Nonlinear Viscoelastic Behavior of Butadiene–Acrylonitrile Copolymers Filled with Carbon Black*

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Synopsis

Various viscoelastic measurements including dynamic mechanical measurements in tension at 110 Hz from −60° to 160°C, tensile stress relaxation measurements with 100% elongation at 25°, 54°, and 98°C, capillary flow measurements at 70°, 100°, and 125°C, and high-speed tensile stress–strain measurements carried to break at 25°, 56°, and 98°C were performed on four samples of carbon black-filled butadiene–acrylonitrile copolymers. All the data were treated with the same equation for time–temperature conversion. The capillary viscosity–shear rate curves were significantly lower than the complex viscosity–angular frequency curves, indicating "strain softening" with extrusion. The viscosity was estimated from the stress–strain relationship at the yield point. The viscosity as a function of the strain rate is significantly higher than the complex viscosity as a function of angular frequency, indicating "strain hardening" with extension. The strain softening and strain hardening are attributable to the structural changes upon deformation of the carbon black-filled elastomers. With the unfilled elastomers, neither strain softening nor strain hardening were observed in similar measurements.

INTRODUCTION

Viscoelastic analyses of elastomer processing may be performed by investigating the material behavior at small and large deformation and its properties at break. These observations may be made over rates and temperature ranges of processing.[1]

In earlier studies, dynamic mechanical measurement, stress relaxation, stress–strain to break, and steady shear measurements were made on butadiene–acrylonitrile uncompounded raw elastomers. Simple correlation schemes were utilized to cross-correlate the results of these various measurements.[2]

This work involves carbon black-filled compounds of the same copolymers. Cross correlation of the results of the same types of viscoelastic measurements is attempted and the resulting correlation compared to those previously obtained for the unfilled materials. The specific interest is to find differences between the deformation mechanism of filled rubber and that of unfilled rubber, recognizing the fact that the former is a highly structured system whereas the latter is amorphous.

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TABLE I
Butadiene–Acrylonitrile Copolymer Samples

Sample code for filled elastomer	Sample code for raw elastomer	Raw elastomer Hycar[a]	T_g, °C	Mooney (ML-4) at 100°C
1	A	1052-30	−37, −24	35
2	B	1042	−36, −24	78
3	C	1042X82	−34, −24	81
4	D	1002	−28	85

[a] Registered Trademark of B. F. Goodrich Chemical Company.

EXPERIMENTAL

Materials

The raw elastomers used in this study are four butadiene–acrylonitrile copolymers having 33% acrylonitrile content. The glass transition temperature T_g observed by DTA and the Mooney (ML-4) values at 100°C are given in Table I. The carbon black-filled compounds were prepared by dispersing 40 parts carbon black FEF-N550 per 100 parts rubber on a roll mill.

Dynamic Measurements

A Rheovibron (Imass, Inc., Accord, Hingham, Massachusetts 02018) was used in tension at a fixed frequency of 110 Hz over the temperature range of −60°–160°C. For some cases, temperatures to 200°C were used.

Stress Relaxation

An MTS high-speed tensile tester (MTS Division, Research Incorporated, Minneapolis, Minnesota 55424) was used to strain the sample to 100% elongation in less than 0.01 sec. At this elongation, the decay of force was observed as a function of time at temperatures of 25°, 54°, and 98.5°C.

Steady Shear Measurements

An Instron capillary rheometer (Instron Corp., Canton, Massachusetts) was used with a die of 0.050 in. in diameter, 0.990 in. in length, and 90° included angle. The temperatures were 70°, 100°, and 125°C. The shear rate range was 2.9–2900 sec^{-1}. Rabinowitsch's[3] correction and the correction for the entrance energy loss[4] were made to a part of the data.

Stress–Strain Measurements

An MTS high-speed tensile tester was used at drive speeds of 3.16, 31.6 and 344 in./sec (677%, 6,770%, and 72,800% per sec) at temperatures of 25°, 56°, and 98°C.
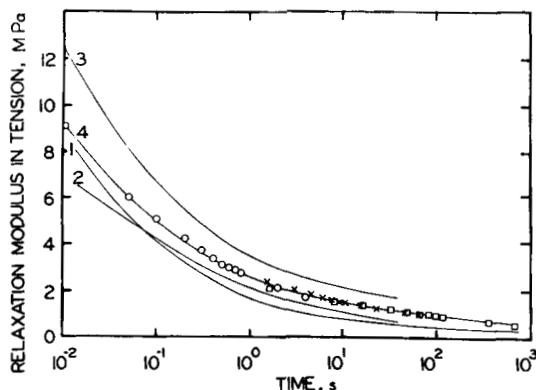
Fig. 1. Stress relaxation curves, reduced to 25°C, of the four carbon black-filled elastomers: (O) 25°C; (X) 54° → 25°C; (□) 98.5° → 25°C.

RESULTS

Time–Temperature Superpositions

The equation for time–temperature superposition was evaluated from stress relaxation measurements and expressed as[8]

$$\log \alpha_T = C_1(T - T_0)/(C_2 + T - T_0) \tag{1}$$
$$= 5.06(T - T_0)/(94.4 + T - T_0)$$

with T_0 taken as 298°K (25°C). Values of the constants C_1 and C_2 are similar to but somewhat smaller than those for the raw elastomers, i.e., $C_1 = 5.95$ and $C_2 = 109$. Equation (1) will be used with all measurements in this work.

Stress Relaxation

The results of the stress relaxation measurements are converted to those at 25°C and shown in Figure 1 for all four samples. The selected data points are shown with only one sample in order to avoid crowding the figure. The modulus $E(t)$ is expressed as

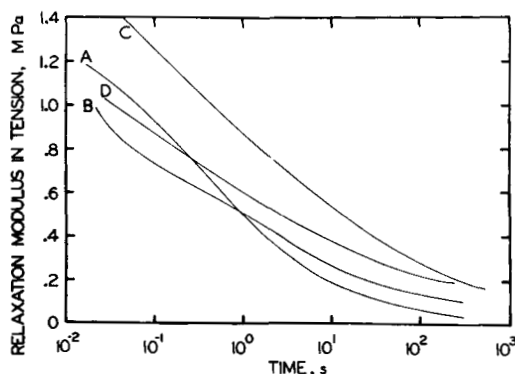$$E(t) = [F(t)/A]\alpha(\alpha - 1)^{-1} \tag{2}$$

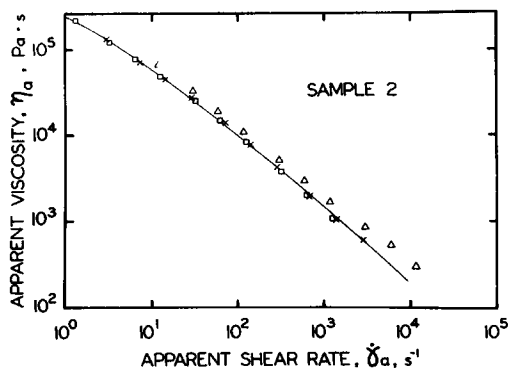Fig. 2. Stress relaxation curves, reduced to 25°C, of unfilled raw elastomers A, B, C, and D.

Fig. 3. Steady shear flow curve of carbon black-filled elastomer—test of temperature reduction: (△) 70° → 100°C, (X) 100°C; (□) 125° → 100°C.

where $F(t)$ is the observed force, A is the original cross-sectional area, and α is the extension ratio, i.e., $\alpha = 2$. The term $[F(t)/A]\alpha$ is the stress and $\alpha - 1$ is the strain.

The relative differences of the relaxation behavior of the four samples are very similar to those of the corresponding raw elastomers.[2] For example, in Figure 2, the relative magnitude of the modulus of the raw polymers at times longer than 1 sec was C, the highest, followed by D, B, and A. At times longer than 0.1 sec, the relative magnitude of the modulus of the filled samples were also the same; that is, 3 was the highest, followed by 4, 2, and 1.

Steady Shear Measurements

The viscosity–shear rate relationship of sample 2 is shown in Figure 3, which is the result of time-temperature superposition according to eq. (1). The data at 125°C after reduction to 100°C were in good agreement with the data at 100°C. However, the data of 70°C were not in agreement with those at 100°C. This was the case with all four samples. The reason why the 70°C data did not obey the temperature dependence of eq. (1) is not known at present.

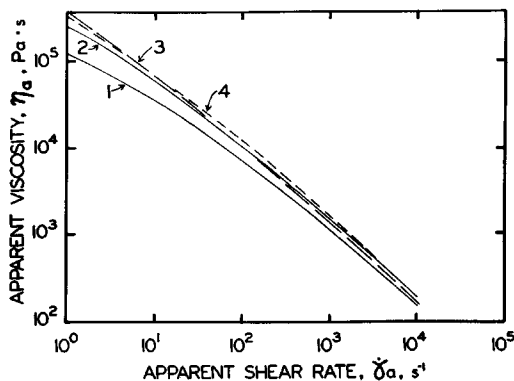The viscosity–shear rate curves of the four samples are shown in Figure 4.

Fig. 4. Steady shear flow curves, reduced to 100°C, of carbon black-filled elastomers.
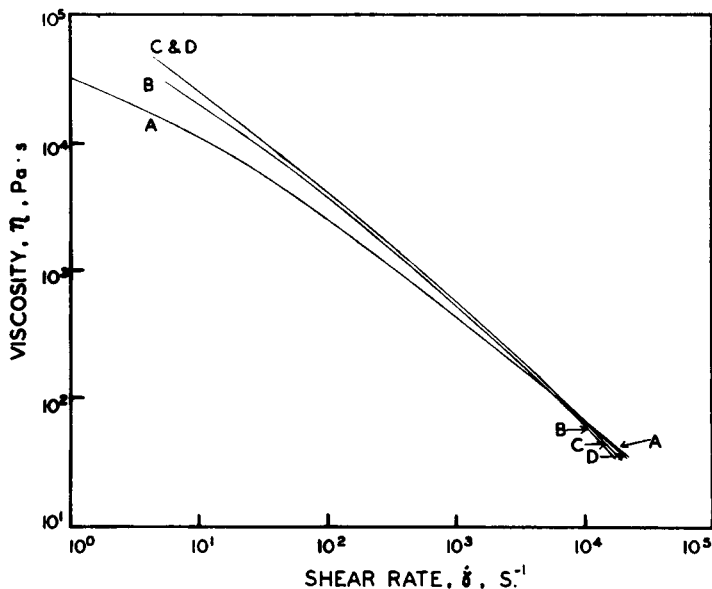
Fig. 5. Steady shear flow curves, reduced to 100°C, of unfilled raw elastomers.

Only the 100° and 125°C data were used. The relative magnitude of viscosities of the four samples are very similar to those of corresponding raw polymers[2,6] (Fig. 5); that is, the viscosities of samples 2, 3, and 4 are very similar, and so are the viscosities of samples B, C, and D. The viscosity of sample 1 is much lower than the rest of the filled samples, and so is the viscosity of A from the rest of the raw polymers.

Figure 6 is a comparison of uncorrected and corrected viscosities of samples 2 and 3. The former are the data shown in Figure 4. The latter are those after Rabinowitsch correction[3] and correction for entrance pressure loss[4] were made. Although the magnitudes of the corrections were large, the relative difference among the two samples remained the same. Therefore, the above comparisons of the behavior between filled and unfilled elastomers (Figs. 4 and 5) are valid.
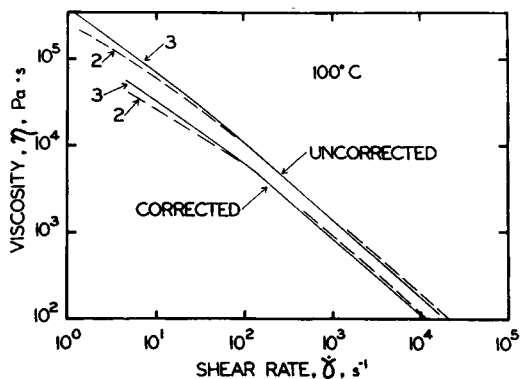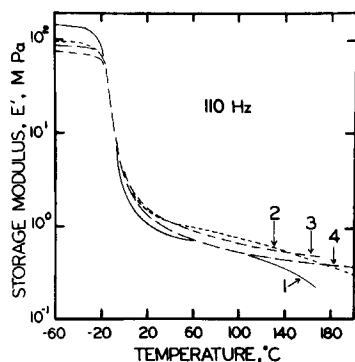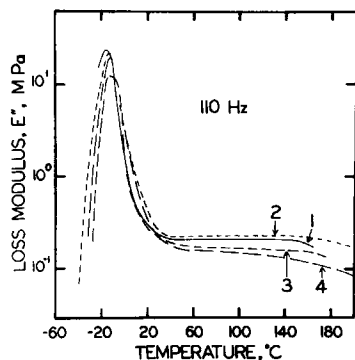

Fig. 6. Magnitude of corrections for steady shear flow data of carbon black-filled elastomers.
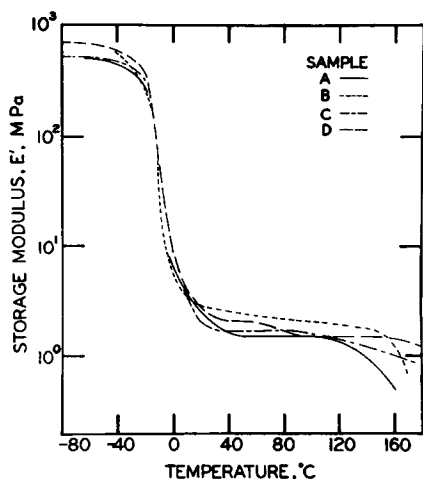
Fig. 7. (a) Storage modulus–temperature curves of carbon black-filled elastomers. (b) Loss modulus–temperature curves of carbon black-filled elastomers.
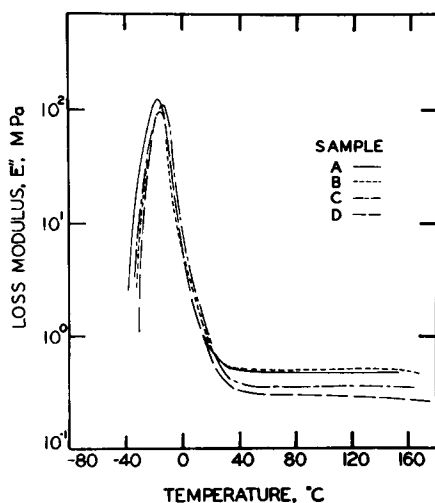
Dynamic Measurements

The results of the Rheovibron measurements are shown in Figures 7(a) and 7(b), where the observed values of the storage modulus and the loss modulus are plotted against temperature. These samples do not appear very different from each other beyond experimental error. This is very similar to the observation with the raw elastomers,[7] Figures 8(a) and 8(b).

Stress–Strain Measurements (Ultimate Properties)

The ultimate properties obtained by the tensile stress–strain measurements are shown in Figures 9(a) and 9(b), where the stresses at break and the corresponding elongations are plotted separately as functions of the strain rate. The strain rates are expressed as linear elongation rates. All data were reduced to those at 25°C. As in the case of raw elastomers[8] and unfilled vulcanizates,[9] the stresses at break increase with an increase in strain rate [Figs. 9(a) and 9(b)]. However, the fairly large sample-to-sample differences observed with raw elastomers[8] are almost completely removed. The data for the strain at break are excessively scattered [Fig. 9(b)]. Neither the sample-to-sample difference nor the dependence on strain rate can be observed. This is very different from the cases for raw elastomers,[8] Figure 10(b).

Fig. 8. (a) Storage modulus–temperature curves of unfilled raw elastomers. (b) Loss modulus–temperature curves of unfilled raw elastomers.

DISCUSSION

Viscoelastic behavior of four butadiene–acrylonitrile copolymers filled with carbon black have been examined by four different techniques. Dynamic measurements were made at elongation of less than 1%. Similar to the behavior of unfilled raw elastomers, sample-to-sample difference was not observed in the temperature range of the test. The stress relaxation experiment performed at 100% elongation showed sample-to-sample differences which were very similar to those observed with the corresponding unfilled elastomers. Steady shear measurements also showed sample-to-sample differences very similar to those observed with the unfilled elastomers. On the other hand, sample-to-sample differences are not very significant in the ultimate properties measured by tensile
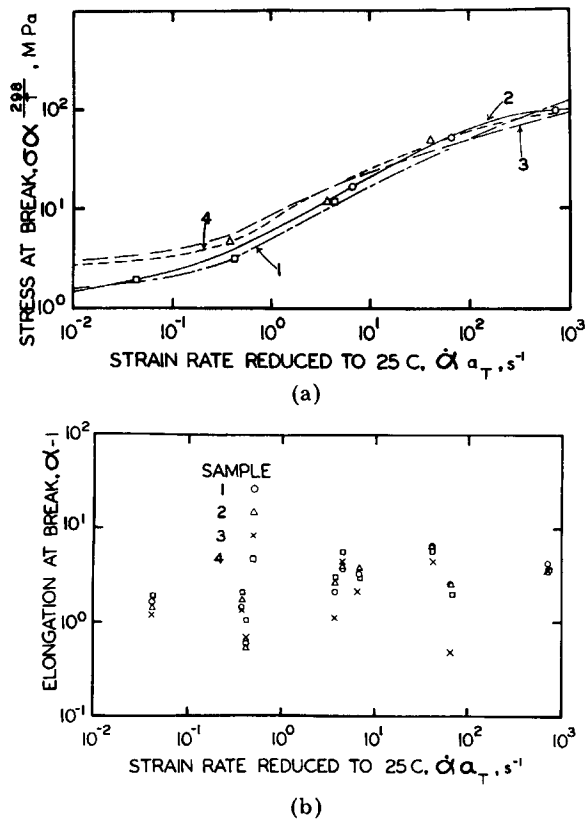
Fig. 9. (a) Stress at break as function of strain rates, reduced to 25°C, of carbon black-filled elastomers: (O) 25°C; (△) 56° → 25°C; (□) 98° → 25°C. (b) Elongation at break as function of strain rates, reduced to 25°C, for carbon black-filled elastomers.

stress–strain tests. This is in contrast to unfilled raw elastomers, where sample-to-sample differences are magnified in this test.

It appears, then, carbon black is playing a dominant role in determining the ultimate properties. The large scatter in the data of elongation at break suggests that the incorporation of carbon black into rubber broadens the distribution of defects, which are probably responsible for determining ultimate properties. On the other hand, failure of unfilled elastomers is known to be significantly influenced by the bulk viscoelastic properties[9]; the question of why the viscoelastic properties of elastomers do not have much influence on ultimate properties of the filled elastomers remains. This question is especially pertinent, when the following facts are recognized: sample-to-sample differences attributable to the elastomer components were seen in the bulk behavior of filled systems such as in stress relaxation and steady shear measurements, but not in the ultimate properties.

Next, the effect of carbon black on the bulk viscoelastic behavior will be examined. A typical approach has been to examine the effect of carbon black concentration on the viscoelastic properties of filled elastomers. Quantitative treatments along this line were based on the analogy of filled rubbers to suspensions consisting of rigid particles dispersed in fluid media.[10,11] However,
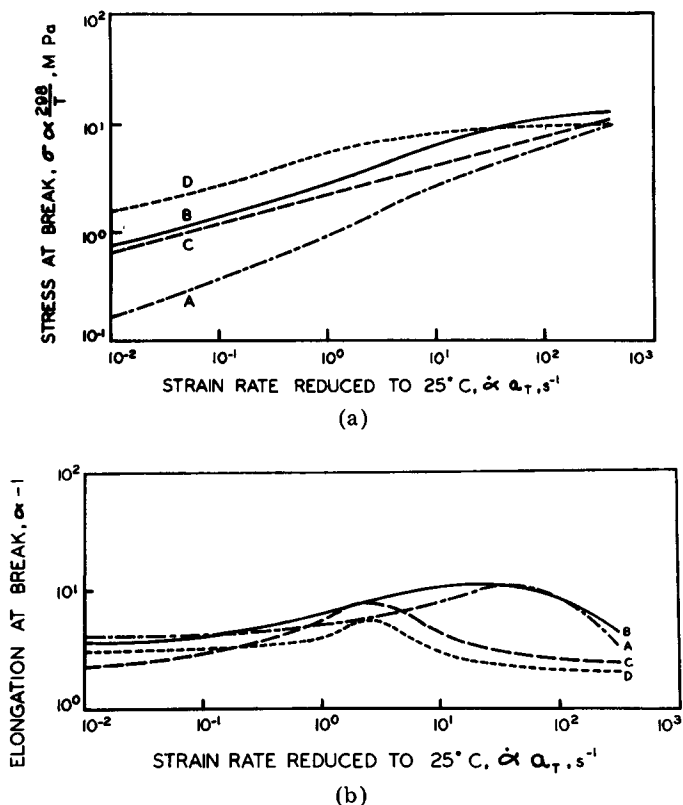
Fig. 10. (a) Stress at break as function of strain rates, reduced to 25°C, of unfilled raw elastomers. (b) Elongation at break as function of strain rates, reduced to 25°C, of unfilled raw elastomers.

this approach is incomplete in that it does not treat the effect of structure introduced by the presence of filler.

In the present work, our interest is to examine the difference in deformational mechanisms between filled and unfilled elastomers. Of particular interest are the three-dimensional structure in the elastomer matrix established by the presence of carbon black, changes in structure with increasing strain, and how such changes are effected in the viscoelastic behavior. This type of investigation was carried out by examining the strain amplitude dependence of the dynamic behavior at fixed frequency and temperature[12] and the shear rate dependence of the viscosity.[13]

In this paper, both strain and strain rate dependences will be examined; dynamic, steady shear, and tensile stress–strain measurements will be used. Interrelations among these three measurements will be investigated to see if there is a unique difference between filled and unfilled elastomers.

The corrected steady shear data of Figure 6 are replotted in Figures 11 and 12 together with the data of the shear complex viscosities calculated from dynamic and tensile stress–strain measurements. The dynamic data were those shown in Figures 7(a) and 7(b). A temperature range of 40°–220°C for sample 2 and 40°–170°C for sample 3 were used. All the data were reduced to 100°C by using eq. (1).

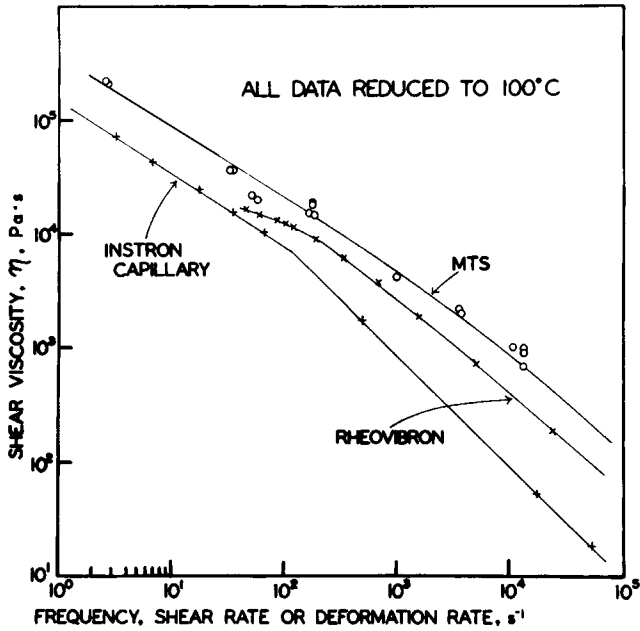The complex viscosities are significantly higher than the steady shear viscosity

Fig. 11. Viscosities of sample 2 obtained by capillary extrusion, dynamic oscillatory, and tensile stress–strain measurements.

when compared at equal values of angular frequency and shear rate.   This is contrary to the results for unfilled elastomers where the two viscosities are in good agreement,[2,6,7] Figures 13 and 14.

The tensile stress–strain data at the yield point were used[2] to calculate
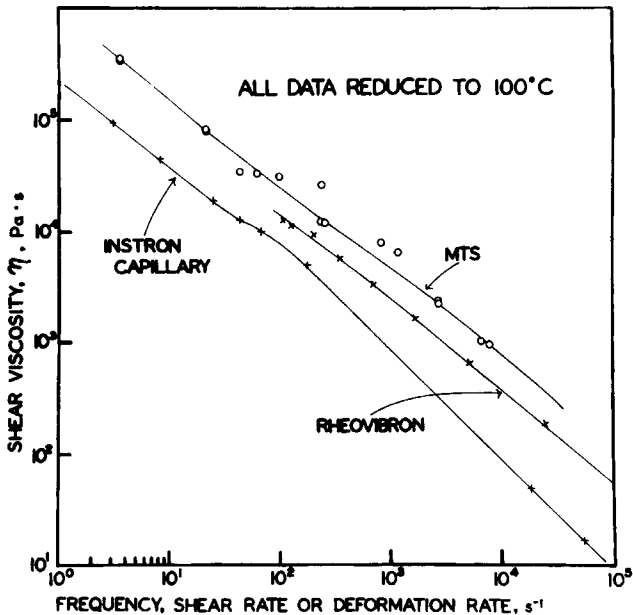

Fig. 12. Viscosities of sample 3 obtained by capillary extrusion, dynamic oscillatory, and tensile stress–strain measurements.
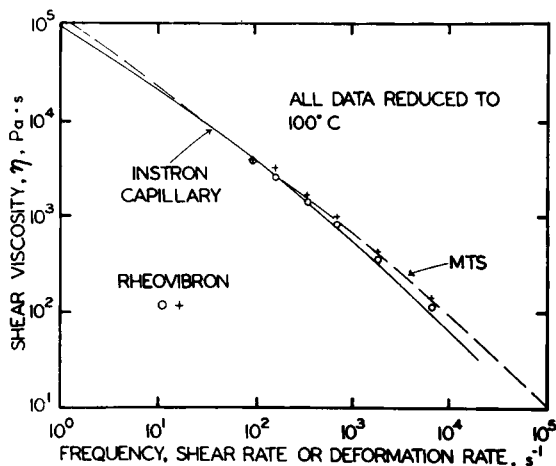
Fig. 13. Viscosities of sample B obtained by capillary extrusion, dynamic oscillatory, and tensile stress–strain measurements.

viscosities η as a function of strain rates $\dot{\gamma}$. The following equations, previously applied to the data of unfilled elastomer, are used:

$$\eta = \tfrac{1}{3}\left(\frac{\alpha\sigma}{\epsilon}\right)(\alpha t) \tag{3}$$

$$\dot{\gamma} = (\alpha t)^{-1} \tag{4}$$

where σ is the tensile force divided by the cross-sectional area of the unstressed specimen; $\sigma\alpha$ is the tensile stress corrected for the change of the cross-sectional area; α is the extension ratio l/l_0; $\epsilon = \alpha - 1$; t is the observed time; and αt is the reduced time.[14] All data were reduced to 100°C, using eq. (1). The viscosities calculated from the tensile stress–strain data are significantly higher than the complex viscosities from the Rheovibron measurements. This is contrary to the observation for unfilled elastomers, where the two viscosities were in good agreement,[7] Figures 13 and 14.
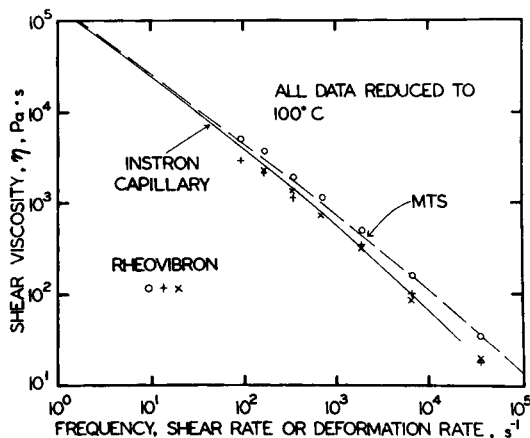

Fig. 14. Viscosities of sample C obtained by capillary extrusion, dynamic oscillatory, and tensile stress–strain measurements.

Because the Rheovibron measurements involve very small deformations, the dynamic data may be regarded as representing the structure with a minimum disturbance. Capillary extrusion involves large deformation and possible structural change as well. Therefore, the difference between the capillary extrusion data and the dynamic data could well be the result of structural changes. The material may be "strain softening" with extrusion. The viscosities calculated from tensile stress–strain behavior are much higher than those from dynamic measurements. The tensile elongation may be altering the material structure resulting in "strain hardening." However, the tendency to harden with increasing strain cannot be detected directly from the shape of stress–strain curves. This interpretation is possible only with reference to the behavior of unfilled elastomers, where corresponding states are found between small and large deformation.[14] Therefore, there is no strain hardening. When the corresponding principle is applied to filled elastomers, the behavior at large deformation does not superpose onto that at small deformation.

It appears that the structure built by the presence of carbon black increasingly jams against elongation until finally the structure yields and, soon afterward, the sample breaks. This mechanism explains why the ultimate properties of filled elastomers are insensitive to the bulk viscoelastic behavior.

Strain softening with extrusion requires further explanation. Although there is no fully satisfactory explanation as to why the steady-state viscosity–shear rate curve and complex viscosity–angular frequency curve are in agreement, such agreements have been observed with unfilled elastomers (Figs. 13 and 14) as well as with many plastic melts. The present argument takes account of this fact.

When carbon black is dispersed in the rubber, the above two curves are not in agreement, but strain softening is observed. The explanation for the softening may be visualized in the following manner. The behavior of material moving from the barrel to the capillary is similar to tensile deformation, where the total elongation corresponds to the reduction of the cross-sectional area.[15] Here, it is 55%, which is far beyond the elongations at break [Fig. 9(b)].

It appears that after passing the yield point and the breakdown of the structure, the compound softens if it is contained in the capillary and kept from breaking. Further investigation is required on the morphologic changes that are manifested by strain hardening and strain softening.

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