical properties do not correlate with the double strain amplitude. A strain called the "total strain" has been defined in order to interpret the experimental results. It is also shown that the dynamic mechanical properties are displacement velocity dependent, while the comparison is made under identical conditions of strain and frequency. Separability of time and strain effects is observed for the storage modulus, whereas the loss modulus is shown to be a nonseparable function. The elastic and the relaxation components, constituting the mixed function representing the storage modulus are shown to have similar deformation dependence. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Technical properties of elastomers are greatly enhanced by the use of different compounding ingredients. Among these, fillers play a very significant role in imparting strength, resistance to tearing force, and higher modulus. Structured fillers, like reinforcing blacks and fumed silica, contribute to the viscoelastic properties of elastomers, and there exists no comprehensive theory that predicts their behavior. The magnitude of strain amplitude dependence of the storage modulus for elastomers filled with structured blacks is influenced by the carbon black type,¹⁻⁶ processing conditions,⁷⁻⁹ volume fraction of filler,¹⁰⁻¹² strain history,^{13,14} and vulcanizing systems and degree of crosslinking.^{15,16}

The effect of static strain with a superposed dynamic strain on the dynamic mechanical properties and the relaxation processes has been studied by many workers.¹⁷⁻²² Chang, Bloch, and Tschoegl²³⁻²⁶ have advanced a linear integral theory that characterizes quite successfully the viscoelastic behavior

of crosslinked and uncrosslinked styrene butadiene rubber (SBR) and uncrosslinked polyisobutylene. Their theory employs a generalized strain measure to account for the stress-strain nonlinearities and assumes that the relaxation spectrum is independent of the static strain.

Recently, a new theory called the generalized solid-liquid (GSL) model has been proposed to account for the nonseparability of time and strain effects for the storage modulus and separability for the loss modulus.^{27,28} These studies have been carried out at high static deformation of the test pieces. Despite the fact that the model applies only to unfilled vulcanizates, it has been used for the successful interpretation of results for filled butyl rubber vulcanizates. The success of the GSL model is attributed to the physical assumption intrinsic to the model; more specifically: (1) the relaxation spectrum is independent of the static strain and (2) the deformational dependences of the elastic and the relaxation contribution to the overall response of the system need not be the same.²⁸

Elastomeric mounts used in automobiles are mostly in the compression-shear mode. These mounts are subjected to a static load of the engine mass and a dynamic load due to the engine vibra-

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Table I Mix Formulation (Figures in Parts Per Hundred Parts of Rubber, phr)

Ingredient	phr
EPDM ^a	100
ZnO ^b	5
Stearic acid ^c	1
HAF N330 black ^d	60
Paraffinic oil ^e	5
Sulfur ^f	1
<i>N</i> -cyclohexylbenzothiazyl 2-sulfenamide ^g	1.5
Tetramethylthiuram disulfide ^h	1
Cured at 160°C, 8 min	
Apparent crosslink density ⁱ	2.2×10^{-4}

^a EPDM, Nordel 1660. Ethylene propylene diene monomer rubber manufactured by Du Pont, USA. Ethylene content 55% by weight. Third monomer: 1,4-hexadiene. Mooney viscosity ML 1 + 4 (120°C), 60; density, 0.86 g/cm³.

^b Specific gravity 5.5.

^c Stearic acid: rubber grade, supplied by Godrej India Ltd.

^d High-abrasion furnace black, Philips Carbon Black Ltd., Durgapur, W. B., India.

^e Highly saturated pharmaceutical grade, supplied by C. D. Pharmaceuticals, Calcutta, India.

^f Soluble sulfur; density, 2.05 g/cm³.

^g Rubber grade vulcanization accelerator, ICI, Rishra, W. B., India.

^h Rubber grade vulcanization accelerator, ICI, Rishra, W. B., India.

ⁱ Test pieces are undercured.¹⁶

tions. The static load varies depending on the vehicle acceleration and the road conditions, due to which the mounts may be compressed for a short period. During this period, the dynamic excitation may vary or remain the same, depending on the engine rpm, and hence the vibration isolation characteristics of the mounts also change. The effect of the variation of static and dynamic strain on the dynamic me-

chanical properties of black-filled ethylene-propylene diene monomer (EPDM) rubber vulcanizate is detailed in the present study. Dynamic strain may be applied in two different ways: (i) by keeping the test piece length constant and varying the dynamic displacement amplitude and (ii) by varying the test piece length for a fixed dynamic displacement amplitude. These two represent different strain histories. This aspect has also been emphasized in the present study.

EXPERIMENTAL

The compound formulation and the details of the materials are given in Table I.

Mixing

The compound mixing is carried out in a laboratory-type two-roll mill, the details of which are given in Table II.

Preparation of Test Pieces

Test pieces of approximate dimensions $0.5 \times 0.3 \times 10$ cm are molded in an electrically heated hydraulic press at 160°C for 8 min.

Testing

Dynamic tests were carried out using a Rheovibron DDV III EP in the extension mode. A detailed study of this instrument is presented elsewhere.²⁹ After fixing the test piece in the clamps, the instrument is adjusted for null stress on the specimen ("balanced"³⁰). The test piece is then stretched to a calculated length and clamped in that position. Instrument is set to the manual mode. The displace-

Table II Mixing Procedure^a

Time (min)	Process
0	Adjust the nip gap to 1.5–2 mm. Raw EPDM is milled and allowed to form a band
2	Add ZnO
3	Add the black part by part until incorporation is complete
8	Add oil and stearic acid
10	Add curatives
12	Sheet out
	Reduce the nip gap to 1 mm and refine the compound 5 times. Increase the nip gap to 3 mm and sheet out.

^a Batch temperature $\approx 80^\circ\text{C}$. Mill roll dimensions, 33×15.25 cm. Friction ratio, 1.08 (front roll rpm, 19.5; back roll rpm, 21).

ment amplitude is changed in an increasing order for a particular static strain. Table III shows the values of the static strain and the corresponding total strain (see, definition of terms). The results reported are at a frequency 3.5 Hz, if not specified otherwise.

Definition of Terms

Dynamic testing: Testing of mechanical properties under sinusoidal deformation of the test specimen.

Displacement amplitude, d_a : This is the maximum displacement of the servo-piston and is equal to the peak deformation of the test specimen. This has three discrete values: 0.0025, 0.008, and 0.025 cm, which are to be set on the instrument by pressing the corresponding knob.

Displacement velocity: This is the velocity of the servo-piston and is equal to the velocity with which a point mass in the immediate vicinity of the clamp moves. Mathematically, this is defined as $d_v = 4fd_a$, where f is the frequency in cycles/s (Hz).

Dynamic strain: This is the peak strain experienced by the test specimen during a dynamic half-cycle. Mathematically, this is defined as $d_s = d_a/L$, where L is the length of the test specimen between the clamps.

Double strain amplitude (DSA): This is a terminology introduced by Payne⁵ and is equal to the ratio of the peak-to-peak deformation of the test piece during a dynamic cycle to its length. This is defined as $DSA = 2 \times d_s$.

Total strain: This is an empirical term mathematically defined as

$$\epsilon = \frac{L_2 - L_1 + d_a}{L_2}$$

where L_1 is the length of the test piece between the clamps in the strain-free state and L_2 is the length

of the test piece between the clamps after the application of a static strain.

RESULTS AND DISCUSSION

The storage modulus of a test specimen, which is not subjected to static strain, is plotted as a function of double strain amplitude (Fig. 1). Phase angle also shows a similar trend (Fig. 2). Figure 3 shows the behavior of the loss modulus; x-marked points were at 11 Hz and a displacement velocity of 0.35 cm/s. The results show considerable influence of the displacement velocity. A similar phenomenon has also been observed in the case of gum vulcanizates.³¹

Effect of Static Strain

Depending on the strain, structural rearrangement of filler network, molecular chain rearrangement, and change in free volume can take place.³² The maximum strain used in this set of experiments is 30% and hence not much change in molecular orientation or free volume is expected to take place. This is evident from the values of the storage modulus (Fig. 4), which do not show any increase compared to that of the unstrained material ("unstrained" denotes the condition where a test piece is not subjected to any static strain before applying a dynamic strain). Earlier workers have reported an increase in the storage modulus with static strain.²⁸

Modulus values are reported after applying area correction using the equation $E_{\text{corrected}} = E_{\text{measured}} \times \lambda$ where λ is the final length/initial length, is the extension ratio. As seen in Figure 4 the values show high scatter when plotted as a function of DSA. Hence, DSA cannot be used to interpret the results when the material is subjected to both static and dynamic strain. Therefore, a new strain is defined

Table III Details of Static Strain, Dynamic Strain, and Total Strain

Length of Test Piece between Clamps (cm)		Static Strain (%)	Dynamic Displacement Amplitude (cm)	DSA (%)	Total Strain (%)
Initial	Strained				
7.01	7.06	0.713	0.0025	0.071	0.749
7.01	7.06	0.713	0.008	0.227	0.827
7.01	7.06	0.713	0.025	0.708	1.07
1.035	1.335	28.99	0.0025	0.374	29.22
1.035	1.335	28.99	0.008	1.2	29.76
1.035	1.335	28.99	0.025	3.74	31.4

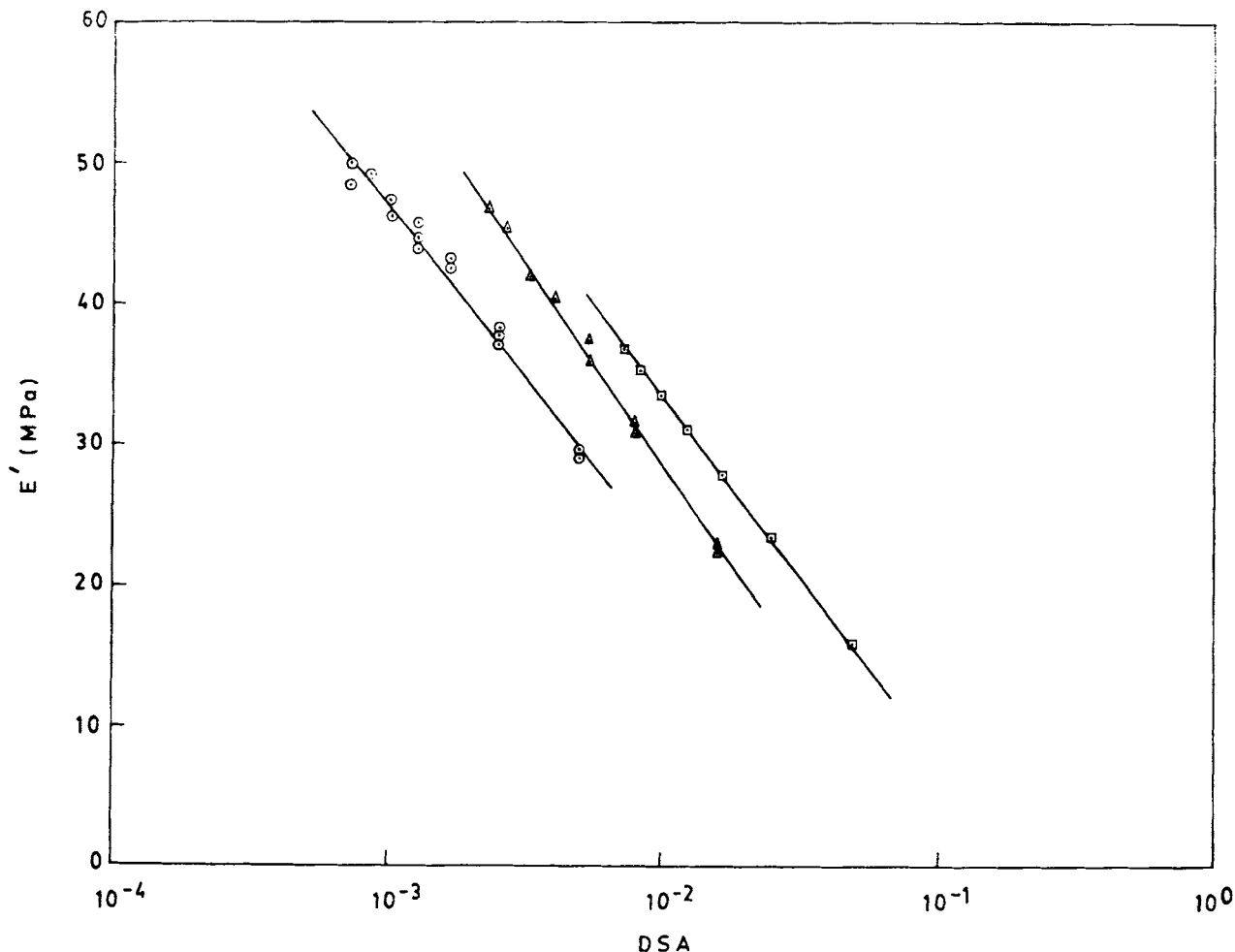


Figure 1 Storage modulus as a function of DSA for unstrained EPDM vulcanizate. The symbols represent displacement velocities. (○) 0.035 cm/s, (△) 0.112 cm/s, and (□) 0.35 cm/s.

as "total strain" (see definition of terms). The total strain may be viewed as the maximum strain experienced by the test specimen during one-fourth of a dynamic cycle compared to the strain-free condition. The results of Figure 4 are plotted again as a function of total strain (Fig. 5). This representation clearly shows that the static strain should be taken into consideration while judging the strain measure. It is seen that as the displacement velocity increases, the dynamic strain rate also increases and hence the storage modulus decreases. Dynamic properties of polymeric materials do depend on the strain rate as much as on strain. The observed separability of the static deformation and the dynamic strain amplitude for the storage modulus of a black-filled natural rubber vulcanizate has been attributed to the formation of a new transient structure network in the deformed state following a static defor-

mation.¹⁷ In the case of black-filled EPDM, under a combined static and dynamic strain (both varying at random), the effects of static strain and dynamic strain are not separable. However, the effects of total strain and displacement velocity are separable. This observation may be attributed to the time-dependent deformation characteristics of the filler-polymer network in the deformed state following static deformation. If a particular curve in Figure 5 is represented as $E = F(\epsilon, d_v, f, L)$ where f is the frequency, then the other curves corresponding to different strain rates may be represented as $E = cF(\epsilon, d_v, f, L)$, where the constant c depends on the strain history of the material.

Figure 6 shows the variation of the storage modulus as a function of frequency and total strain at a displacement velocity of 0.035 cm/s. It is also seen by the comparison of Figures 5 and 6 that the effect

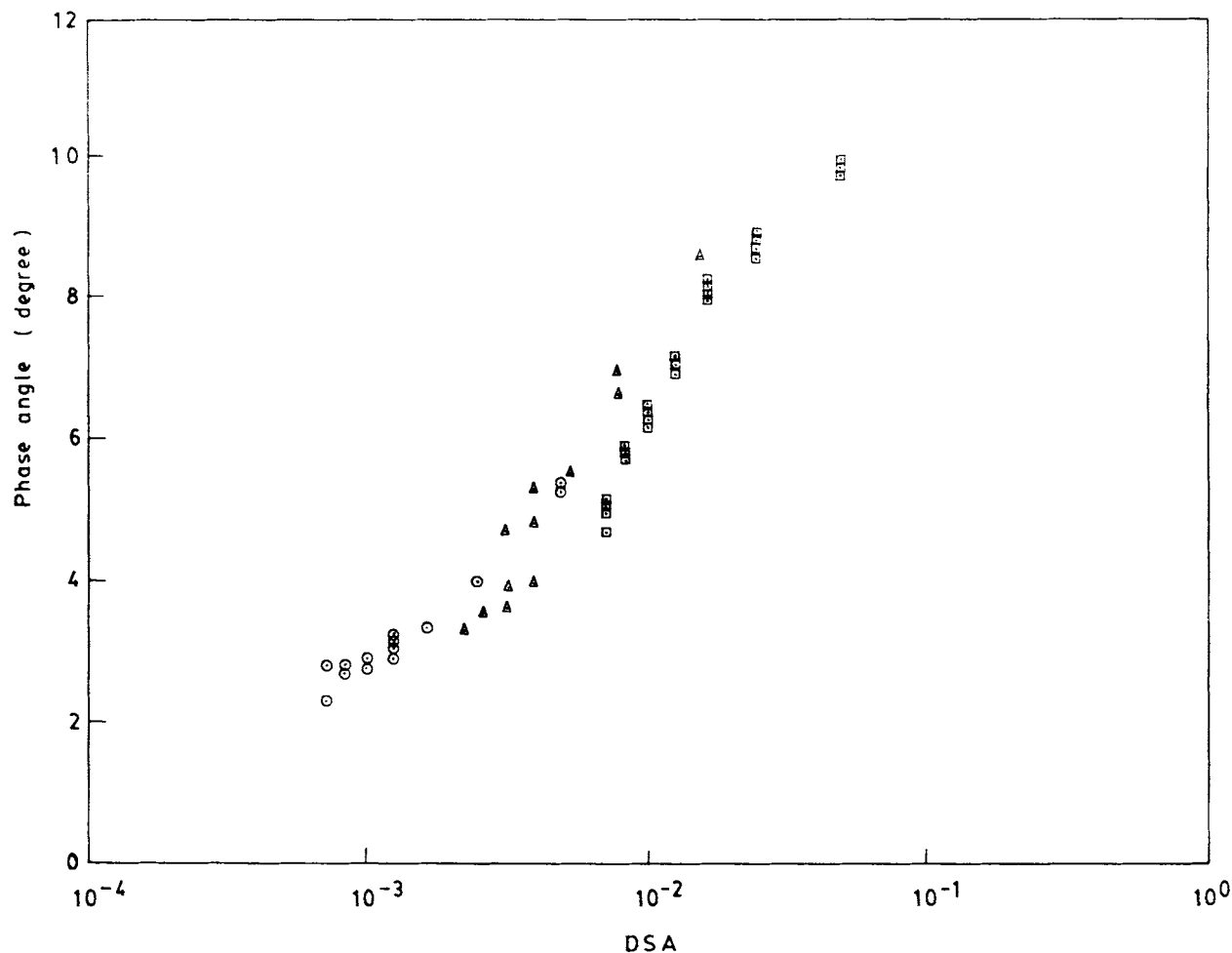


Figure 2 Mechanical phase angle as a function of DSA for unstrained black-filled EPDM vulcanizate. Legends are as in Figure 1.

of increasing frequency for a given displacement velocity is equivalent to decreasing the displacement velocity for a given frequency (E' increases in both cases). This shows an inverse equivalence of the displacement velocity and frequency in two domains (that of "strain" and "time"). This has been found to be true in the case of filled EPDM vulcanizates tested under combined fields of static as well as dynamic strain.

As mentioned, equivalence of E' for different displacement velocities (and hence different strain rates) shows that the constitutive equation for the storage modulus is a separable function of strain and time effects. In such a case, if the storage modulus is plotted as a function of frequency, it forms a set of parallel lines corresponding to different strains. In the present case, the above condition is satisfied (Fig. 7). The GSL model does not predict separability for storage modulus. It has been reported that for natural rubber and butyl rubber vul-

canizates, nonseparability of strain and time effects are observed for storage modulus.^{27,28} It has been argued²⁸ that the nonseparable behavior for natural rubber vulcanizates can be explained by the different deformational dependence of the elastic and the relaxation terms of the mixed response function characterizing the storage modulus. Experimentally it is seen that for black-filled EPDM vulcanizates the above referred case is not true since the storage modulus does show separability behavior. This may suggest that the GSL model need not be a general one, but a typical solution for a more general form of constitutive equation. Hence, it is presumed that in the case of black-filled EPDM vulcanizates, the elastic and relaxation terms in the mixed response function for storage modulus may have similar deformational dependence.

As stated earlier, the displacement velocity dependence of the dynamic mechanical properties at a particular frequency becomes more prominent on

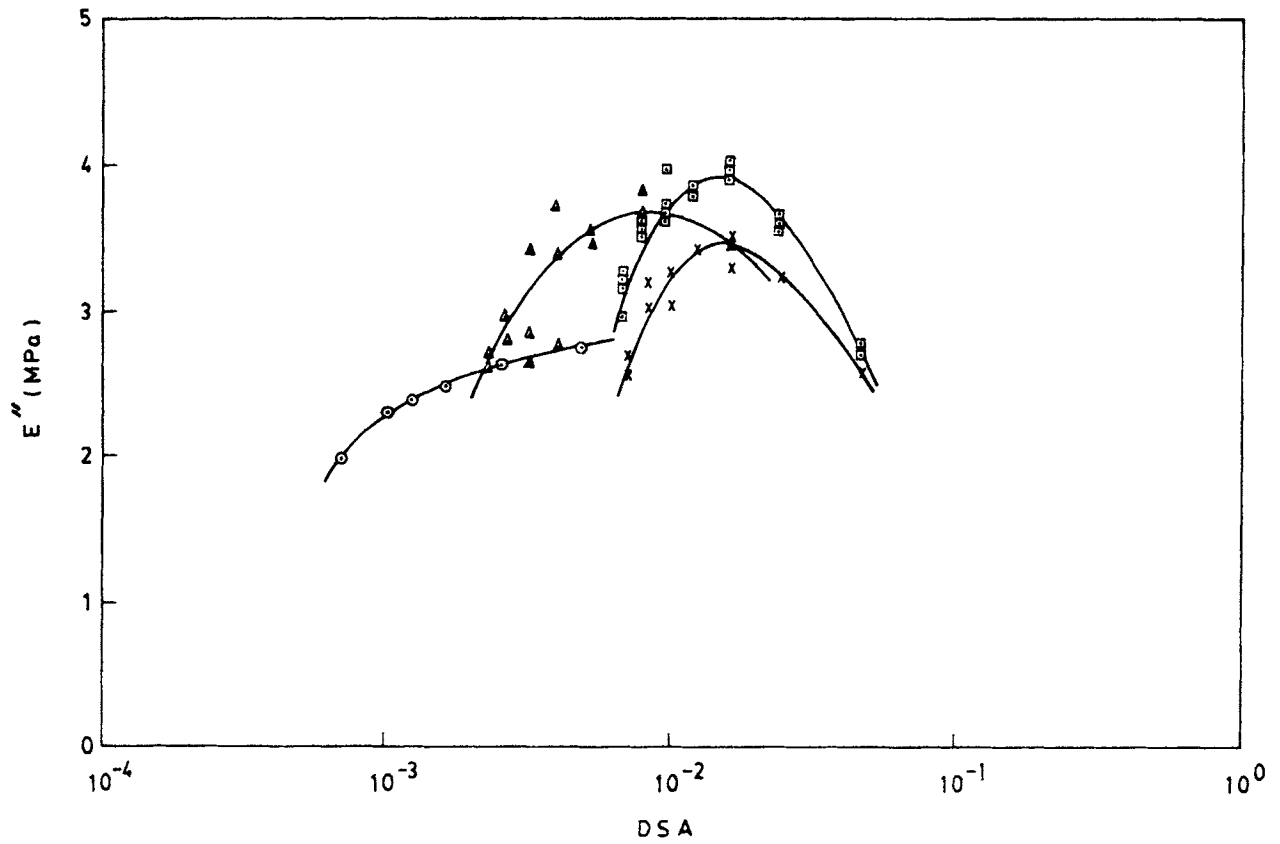


Figure 3 Loss modulus as a function of DSA for unstrained vulcanizates of carbon black-filled EPDM. Legends are as in Figure 1. x is at 11 Hz and a displacement velocity 0.35 cm/s.

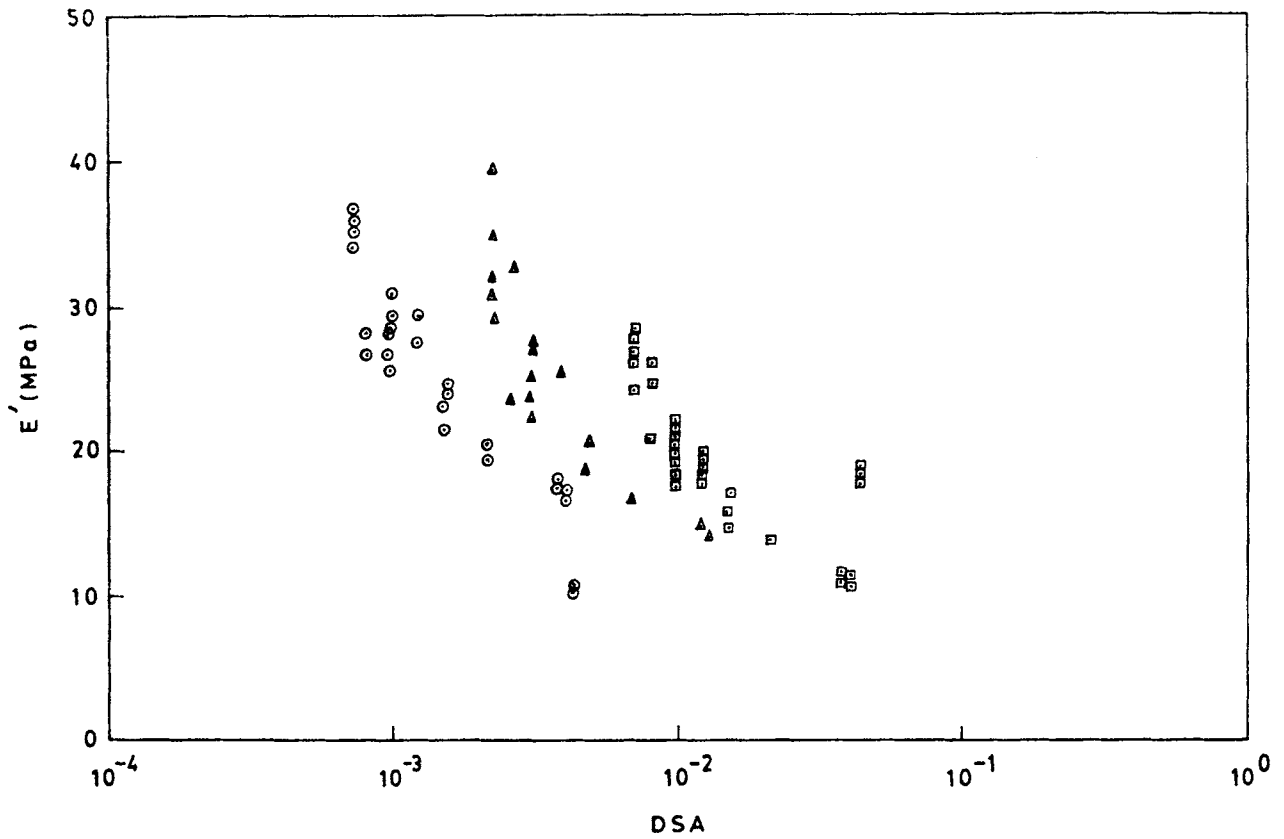


Figure 4 Storage modulus as a function of DSA for black-filled EPDM vulcanizates. The test piece is subjected to a static strain on which a dynamic strain is superposed. Details are as in Figure 1.

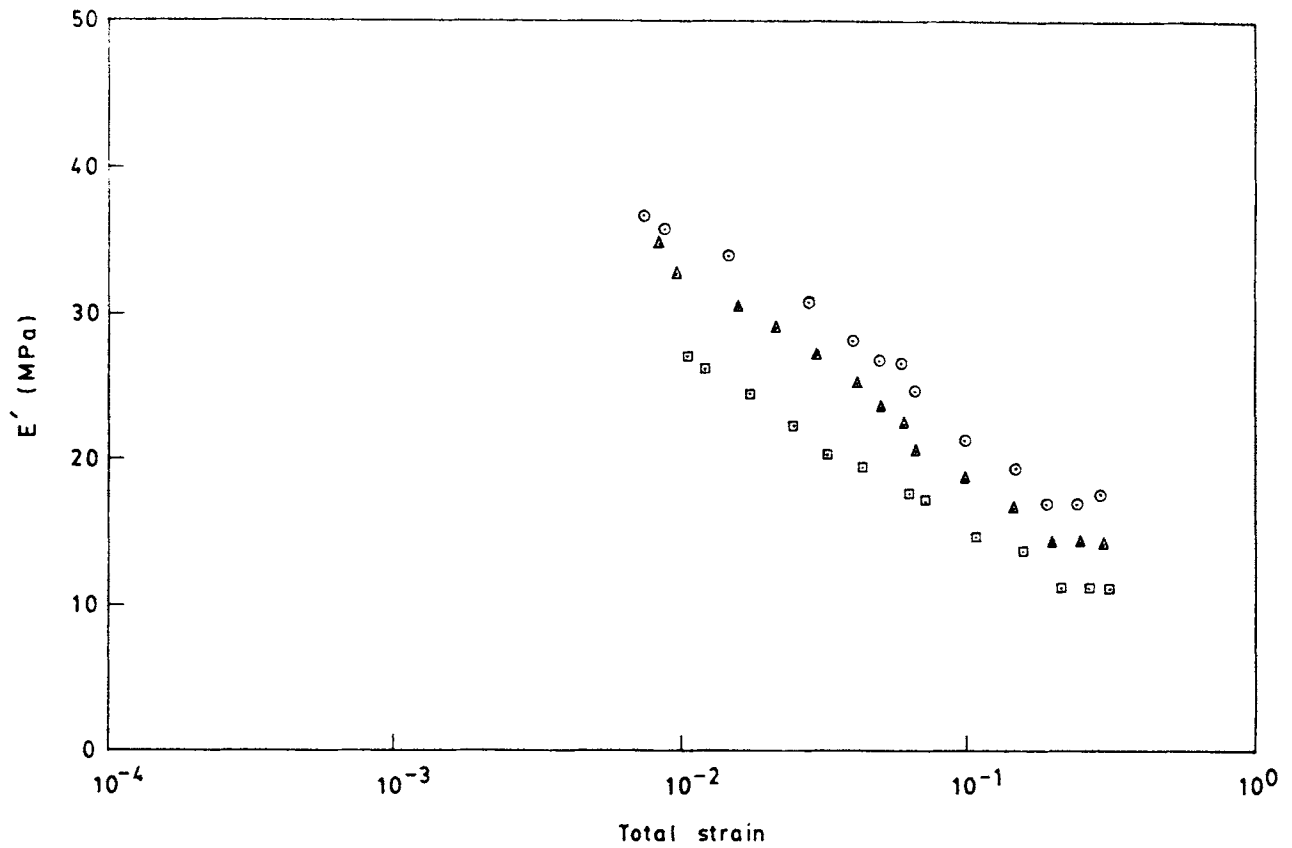


Figure 5 Storage modulus as a function of total strain for black-filled EPDM vulcanizates. Details are as in Figure 1.

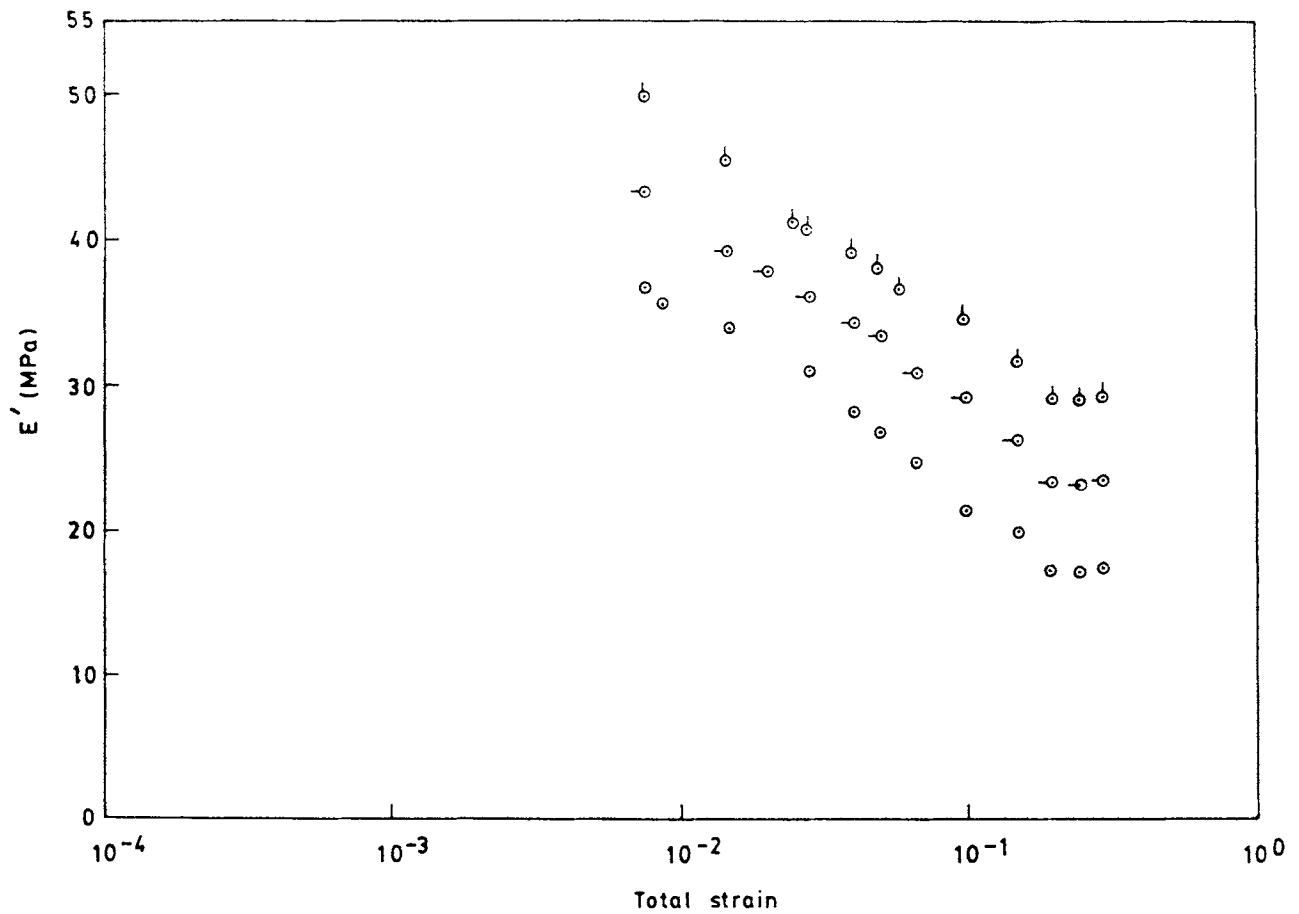


Figure 6 Storage modulus as a function of total strain for black-filled EPDM vulcanizates. Test conditions are as in Figure 4. (○) 35 Hz, shifted by +10 MPa; (○) 11 Hz, shifted by +5 MPa; (○) 3.5 Hz.

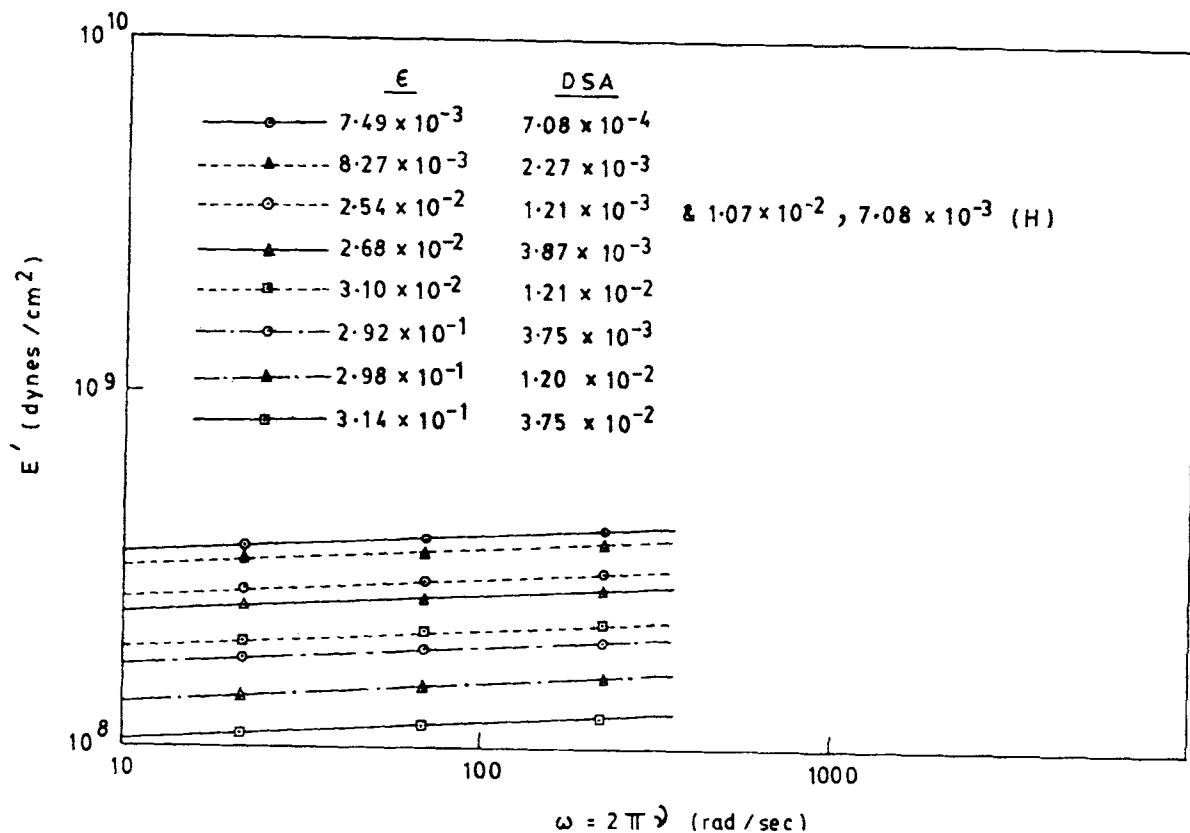


Figure 7 Storage modulus as a function of frequency. Details are as in Figure 1. No shift factors are used.

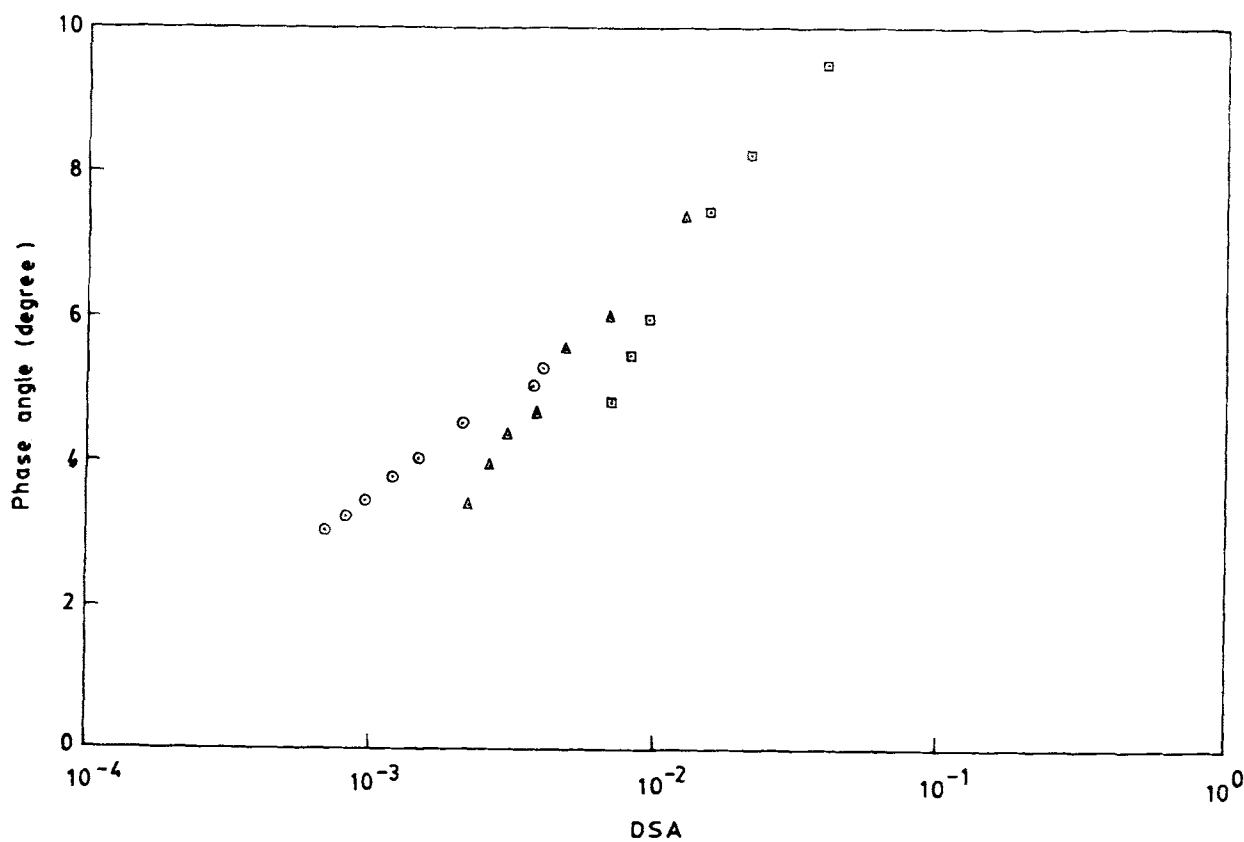


Figure 8 Mechanical phase angle versus DSA for black-filled EPDM. Details are as in Figure 4.

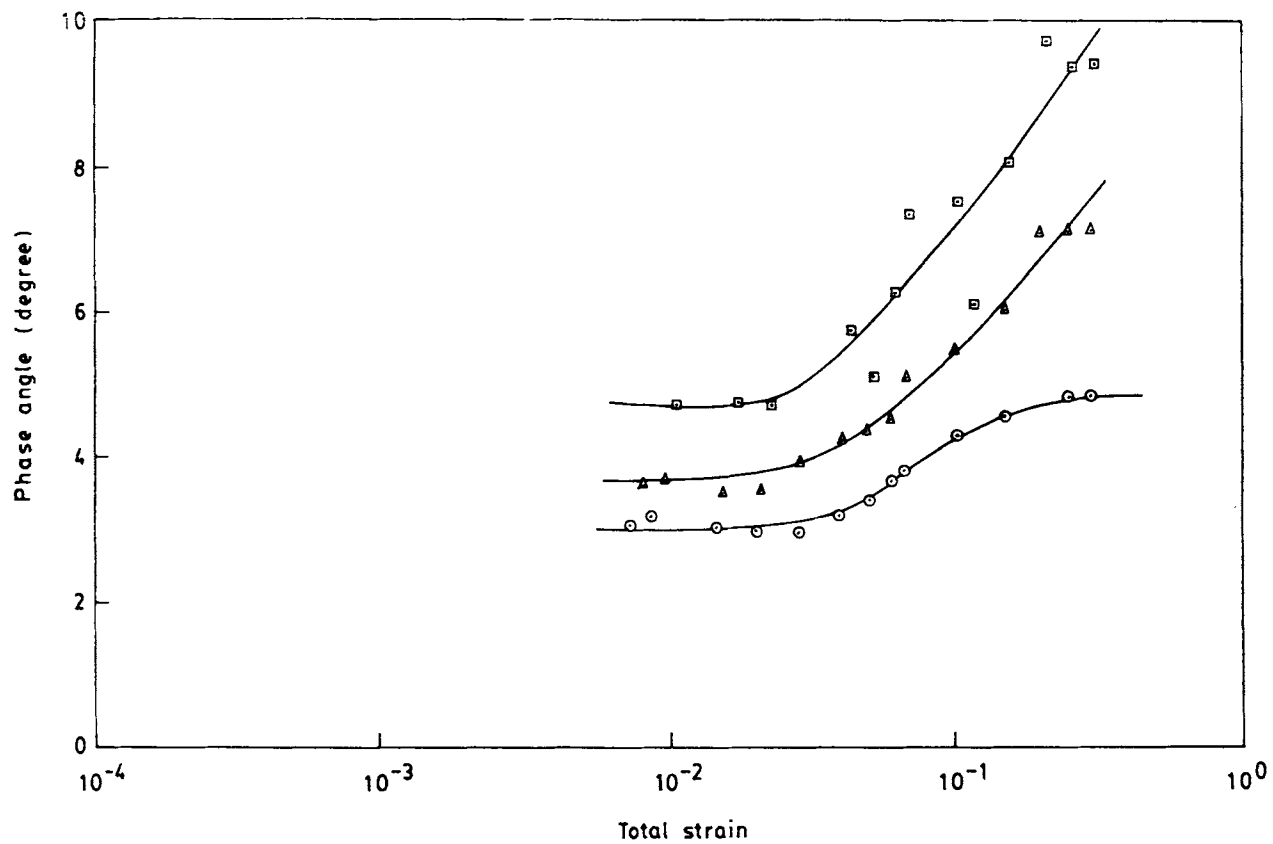


Figure 9 Phase angle as a function of total strain for black-filled EPDM vulcanizates. Details are as in Figure 4.

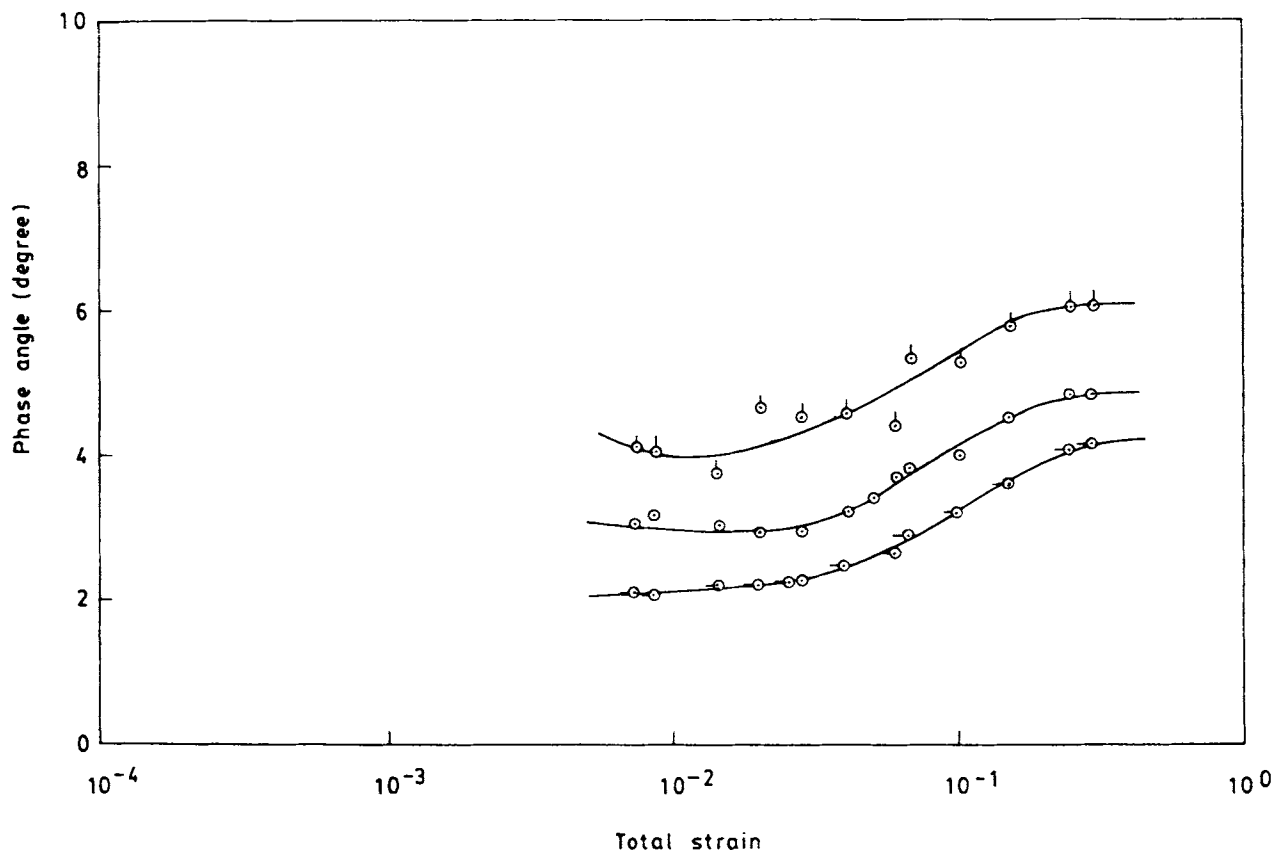


Figure 10 Phase angle as a function of total strain for black-filled vulcanizates of EPDM. Legends are as in Figure 6.

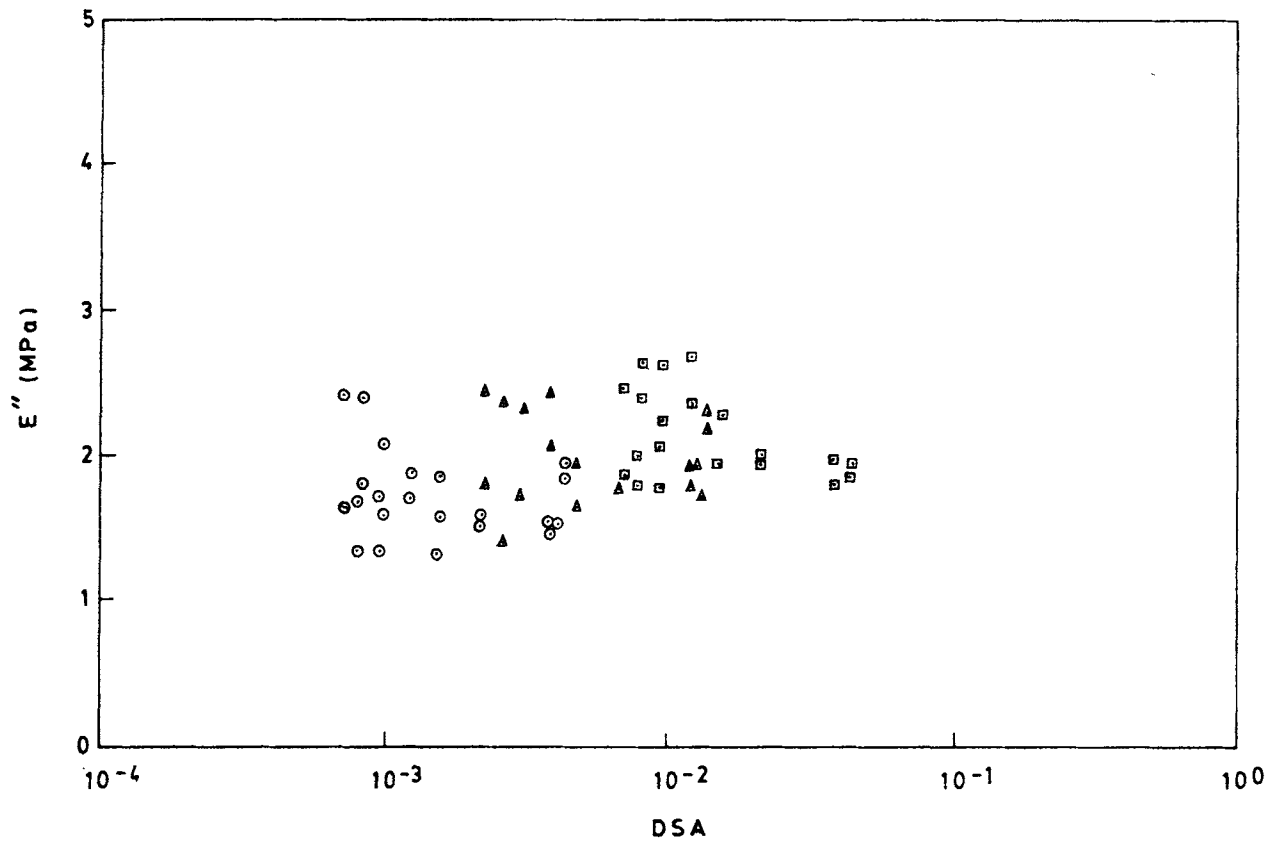


Figure 11 Loss modulus as a function of DSA for black-filled EPDM vulcanizates under static strain. Legends are as in Figure 1.

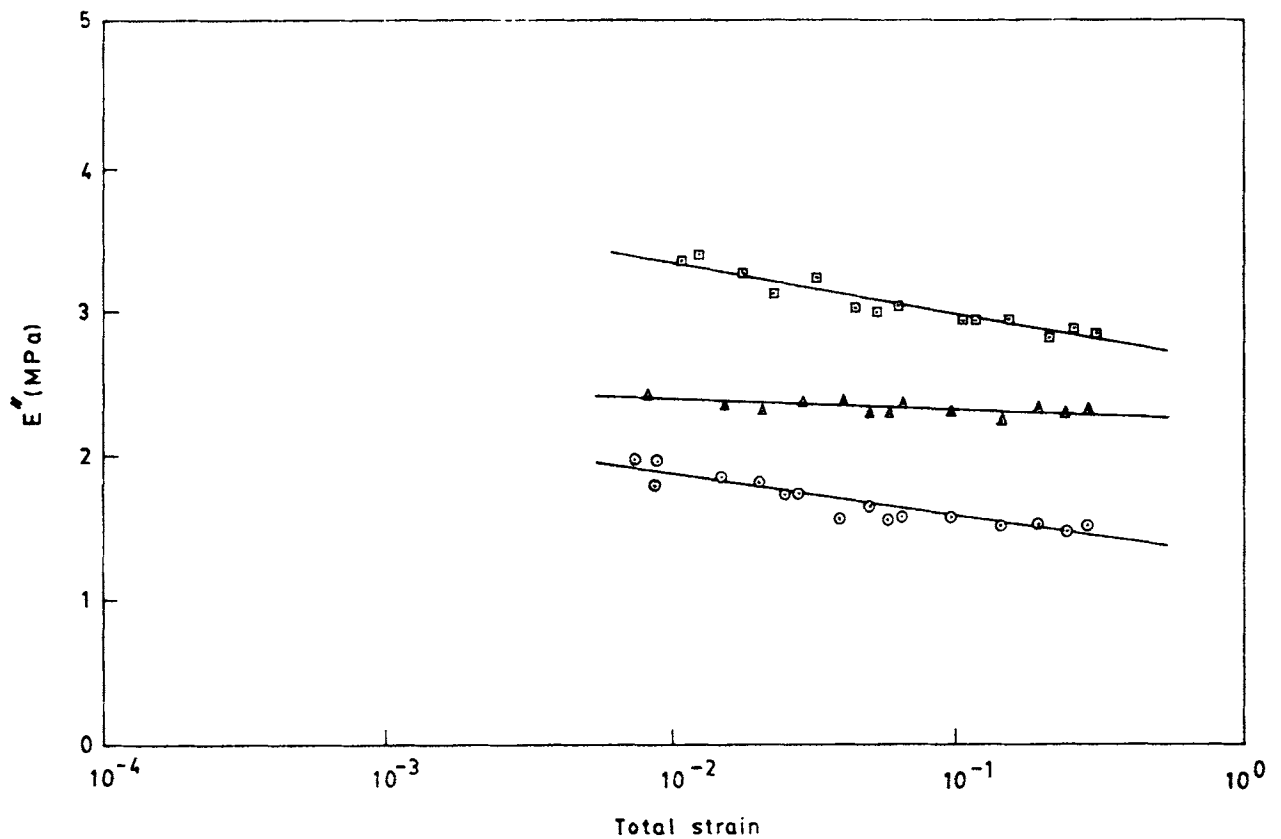


Figure 12 Loss modulus as a function of total strain for black-filled EPDM vulcanizates. Details are as in Figure 4. (Δ) shifted by +0.5 MPa; (\square) shifted by +1 MPa.

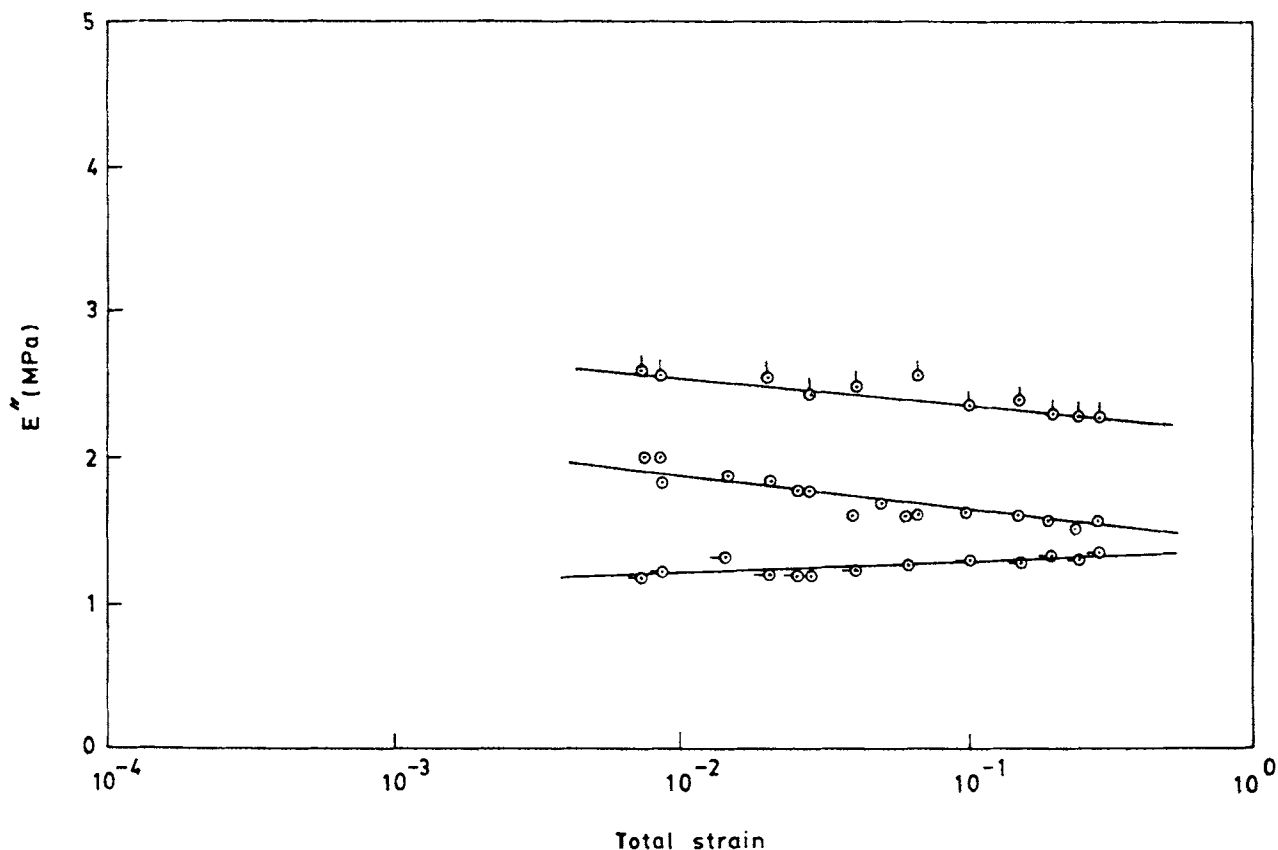


Figure 13 Loss modulus as a function of total strain. Legends are as in Figure 6.

the application of a static strain. Comparing Figures 2 and 8 it is seen that the deviation in the phase angle with displacement velocity is more prominent at lower static strains than at higher values of strain.

As in the case of the storage modulus, the strain measure taken for comparing the dynamic phase angle, δ , is changed to total strain (Fig. 9). It is seen that the curve corresponding to each displacement velocity is separate and, for identical conditions of total strain, δ increases with the displacement velocity. It is noted that each of these curves has a maximum of its own. Plotting the phase angle for different frequencies, it is seen that the shape of the curves remains unchanged provided that the comparison is among those of the same displacement velocity (Fig. 10).

It has been observed that the $\tan \delta$ versus frequency plots are not a set of parallel lines (figure is not included). Since $\tan \delta = E''/E'$, and E' is a separable function of time and strain effects, it is expected that E'' is also not a separable function of time and strain effects. The loss modulus values show considerable scatter when plotted as a function of DSA (Fig. 11). When the same results are plotted

as a function of the total strain (Fig. 12) the lines are separated according to the displacement velocity. In the tested range of total strain, the loss modulus shows a linear relation to the total strain. A plot of the loss modulus as a function of the total strain at different frequencies shows a trend similar to that of $\tan \delta$ (Fig. 13). Figure 14 shows a plot of the loss modulus as a function of frequency. This shows that the loss modulus is not a separable function of time and strain effects.

The strain parameter defined as the total strain has been used successfully to interpret the experimental observations. The concept of combining the dynamic strain and the static strain may have empirical connotations. In the case of superposition of a sinusoidal oscillation on the statically strained test piece, the dynamic strain acts as a step strain of periodic nature. Under such conditions the strain rate as well as the displacement velocity may have a major influence on the measured properties. This may also be the reason that the normally applied viscoelastic parameters are not considered as the primary properties to describe a statically deformed material.²²

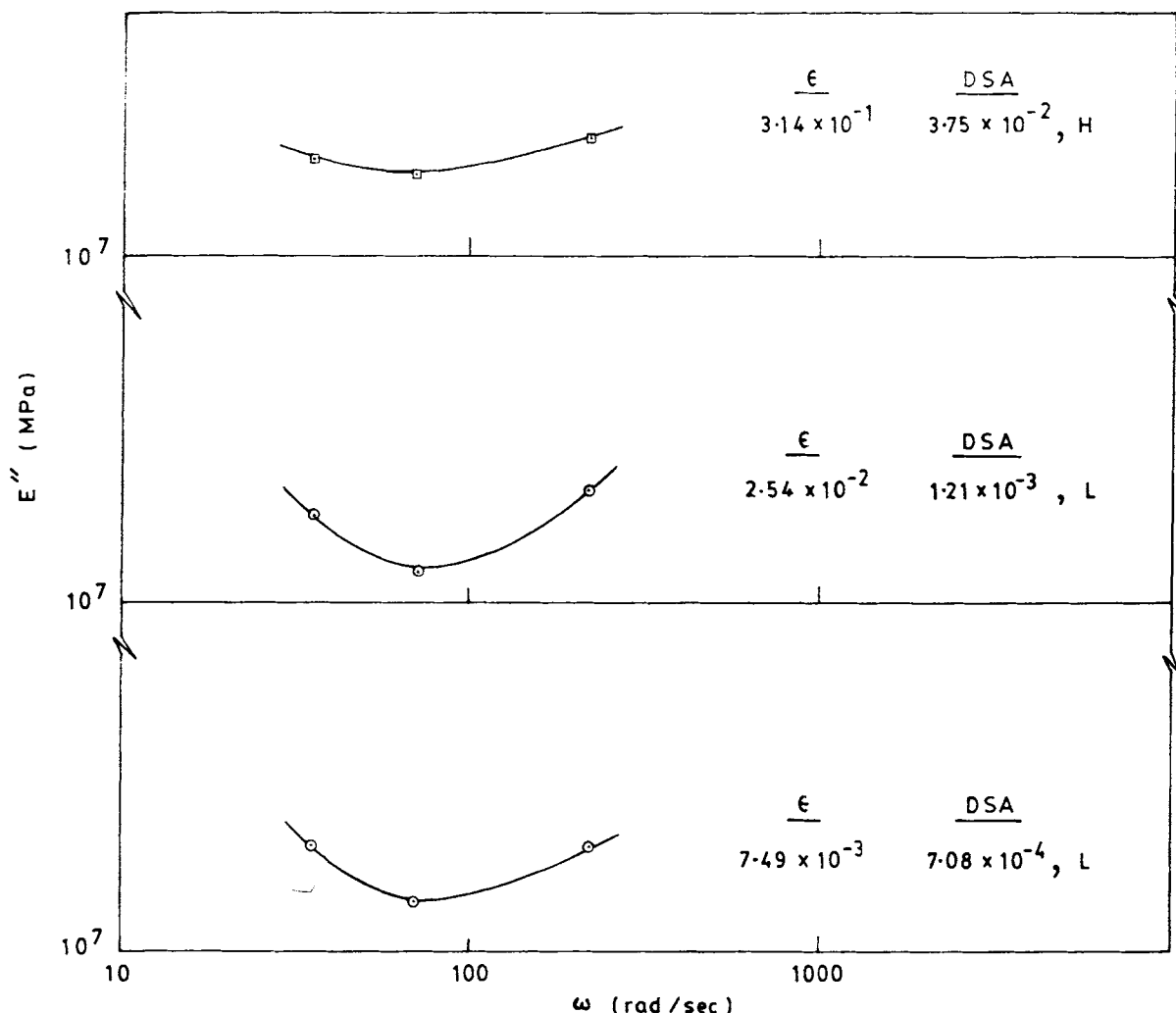


Figure 14 Loss modulus as a function of frequency for black-filled EPDM vulcanizate. Details are as given in Figure 4.

CONCLUSION

During the dynamic mechanical analysis of polymeric materials, the dynamic strain can be varied by two methods as stated in the text. The results show that these are not identical conditions. This becomes more evident when the test piece is pre-strained and a sinusoidal oscillation is superposed on it. The double strain amplitude is found not suitable for the proper representation of the experimental results. A strain called the total strain is defined in order to interpret the experimental results. The total strain is equal to the maximum strain experienced by the test piece during one-fourth of a dynamic cycle. The dynamic mechanical properties of the statically strained test specimen show a dependence on the displacement velocity. The properties show a definite relationship to the

total strain rather than the static or the dynamic strain. Separability behavior is observed in the case of the storage modulus and nonseparability in the case of the loss modulus. The elastic and the relaxational terms, constituting the mixed response function representing the storage modulus, are theorized as having similar deformational dependence.

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