

Rheological and Solid Wall Boundary Condition Characterization of Unvulcanized Elastomers and Their Compounds

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Synopsis

An extensive fundamental investigation of the rheological properties and solid wall boundary condition shear stress of elastomers and elastomer-carbon black compounds has been carried out. The elastomers were an emulsion butadiene-styrene copolymer (SBR 1500) and a polybutadiene. Shear flow rheological properties were measured using a newly designed sandwich rheometer, in both constant shear rate and creep modes as well as in a capillary rheometer. A constant elongation rate rheometer for elastomers was developed. Stress relaxation measurements were also carried out in the sandwich rheometer. The shear viscosity of the gum elastomers exhibits a constant very high shear zero viscosity (8×10^8 Pa·s for SBR 1500 at 100°C) and decreases with increasing shear rate. The compounds exhibit yield values of similar magnitude to carbon black compounds of molten plastics. Only the SBR 1500 and its compounds were studied in the elongational flow mode. It was not possible to achieve a steady state in these experiments. An apparatus for measurement of shear stress as a function of velocity (shear rate) at a specified pressure was developed. The instrument, which we call a friction tester, was used not only to determine wall shear stress but to investigate the regime of flow and potentially determine conditions for the onset of slip. Evidence of changing flow regimes were found, and the implications discussed.

INTRODUCTION

The fabrication of parts from elastomers forms the basis of a major world-wide industry. Despite this importance, there have been very few basic studies of the rheological characterization of elastomers and their compounds or analysis of processing from a fundamental point of view. The situation is quite different for the case of molten plastics where shear and elongational viscosity and other functions have long been measured over a range of deformation rates.¹⁻⁶ It is well established that such melts respond both to small and large strains as viscoelastic fluids which obey "no-slip" boundary conditions.⁵⁻⁸ The theory of viscoelastic non-Newtonian fluids with the no slip boundary condition has been used to analyze flow in a range of melt processing operations such as flow in extruder screws⁹ and dies,¹⁰ extrudate swell from dies,^{11,12} and the filling of molds.^{13,14}

The situation with elastomers and their compounds is rather different. While it is established that pure elastomers do respond to applied deformations as viscoelastic fluids,¹⁵⁻¹⁸ there is little shear viscosity or elongational viscosity data over a range of deformation rates available though the studies of Vinogradov and his co-workers¹⁹⁻²² and Stevenson²³ should be noted. (For reviews see White^{24,25}). Elastomers are generally processed as highly filled carbon black

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compounds. There have been almost no serious studies of these materials, which do more than indicate the increase in viscosity caused by the presence of carbon black. Vinogradov and his co-workers²⁶ have shown that polyisobutylene filled with carbon black exhibits yield values. The material responds as a polymer-black gel at small stresses and like a (nonlinear) fluid above it. A similar response is observed in molten plastics filled with carbon black and other small particles.²⁷⁻³⁰ Slip is recognized as a serious problem in rheological experiments, but little effort has been made towards determining its character. Elastomers and their carbon black compounds have long been known to exhibit slippage,^{31,32} but little is known of its relation to flow conditions. With the constitutive equation and boundary conditions unknown, it is not surprising that little progress has been made in the rational analysis of processing rubber compounds. Indeed, how can one rationally design a screw extruder if it is not known where the rubber compound adheres to the screw and barrel and where it slips relative to either or both surfaces.

We seek in this paper to describe a series of experimental apparatus and experiments for the purpose of the rheological characterization and determination of processability of elastomers and their compounds.

EXPERIMENTAL

Creep sandwich rheometer: Sandwich rheometers for elastomers have been reported by earlier investigators,^{17,18,33} but their data has largely been obtained under transient conditions. We have built a sandwich rheometer with a much greater aspect ratio than previously described in the literature. The distance between the plates is 0.065 cm, the width of the plates is 2.54 cm, and it is 20.32 cm long. For creep tests, it is placed in an air oven (Fig. 1) and weights ranging from 500 to 10,000 g are used. The shear stress $\sigma_{12}(t)$ and shear rate $\dot{\gamma}$ may be computed from

$$\sigma_{12} = F/2A \quad (1a)$$

$$\dot{\gamma} = V/H \quad (1b)$$

Here F is the force of the sandwich, A its shear area, V the velocity of the central member, and H the distance between the plates. F is constant and V varies with time in the creep mode. This allows shear stresses as small as 100 Pa to be

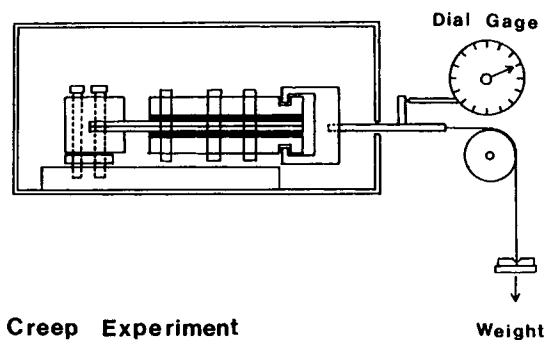


Fig. 1. Creep sandwich rheometer.

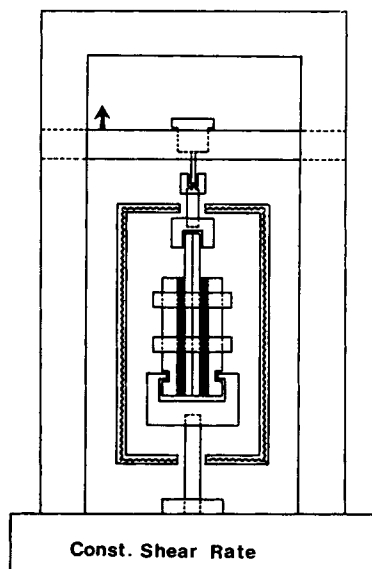


Fig. 2. Constant shear rate sandwich rheometer.

measured. The oven which controls temperatures within $\pm 0.5^\circ\text{C}$ has a temperature range of 20–180°C.

For long-time high- $\dot{\gamma}$ experiments, the decrease in contact area $A(t)$ from the initial $A(0)$ must be considered. Specifically

$$\sigma_{12} = F/2 \left[A_0 - W \int_0^t V(t) dt \right] \quad (1c)$$

where W is the width of the plate.

The creep data was converted to shear viscosity η at low shear rates using the method of Ninomiya.³⁴ The high t asymptote intercept of a plot of $\dot{\gamma}/\sigma_{12}$ vs. t is interpreted as $1/\eta$, where η is the viscosity.

Constant shear rate sandwich rheometer: The same sandwich apparatus that was described in the previous section may be placed in the frame of an Instron tensile tester (Fig. 2). The sandwich rheometer is then placed in a second air oven. Equations (1) may again be used to determine σ_{12} and $\dot{\gamma}$. Here V is a constant, and F varies with time. The Instron crosshead may be moved in the velocity range of 0.05–20 mm/min. This represents a shear rate range of 10^{-4} – 10^{-1} s $^{-1}$. The oven has a control of $\pm 0.5^\circ\text{C}$ and a range of 20–200°C.

Capillary rheometer: We have also used a Merz–Colwell type Instron rheometer in the higher shear rate range. The shear stress is determined from the pressure drop through the capillary. It may be shown that

$$p_T = \Delta p_{\text{ends}} + \Delta p_c \quad (2a)$$

$$= \Delta p_{\text{ends}} + 4(\sigma_{12})_w L/D \quad (2b)$$

where D is the die diameter, L the length, and Δp_c the pressure drop within the capillary. To compute $(\sigma_{12})_w$, we must follow Mooney³⁵ and Bagley³⁶ and correct for Δp_{ends} . This is done using a series of dies of the same diameter but varying length. Forces ($p_T A$ [barrel]) as low as 67 N (15 lbs) may be measured. The die wall shear rate $\dot{\gamma}_w$ is computed from Weissenberg's equation^{37,38}

$$\dot{\gamma}_w = \left(\frac{3n' + 1}{4n'} \right) \frac{32Q}{\pi D^3} \quad (3a)$$

where

$$n' = d \log(D \Delta p_c / 4L) / d \log(32Q / \pi D^3) \quad (3b)$$

with Q the extrusion rate. Capillaries of diameter of 0.15 cm (0.058 in.) were used.

We may also measure the viscosity in this rheometer if we remove the capillary. The large barrel diameter (D_B) is now used in eqs. (2) and (3) in place of D . The effective shear rates are substantially reduced.

Elongational flow rheometer: We have investigated various designs and eventually decided in favor of one based on the work of Cotten and Thiele.³⁹ The other instruments had difficulties in slipping samples. This apparatus is shown in Figure 3. The sample is held in the frame of an Instron tensile tester with the sample wrapped around a pulley. At a fixed position L (20.0 cm) below the chuck, it is held by a pair of rotating rolls pressed into the sample by a spring. The elongation rate $\dot{\gamma}_E$ and tensile stress are

$$\dot{\gamma}_E = R\Omega/L \quad (4a)$$

$$\sigma_{11} = F/A \quad (4b)$$

where A is the cross-sectional area of the sample and Ω are the radius and angular velocity of the rolls. The apparatus sits in an air oven with a temperature range of 20–250°C and a control of $\pm 0.5^\circ\text{C}$.

The samples were prepared by a 0.75-in. Brabender Extruder with a special die ($D = 0.63$ cm, $L = 15.0$ cm). The screw speed was 10 rpm.

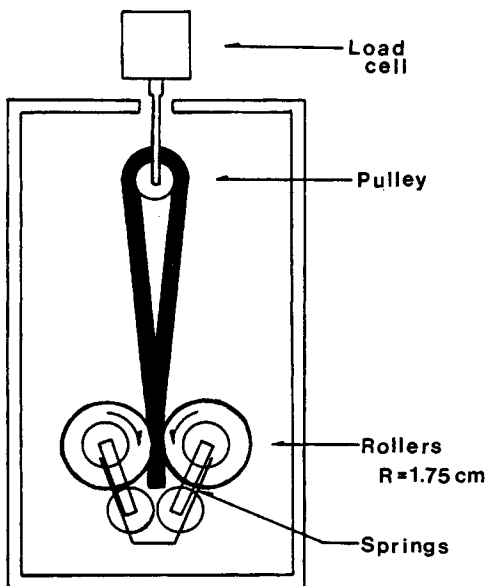


Fig. 3. Elongational flow rheometer for elastomers.

Stress Relaxation Measurements

The relaxation modulus $G(t)$ may be determined using the sandwich rheometer if there is a step shear strain input $\Delta L/H$ to the sample. Specifically

$$G(t) = \frac{\sigma_{12}(t)}{\gamma_0} = \frac{(F(t)/2A)}{(\Delta L/H)} \quad (5)$$

Friction Tester

The search for methods of measurement of slippage has a long history. Originally, Mooney⁴⁰ tried to use the variation in extrusion rate at constant shear stress to evaluate slippage. Later he proposed using smooth and rough serrated disks in a Mooney shearing disk viscometer.^{31,41} Both have the disadvantage of not considering the important influence of pressure. We have chosen instead an apparatus based on earlier concepts and designs of den Otter and Wales.⁴² This apparatus consists of a heated steel annular cylinder with inside diameter of 0.25 in. (see Fig. 4). The rubber sample used is placed between an upper force sensing piston and a lower (also force sensing piston). The apparatus is generally placed in a floor model Instron tensile tester. The temperature may be controlled in the range of 20–180°C and pressures measured from 5×10^8 Pa to 5×10^9 Pa. The mean shear stress on the wall of the cylinder is

$$\overline{\sigma_{12}(R)} = F_{\text{shear}}/2\pi RL_p \quad (6)$$

where R is the cylinder radius and L_p the length of the plug. [The local shear stresses $\sigma_{12}(R, x_1)$ must vary with position along the length of the plug, especially in the neighborhood of the pistons.] More details are given by Toki.⁴³

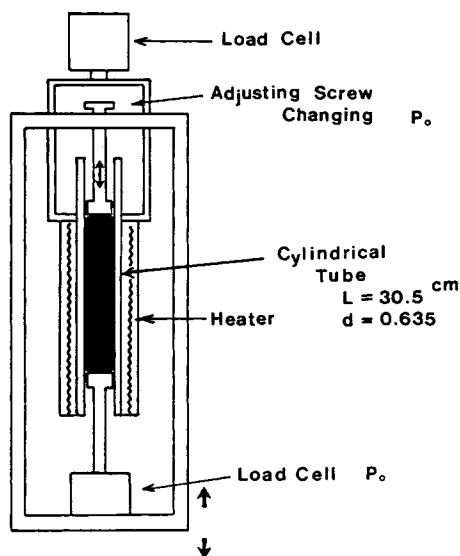


Fig. 4. Friction tester for elastomers.

MATERIALS

The elastomers investigated in this study were an emulsion-polymerized butadiene-styrene copolymer, an SBR 1500, supplied by B. F. Goodrich, and an alkyl lithium-polymerized polybutadiene, Firestone Diene 35 NFA (BR).

Compounds of SBR 1500 with R-HAF (N-326) carbon black were prepared on two-roll mill at 80°C. Carbon black loadings with volume fractions $\phi = 0.05$, $\phi = 0.15$, and $\phi = 0.3$ vol % were prepared.

RESULTS OF RHEOLOGICAL EXPERIMENTS ON GUM ELASTOMERS

Shear Viscosity

We present the shear viscosity as a function of shear rate for both the SBR and BR at 100°C in Figure 5. The gum elastomers generally exhibited severe extrudate distortion in the capillary rheometer.

It may be seen that the shear viscosity approaches a constant η_0 at low shear rates and decreases with increasing shear rate. The zero shear viscosity is approached at a shear rate of 10^{-5} s^{-1} for the BR and 10^{-7} s^{-1} for the SBR. It has a magnitude of $4.0 \times 10^6 \text{ Pa}\cdot\text{s}$ for the BR and around $8 \times 10^8 \text{ Pa}\cdot\text{s}$ for the SBR. Data on a commercial polystyrene (PS) (Dow Styron 678U) at 170°C²⁶ are shown to represent this type of material. The zero shear viscosity is $10^5 \text{ Pa}\cdot\text{s}$ and is orders of magnitude lower than that of the SBR. The viscosities at higher shear rates are much closer.

Discrepancies between sandwich and capillary data are seen at high shear rates. This may come from unstable flow and slip occurring in capillary extrusion of elastomers. Slippage effects are well known in these materials.^{21,42,44}

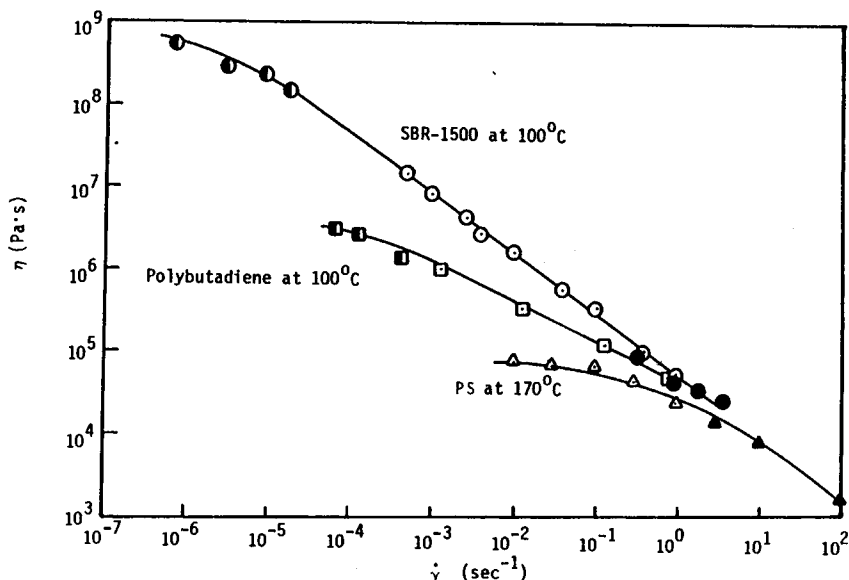


Fig. 5. Steady state shear viscosities of SBR-1500, polybutadiene, and polystyrene as a function of shear rate. Measured by: (●, ■) creep experiment; (○, □, △) constant shear rate sandwich viscometer; (●, ▲) capillary rheometer.

Elongational Flow

Transient elongational viscosity data for SBR 1500 at 100°C are shown in Figure 6. A steady state was not achieved. Transient viscosities as high as 5×10^7 Pa·s were obtained.

Stress Relaxation

Stress relaxation data for the SBR 1500 at 100°C are shown in Figure 7.

We have sought to analyze this data using the Tobolsky–Murakami⁴⁶ Procedure X. This involves writing

$$G(t) = \sum G_i e^{-t/\tau_i} \quad (7)$$

where the τ_i are relaxation times. The maximum τ_i , i.e. τ_m , is determined by plotting $\log G(t)$ vs. t . This leads to a maximum relaxation time τ_m of order 10^5 s at 100°C.

RESULTS OF RHEOLOGICAL PROPERTIES OF RUBBER COMPOUNDS

Shear Viscosity

Viscosity-shear rate (Fig. 8) and viscosity-shear stress (Fig. 9) data on the compounds indicate that the viscosity level is raised and yield values Y are developed. No yield value is observed with a volume loading of 0.05. As carbon

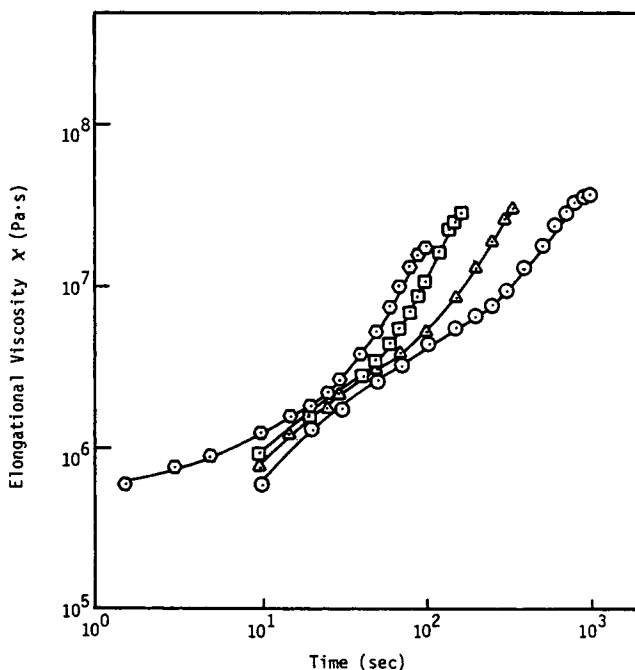


Fig. 6. Elongational viscosity E as a function of time for SBR-1500 at 100°C (s^{-1}): (○) 2.49×10^{-3} ; (Δ) 8.09×10^{-3} ; (◻) 1.85×10^{-2} ; (◇) 2.80×10^{-2} .

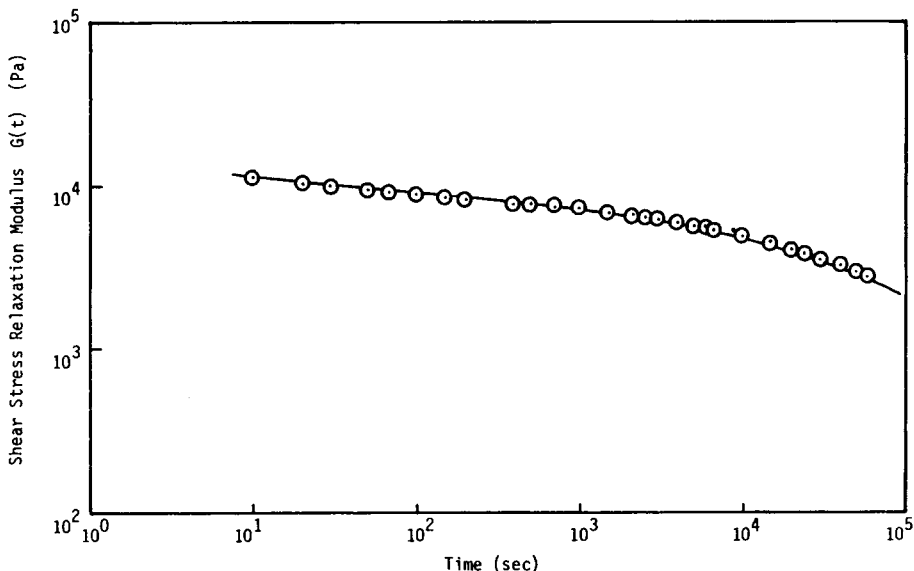


Fig. 7. Shear stress relaxation modulus as a function of time for SBR-1500 at 100°C. The solid line represents calculated values of discrete relaxation terms.

black volume loading varies from 0.15 to 0.3, Y varies from 7×10^2 to 1.2×10^4 Pa.

Clear evidence of slip in the sandwich viscometer at higher shear rates was found and is indicated in Figures 8 and 9. Some discrepancies with capillary data were also found.

Elongational Flow

Transient elongational viscosity-time curves at various elongation rates are shown in Figure 10. Though values of the transient elongational viscosity as high as 10^8 Pa·s were obtained, a steady state was not achieved. The addition of carbon black reduces the elongation to break.

FRICION TESTER RESULTS

We present the measured mean shear stress as a function of pressure for SBR-1500 at 100°C in Figure 11. At low velocities or shear rates, the shear stress is independent of pressure. At higher velocities, the shear stress increases with pressure. At these higher velocities, under some conditions the straight lines change slope or jump in magnitude at certain pressures. The pressure at the inflection point or discontinuity increases the shear rate.

Clearly there seems to be a change in deformation regime occurring here. At low velocities, we seem to be seeing the response of a pressure independent viscosity. At higher velocities, the pressure dependence of the shear stress implies a transition toward a mechanism of a solid slipping over a steel surface. We generally observe an inflection or point of discontinuity. These results may be an indication of the occurrence of slip. Comparison of elastomers and com-

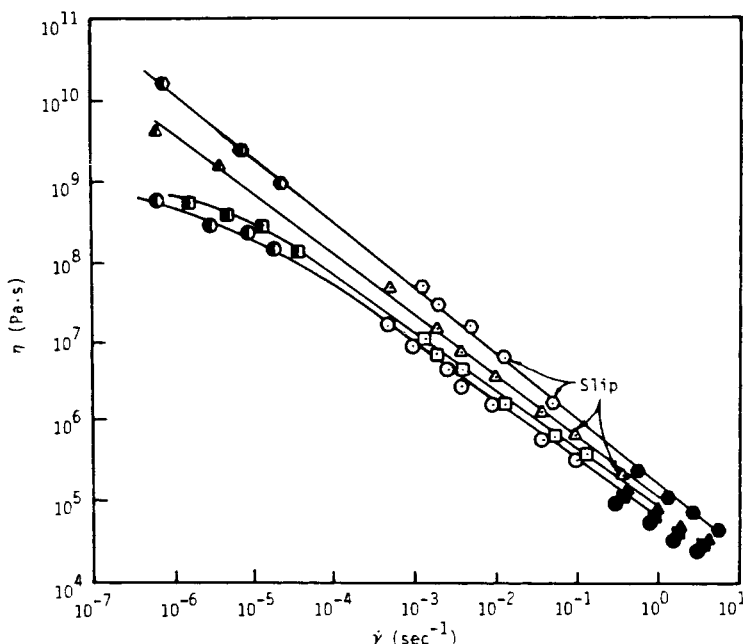


Fig. 8. Steady state shear viscosities of SBR-1500 and its compounds as a function of shear rates: Measured by: (●, ■, ▲, ●) creep experiments; (○, □, △, ○) constant shear rate sandwich viscometer; (●, ■, ▲, ●) a capillary rheometer: $\phi = 0.0(\circ), 0.05(\square), 0.15(\triangle), 0.30(\odot)$.

pounds (Fig. 12) shows carbon-black-filled rubbers are more likely to exhibit such inflections than pure rubber at the same shear rate/velocity.

DISCUSSION

The results of the present study must be considered preliminary, but they do bring out certain very important points. The first important results are the very high viscosities and relaxation times of the elastomers, especially the SBR-1500 at its processing temperature compared to those of molten polyolefins and polystyrene at their processing temperatures. The polystyrene (PS) of Figure 4 has an η_0 of 10^5 Pa·s at 180°C as opposed to near 10^9 for the SBR. The PS has a maximum relaxation time τ_m of order 10 s as opposed to nearly 100,000 s for the SBR. There is a difference of four orders of magnitude in both η_0 and τ_m . One should not be misled by relatively low viscosities at high shear rates.

The measured characteristics of the BR suggest that narrower molecular weight distribution commercial elastomers will have much lower η_0 than broad distribution polymers such as the SBR. This is inherent in the Vinogradov-Malkin formulation^{6,47}:

$$\eta(\dot{\gamma}) = \eta_0 F_{\text{MWD}}[\eta_0 \dot{\gamma}] \quad (8)$$

where we have indicated that F_{MWD} depends upon molecular weight distribution. F_{MWD} falls off more rapidly with broadening molecular weight distribution. If $\dot{\gamma}$ and the value of η at this $\dot{\gamma}$ are fixed, η_0 must be larger for materials where F_{MWD} falls off more rapidly.

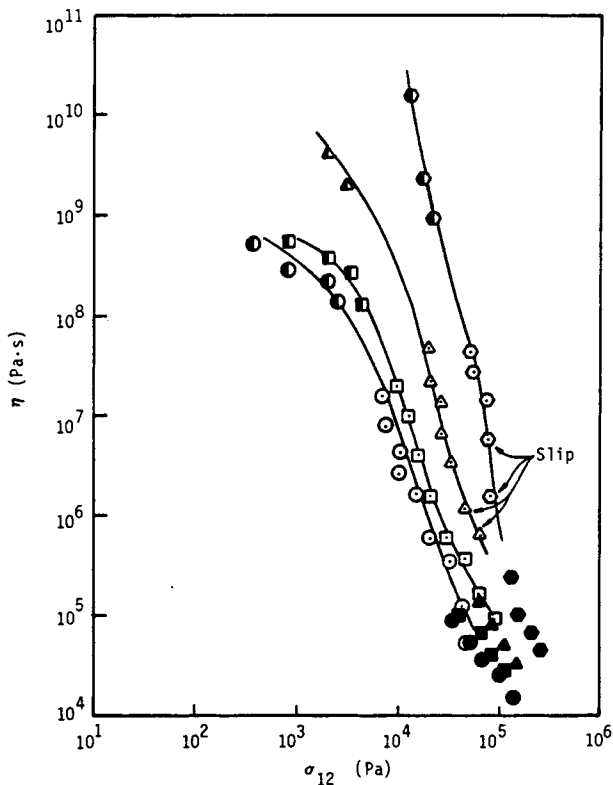


Fig. 9. Steady state shear viscosities as a function of shear stress of SBR-1500 and its compounds: Measured by: (●, ■, ▲, ●) creep experiment; (○, □, △, ⊙) constant shear rate sandwich viscometer; (●, ■, ▲, ●) a capillary rheometer. $\phi = 0.0(\circ), 0.05(\square), 0.15(\triangle), 0.30(\diamond)$.

Rubber compounds are soft solids rather than fluids. The yield value of a 30 vol % carbon black compound of SBR is in excess of 10^4 Pa. These yield values are very similar to those exhibited by polystyrene-carbon black compounds at the same volume loading.^{28,29} Tanaka and White²⁹ report no yield value at a volume loading of 0.1 and a value of 1.0×10^4 Pa for a 0.3 loading of N542 carbon black. The magnitude of yield values seems largely dependent on the type and loading level of the carbon black rather than the polymer matrix.

The problem of cold flow of elastomers is well known to be related to η_0 .¹⁸ Elastomers exhibit orders of magnitude less cold flow than molten plastics. The narrower molecular weight distribution elastomers exhibit more cold flow than broader distribution elastomers. The presence of carbon black in elastomers is known to eliminate cold flow. This is due to the existence of a yield value.

In analyzing the flow of rubber compounds, one must use rheological models which contain yield values and exhibit memory effects. Such a model has been developed by one of us^{28,48} and applied to polystyrene filled with carbon black, calcium carbonate, and titanium dioxide.^{28,49}

Elastomers and their compounds appear subject to slip upon conditions akin to those in processing operations. The specification of slip and its dependence upon dual shear stress, pressure, and temperature remains one of the most im-

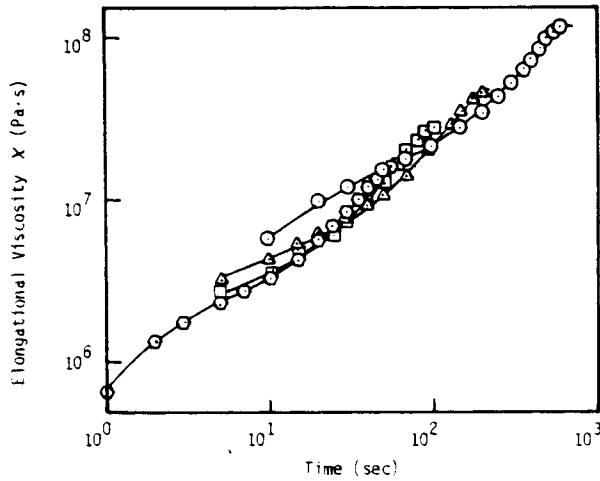


Fig. 10. Elongational viscosity E as a function of time for SBR-1500 compounds ($\phi = 0.3$) at 100°C (s^{-1}): (\odot) 2.49×10^{-3} ; (Δ) 8.09×10^{-3} ; (\square) 1.85×10^{-2} ; (\diamond) 2.80×10^{-2} .

portant unsolved problems in polymer processing. The shear stress levels we observed at the apparent discontinuities are generally of the same order as those found by Vinogradov et al.^{21,42} for extrusion through dies.

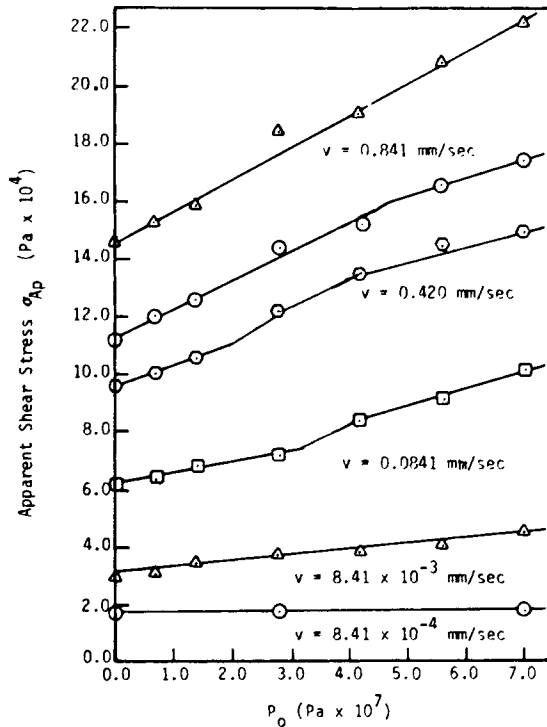


Fig. 11. Apparent shear stress as a function of pressure P_0 for SBR-1500 at 100°C . $V = 2.10$ mm/s.

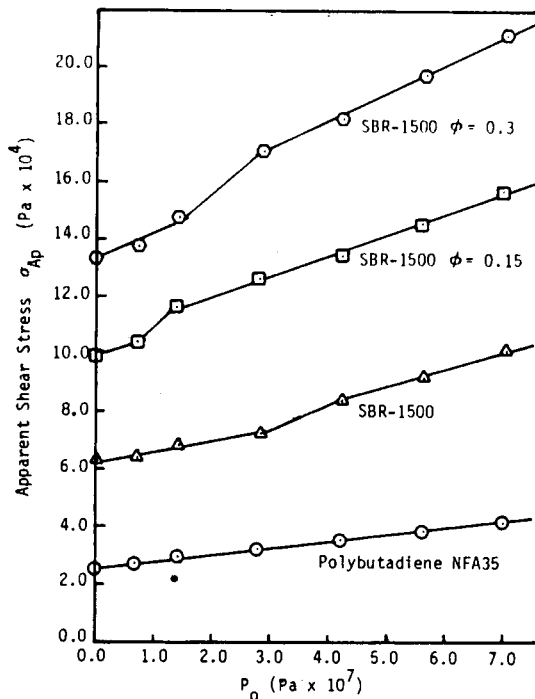


Fig. 12. Apparent shear stress of elastomers and compounds at $v = 8.41 \times 10^{-2}$ mm/s, $\dot{\gamma} = 1.06 \times 10^{-1}$ s $^{-1}$.

CONCLUDING REMARKS

The major contribution of this paper was the presentation of new experimental data on elastomers and compounds from a series of newly built instruments: (i) a sandwich viscometer for creep, constant shear rate and stress relaxation modes; (ii) an elongational rheometer; (iii) a friction tester. Specific important results are given below

(1) SBR 1500 at 100°C was found to exhibit a constant viscosity η_0 at low shear rates which decreases with increasing shear rate. The value η_0 is quite large (8×10^8 Pa·s) compared to data for typical thermoplastic melts (10^4 – 10^5 Pa·s) under the conditions they are processed. The maximum relaxation time τ_m was determined to be 10^5 s compared to about 10 s for thermoplastics. It was not possible to obtain steady state elongational viscosity. The polybutadiene studied had an η_0 of 4×10^6 Pa·s and did not exhibit as large deviations from Newtonian flow.

(2) The SBR 1500–carbon black compounds exhibited yield values in shear flow at volume loadings of 0.15 and higher. The magnitudes of these yield values are close to those observed in studies of carbon black–polystyrene compounds of similar value loadings. This suggests that, at low deformation rates, it is the filler rather than the matrix which is determining the rheological properties.

(3) The SBR 1500 and its compounds were found to slip in the sandwich rheometer at higher shear rates and probably also in the capillary rheometer. The extrudates were always rough and computed shear stresses and viscosities lower than expected.

(4) Friction tester experiments indicated that the shear stress was independent of pressure at low velocities suggesting there was no slip in the instrument and the viscosity independent up pressure. At higher velocities, the shear stress becomes an increasing function of linear velocity, sometimes exhibiting possible near discontinuities in the shear stress–pressure curve. This suggests a transition to a solid slipping process, especially at low pressures. This was most accentuated in the SBR compounds.

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