

The Influence of Carbon Black on the Extrusion Characteristics and Rheological Properties of Elastomers: Polybutadiene and Butadiene-Styrene Copolymer

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Synopsis

An experimental study of the influence of carbon black loading, particle size, and structure on the extrusion characteristics of polybutadiene and butadiene-styrene copolymer synthetic rubber is described. The development of extrudate distortion and its mechanisms are considered. The viscosity and die swell have been related to black loading, particle size, and structure. Generally, it is found that black surface area and structure acts to increase viscosity and decrease elastic memory. This situation is analyzed in terms of the theory of nonlinear viscoelasticity. Two mechanistic theories are described which may explain this behavior. One theory is based on the continuum mechanics analysis of suspensions of particles in viscoelastic media. The rheological behavior of the black compounds is explained in terms of the increased severity of deformation in the polymer matrix surrounding the particle agglomerates. The second theory is based on the view of an entanglement network containing black particles. Polymer chains may be adsorbed onto the surface giving rise to increased entanglement densities.

INTRODUCTION

Certainly, the introduction of carbon black in 1912 as an additive or compounding ingredient ranks second only to the development of the vulcanization process in its importance as a technological innovation in the rubber industry. The presence of carbon black in vulcanized rubber enormously enhances such properties as elastic modulus, tensile strength, and abrasion resistance¹⁻⁶ and through these makes possible high-quality products of commerce such as the modern tire. These commercial carbon blacks are spherical particles with diameters of order 150-500 Å and tend to exist in fused chain-like agglomerates which are referred to as structure.^{3,7,8}

Discussions of the influence of carbon black on rubber usually center on the characteristics of the vulcanizate, and little mention is given to the effects of black on unvulcanized elastomers. This is, however, also an

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important problem, for rubber compounds must be fabricated in this state to produce the components which are to be vulcanized. Experimental studies of the processing, especially the extrusion of rubber compounds, date back twenty to fifty years.⁹⁻¹⁷ There have been a number of reports indicating the qualitative features of the influence of carbon black on the rheological properties of unvulcanized rubber. The first characteristic noted was the increase in viscosity with increasing black loading^{4,18-22} and the apparent thixotropic behavior of the compounds.²³ It was also found that, at constant loading, viscosity increased with decreasing particle size or increasing surface area.^{3,19,21} Perhaps even more important from a practical fabricating point of view was the great improvement in extrusion characteristics, particularly decreases in die swell and extrudate distortion with not only increasing carbon black loading^{3,4,19,20,22} but also with increasing black surface area at constant loading.^{3,4,19,20} As uncompounded elastomers usually exhibit severe extrudate distortion even at rather low extrusion rates,^{21,24} it is probably no understatement to say that modern rubber-processing techniques would not be possible for many products without the beneficial influence of carbon black. However, the available information on the influence of carbon black on the rheological properties of unvulcanized rubber compounds is far from complete. (For discussions of rubber-processing equipment and the interaction between rheology and processing, see the surveys of Mooney¹⁷ and White and Tokita.^{25,26})

The rubber industry has come to realize during the past five or so years that it is moving into a new era. The past few years have seen the introduction of superior performing radial ply tires in the American market place which require greater uniformity and quality of their components during building. The inadequacy and inefficiency of traditional processing equipment and materials handling has been realized, and there has been a major effort made to develop new process designs, largely based on extrusion to fabricate new products such as radial ply tire components. Indeed, from a period in which processing was to some extent ignored, the rubber industry must enter a new age in which considerable sophistication is required. Claude Allard, President of the Uniroyal Tire Company, has recently written²⁷:

"The conversion of the tire industry to radial ply tires further complicates the needs placed on polymers because at the high order of stable properties required by these much more precise constructions. The degree of sophistication dictates a whole order of magnitude of improvement in polymer uniformity particularly rheological uniformity. This is an area in which our older standard test procedures are proving inadequate. . . . Intensive mixers other than the time honored Banbury-mill combinations are needed. One example of the type of equipment required . . . exists in . . . [the] . . . Transfermix. . . . The Transfermix provides enforced mixing through the shearing action of stock changing its direction of flow as it passes four times through the interface between the barrel and the screw [of an extruder]."

Allard and others²⁰⁻³¹ (including various individuals in the rubber industry who have privately spoken with the author) see extrusion-type operations

playing an increasing role in a rubber fabrication industry with tightening quality control.

This growth of importance of extrusion of rubber compounds demands basic studies of the rheology of unvulcanized compounds and of the extrusion process. This paper, we hope, represents a step in this direction. Specifically, it is the purpose of this paper to (1) present an experimental study of the influence of carbon loading, particle size, and structure on the extrusion behavior and rheological properties of three synthetic elastomers (two polybutadienes and a butadiene-styrene copolymer), (2) to attempt to explain these rheological characteristics within the framework of the theory of viscoelastic fluids by looking at the influence of black on the relaxation modulus function, and (3) to discuss mechanistic theories which explain the variation in the relaxation modulus function.

EXPERIMENTAL

Materials

The elastomers studied in this program were two polybutadienes, made by a Ziegler catalyst (Phillips Cis-4) and an alkyl lithium catalyst (Firestone Diene 35NF) and a 23.5% styrene copolymer of butadiene which is polymerized in emulsion (Texas-US Chemical Synpol 1500). The three elastomers will be designated BR-1, BR-2, and SBR in this paper. The microstructures and molecular weight distributions determined by osmometer and gel permeation chromatograph³² are summarized in Table I.

A series of five different types of carbon blacks manufactured by Continental Carbon were used. The blacks were chosen so as to exhibit variations in particle diameter and structure, which allows studies of compounds with constant volume loading and structure but varying particle diameter and at constant volume loading and particle diameter but varying structure. The carbon blacks and their characteristics are summarized in Table II.

TABLE I
Characteristics of Elastomers Studied

Code	Material	Styrene content	Butadiene microstructure			$\frac{M_w}{M_n}$ (GPC)	M_n (osmometer)
			<i>cis</i> -1,4	<i>trans</i> -1,4	1,2		
BR-1	polybutadiene (Phillips Cis-4)	0	93%	—	—	3.35	118,500
BR-2	polybutadiene (Firestone Diene 35 NF)	0	37	65	8	2.8	90,000
SBR	butadiene-styrene copolymer (Texas-US Chemical Synpol 1500)	23.5	10	70	20	5.4	72,000

TABLE II
Characteristics of Carbon Blacks

Carbon black type (continental carbon designation)	Surface area, m ² /g	Particle diameter, Å	Surface DBP absorption, cm ³ /100 g
ISAF-LS ASTM N-219	123	230	78
FEF-LS ASTM N-542	47	450	67
SRF-LM	25	800	72
FEF-LM ASTM N-539	42	470	108
FEF ASTM N-568	50	440	133

Compound Preparation

All compounds were prepared using a basis of 400 g elastomer, and mixing was carried out on a laboratory mill having 3-in. by 7-in. rolls. The front and rear rolls were run at 20 and 24 rpm, respectively, and were heated to 95°C. The average milling time was 15 min. As a control, 400 g uncompounded batches of each elastomer were also milled for approximately the same period at 95°C. All batches were allowed to stand at room temperature for 24 hr before their rheological properties were determined.

Extrusion Studies

The extrusion characteristics of each compound were determined with an Instron capillary rheometer operating in an Instron tensile testing machine. This is the same rheometer used in many of our earlier studies on extrusion.^{24,33} A series of stainless-steel 180°-entrance-angle capillary dies with an average diameter of 0.052 in. and L/D ratios of 5.01, 9.88, and 20.22 were used. The extrusion was carried out at 100°C.

Visual observations were made of the extrudates over the entire operating range using a laboratory optical microscope. The character of the extrudate was noted and the approximate diameter measured with a calibrated eyepiece.

Plots of the total pressure drop in the rheometer as a function of L/D were used to determine the entrance pressure loss Δp_e and capillary wall shear stress $(\sigma_{12})_w$ through the expression^{24,34,35}

$$P_T = 4(\sigma_{12})_w \left(\frac{L}{D} \right) + \Delta p_e \quad (1)$$

where 1 is the direction of flow and 2 is the direction of shear. Presuming that there is no slippage and the flow is laminar and fully developed, the capillary wall shear rate may be determined³⁶ from

$$\Gamma_w = \left(-\frac{du}{dr} \right)_w = \left(\frac{3n' + 1}{4n'} \right) \frac{32Q}{\pi D^3} \quad (2a)$$

with

$$n' = \frac{d \log (\sigma_{12})_w}{d \log 32Q/\pi D^3} \quad (2b)$$

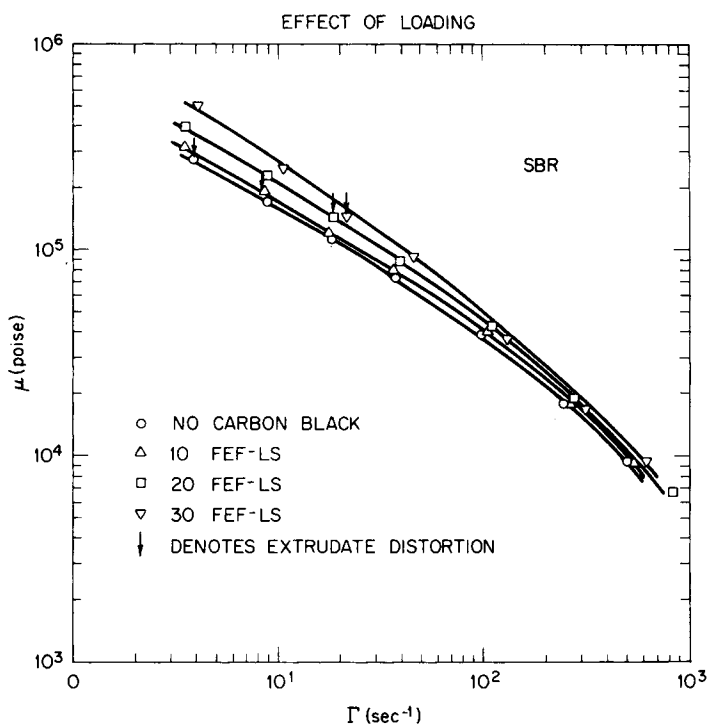


Fig. 1. Influence of carbon black loading (parts black per 100 parts of rubber) on the viscosity-shear rate behavior of SBR compounds. The data for the SBR without carbon black are for the milled sample.

RESULTS

Shear Viscosity

Despite the existence of varying levels of extrudate distortion, the viscosity for the materials under study was determined using eqs. (1) and (2). The results are presented in Figures 1 through 7. In general, the loading parameter seems to contribute most to the reinforcement of the elastomers. An increase in the viscosity is noted as the carbon black loading is increased, with the greatest effect being at low shear rates.

The effect of carbon black particle size on the viscosity was studied by holding the loading and structure levels constant. Specifically, it was found that decreasing particle sizes produced corresponding increases in the viscosity of all materials.

By holding the loading and particle size constant, the effect of carbon black structure on the viscosity was examined. While increases in structure did indeed produce increases in viscosity, in general the effect was not as pronounced as that obtained with decrease in particle size.

Extrudate Character

Visual observations were made of the elastomer extrudates over the range of capillary wall shear rates from 3 to 1000 sec^{-1} , calculated from eq. (2).

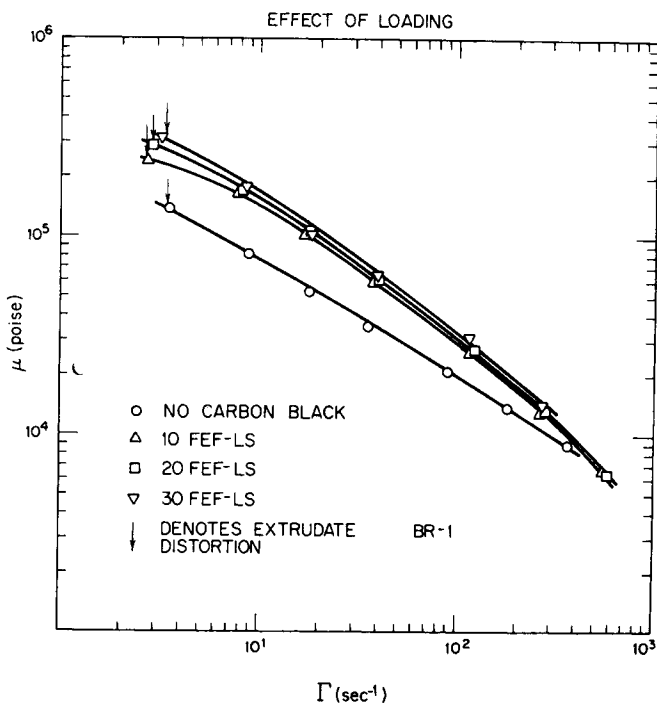


Fig. 2. Influence of carbon black loading (parts black per 100 parts of rubber) on the viscosity-shear rate behavior of BR-1 compounds. The data for the BR-1 without carbon black are for the milled sample.

It is difficult to pinpoint the extrusion rate or capillary wall shear rate at which extrudate distortion begins; because the Instron rheometer operates with finite jumps in extrusion rate, the actual point at which distortion begins and the point at which it was first observed will differ. This problem presents some difficulties in reporting the effects of carbon black on extrudate distortion. In some cases, while the severity of the distortion is observed to decrease with a change in carbon black parameter, the phenomenon is still observed to occur at the same extrusion rate. However, since it was also observed that, once distortion occurs, increasing the extrusion rate tends to increase the severity, the decrease in severity at a given extrusion rate may be interpreted as an increase in the extrusion rate at which the distortion actually first began.

The extrudates of unmasticated uncompounded SBR were found to be grossly distorted over the entire range of extrusion rates studied. Increasing the extrusion rate increased the severity of the distortion and sometimes gave rise to circular ridges on the grossly distorted extrudate. The extrudates of masticated SBR exhibited much the same behavior as that seen with the unmasticated samples. Although there was some hint of a screw thread distortion at the lowest extrusion rates, the samples remained grossly distorted over the entire range of study.

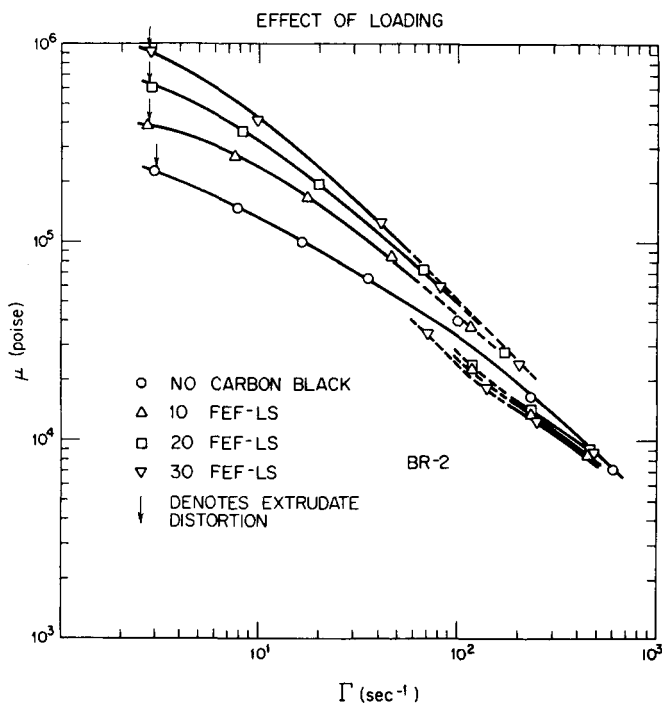


Fig. 3. Influence of carbon black loading (parts black per 100 parts of rubber) on the viscosity-shear rate behavior of BR-2 compounds. The data for the BR-2 without carbon black are for the milled sample.

The addition of carbon black to the SBR resulted in smoother extrudates. With the exception of a few extrudates with fine-scale roughness, the majority exhibited smooth surfaces at the lowest extrusion rates. As the extrusion rate was increased, a surface irregularity of a mesh or ridged form was observed, and further increases in rate brought the gross distortion observed in the compounded samples. Increases in carbon black loading and structure and decreases in particle size gave definite increases in the extrusion rate required to produce both surface irregularities and gross distortion. In general, there was no L/D effect observed for the surface irregularities of the SBR compounds, but the gross distortion was found to decrease with increasing L/D .

The extrudate characters of both unmasticated polybutadienes were found to be very similar. At the lowest shear rates, a surface irregularity of the mesh type was observed. As the extrusion rate was increased, the irregularity first took the form of joined ridges and then progressed into separate ridges somewhat resembling a cone within a cone. Further increases resulted in a region of oscillating forces (measured by the Instron load cell), with the extrudate being ridged during increasing force and grossly distorted during decreasing force. The oscillations were much larger for the BR-2. As the extrusion rate was increased through this

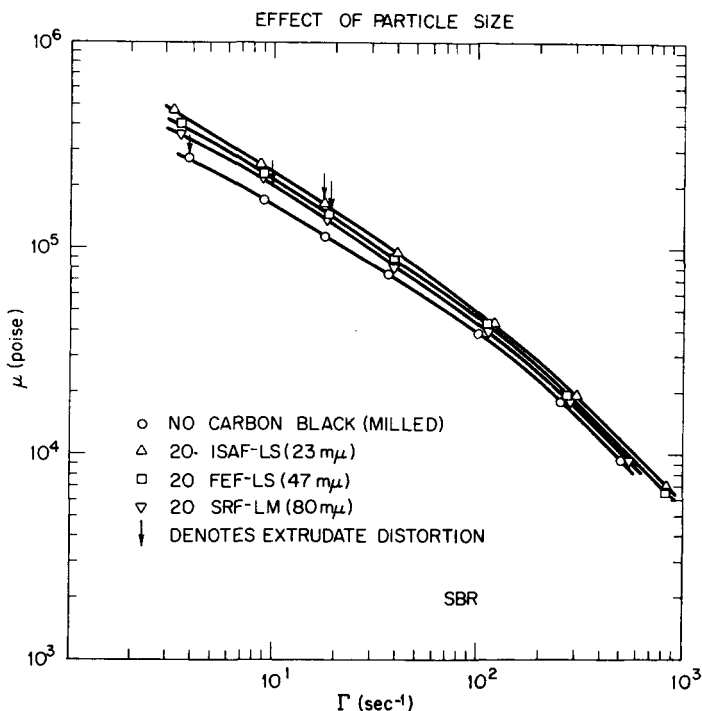


Fig. 4. Influence of carbon black particle size on the viscosity-shear rate behavior of SBR compounds at constant loading and structure.

region, the ratio of the amount of grossly distorted extrudate to the amount of ridged extrudate increased. At higher extrusion rates, the extrudates were grossly distorted. An illustration of the different types of distortion observed is given in Figure 8. After mastication, both polybutadienes began to exhibit gross distortion even at the lowest shear rates. While some surface irregularity was observed at intermediate extrusion rates in the BR-2 samples, the BR-1 samples exhibited only gross distortion throughout the entire range of shear rates studied. The region of oscillating force found in the unmasticated samples was not observed.

Addition of carbon black and increases in carbon black loading and structure and decreases in particle size reduced the severity of the distortions and force oscillations during extrusion of the polybutadiene. However, the various distortion phenomena were observed to occur in the same manner and at approximately the same extrusion rates as in the unmasticated samples.

The effect of die L/D ratio on the distortion of the polybutadienes was the same regardless of whether the sample was unmasticated, masticated, or uncompounded. In general, there was no L/D effect observed for the surface irregularity or stress oscillation regions, but the gross distortion was found to decrease with increasing L/D .

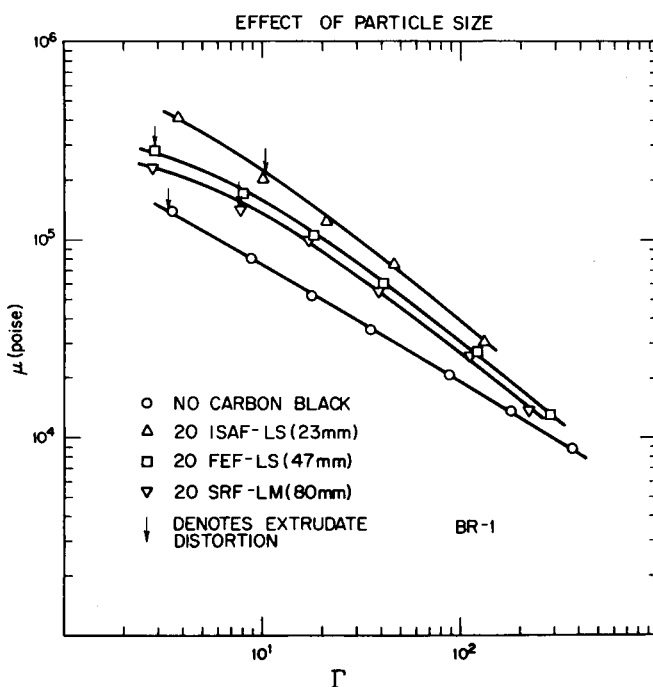


Fig. 5. Influence of carbon black particle size on the viscosity-shear rate behavior of BR-1 compounds at constant loading and structure.

Die Swell

Because of extrudate distortion, the amount of die swell information obtained is somewhat limited. The greatest amount of reliable data was obtained at the lowest extrusion rate studied corresponding to a capillary wall shear rate of (approximately 3 sec^{-1}) and is presented in Figures 9 through 11 as a function of L/D . The level of the die swell of the polybutadienes was generally higher than the SBR's. The die swell of all materials measured was found to increase with increasing extrusion rate and to decrease with increasing L/D . Since increasing extrusion rate and decreasing L/D result in shorter capillary residence times, the emerging materials more clearly remembers its state prior to capillary entry and the resulting extrudate die swell is greater.

The effect of the addition of carbon black to the elastomers was as expected. Generally, increases in carbon black loading and structure and decreases in particle size produced corresponding decreases in extrudate die swell. There was a reversal in the effect of structure on the die swell of BR-1. While examination of the data would seem to indicate an approximately equal effect of the three parameters on the die swell of the elastomers, it should be realized that the absolute accuracy of the measurements may not be reliable due to the presence of surface roughness on some of the samples.

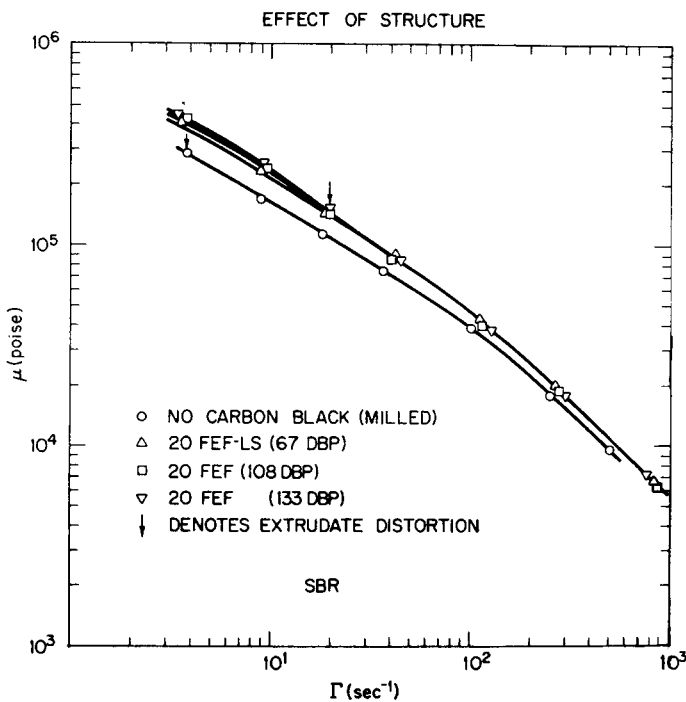


Fig. 6. Influence of carbon black structure on the viscosity-shear rate behavior of SBR compounds at constant loading and particle size. Structure is given in DBP adsorbed in cm^3 per 100 g rubber.

Entrance Pressure Drop

Typical experimental entrance pressure drops are illustrated in Figures 12 and 13. The effect of increased carbon black loading and decreased particle size was to decrease the entrance pressure drop at low shear rates. The effect of structure is not clear. The somewhat random nature of the data at lower extrusion rates is probably due to inaccuracies in determination of pressure (L/D) ratio slopes. At high extrusion rates, the data have inaccuracies due to unstable flow.

DISCUSSION

Shear Viscosity

The incorporation of carbon black into the elastomers resulted in increased viscosities for all samples studied, with the greatest effect being at the low shear rates. The influence of the black on viscosity decreases as shear rate increases.

The relative effects of the carbon black loading (as volume fraction of black ϕ), particle size, and structure on the viscosity of each elastomer can be seen in Figures 14 through 17. Also included on these plots are data from Thomas³⁷ for uniform spheres in Newtonian liquids. The viscosity

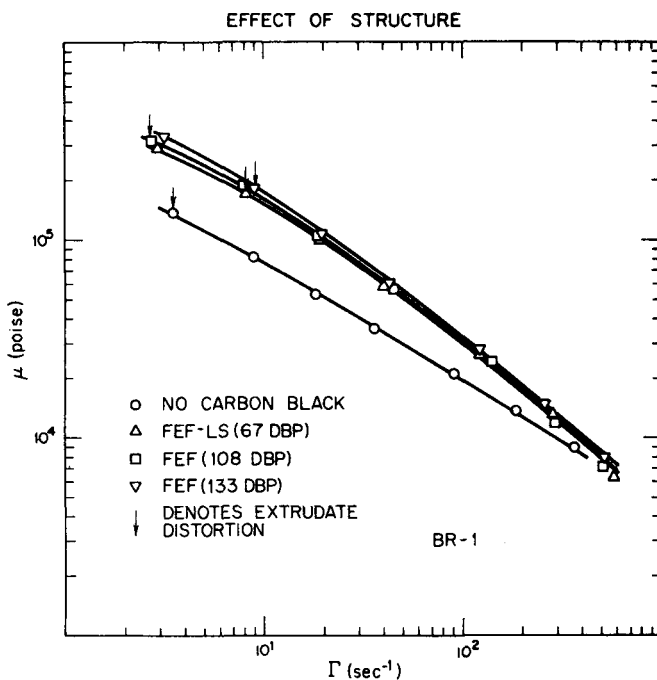


Fig. 7. Influence of carbon black structure on the viscosity-shear rate behavior of BR-1 compounds at constant loading and particle size. Structure is given in DBP adsorbed in cm^3 per 100 g rubber.

level increases with loading and the BR-1 and BR-2 data are substantially higher than the sphere data. Note that the relative viscosity for the SBR is in the range of the data for uniform spheres in Newtonian liquids. This is an interesting result, since the effect of incorporating carbon black is generally assumed to be greater than that arising from hydrodynamic interaction. Part of the apparent lower reinforcing quality of the viscosity may well be due to the greater rate of mastication-induced degradation of SBR relative to BR.³⁸

Decreasing particle diameter d_p at fixed loading decreases viscosity. This suggests that black surface area (proportional to ϕ/d_p) may be a key parameter in correlating the data. Our experimental data are plotted in Figure 17, where the relative increase in shear viscosity $(\mu - \mu_0)/\mu_0$ is plotted versus carbon black surface area for blacks with varying particle diameter but similar structure. A very much improved correlation is found.

Increasing the level of black structure at constant loading acts to increase the viscosity. If we take into consideration the discussion of the previous paragraph, it would seem that, if we were to write the increase in relative viscosity with black addition as the general function

$$\frac{\mu - \mu_0}{\mu_0} = F(\phi, d_p, k, \Gamma^2) \quad (3)$$

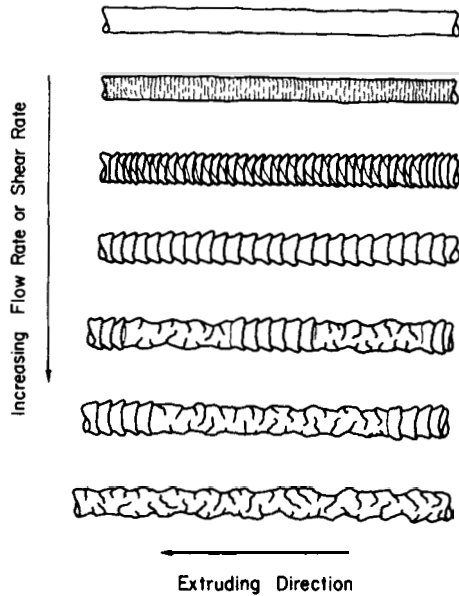


Fig. 8. Figure represents regions of extrudate distortion observed in gum and compounded elastomers. Beginning at the lowest flow rate, the first extrudate sketched is considered smooth. The second, third, and fourth extrudates possess increasing levels of " L/D -independent" surface irregularity distortion. The fifth and sixth extrudates exhibit a mixed region of distortion where there are often force oscillations. The sixth extrudate represents a grossly distorted extrudate.

where k is a measure of black structure. To a first approximation we may regroup the variables as

$$\frac{\mu - \mu_0}{\mu_0} = F\left[\frac{\phi k}{d_p}, \Gamma^2\right]. \quad (4)$$

A plot of this function is given in Figure 18 where we have used masticated gum polymer data for μ_0 . Use of the masticated polymer properties should minimize that influence of molecular degradation on the form of eq. (4). We have fit our data (seven compounds, plus the gum at seven shear rates or 56 data points for each polymer) with the equation

$$\frac{\mu - \mu_0}{\mu_0} = A(\Gamma^2) \left(\frac{\phi k}{d_p}\right) + B(\Gamma^2) \left(\frac{\phi k}{d_p}\right)^2 \quad (5)$$

where for k we have used the dibutyl phthalate adsorption in $\text{cm}^3/100 \text{ g}$. For the functions A and B we have obtained

$$\begin{aligned} A(\Gamma^2) &= a_1 - a_2[\Gamma^2]^{1/2} \\ B(\Gamma^2) &= b_1 - b_2[\Gamma^2]^{1/2}. \end{aligned} \quad (6)$$

The coefficients in eq. (6) are summarized in Table III for the three elastomers studied. Most attempts in the literature to develop expressions

TABLE III
 Constants in Equation (6) Relating Viscosity to Carbon Black Loading and Character^a

Material Code	a_1	a_2	b_1	b_2
SBR	3.4	0.015	6.0	0.024
BR-1	9.6	0.046	16.1	0.072
BR-2	14.3	0.150	18.0	0.140

^a Equations (5) and (6).

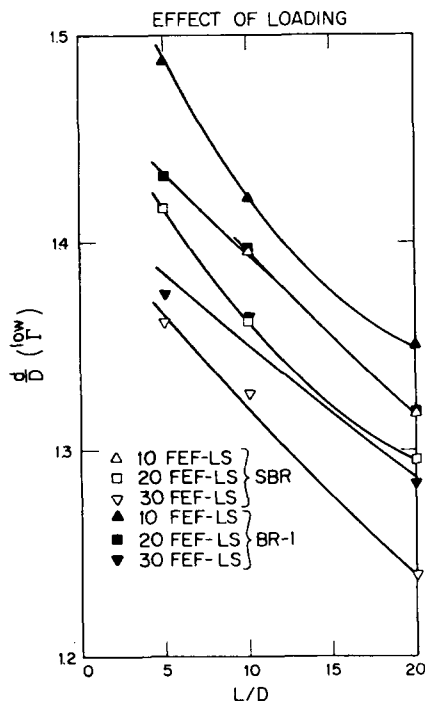


Fig. 9. Die swell of SBR and BR-1 extrudates as a function of carbon black loading (parts black per 100 parts of rubber) at a shear rate of 3 sec^{-1} at constant particle size and structure.

for the viscosity of rubber compounds in terms of filler content consider only the loading parameter³⁹.

Extrudate Character and Die Swell

The general distorted character of the extrudates investigated makes quantitative determination of die swell difficult. Increasing black levels, decreasing particle diameter, and increasing black structure decreased both extrudate distortion and die swell. This suggested that an attempt to correlated die swell at constant extrusion conditions (output rate, die diameter, L/D ratio) with the grouping $\phi k/d_p$. Such a correlation is

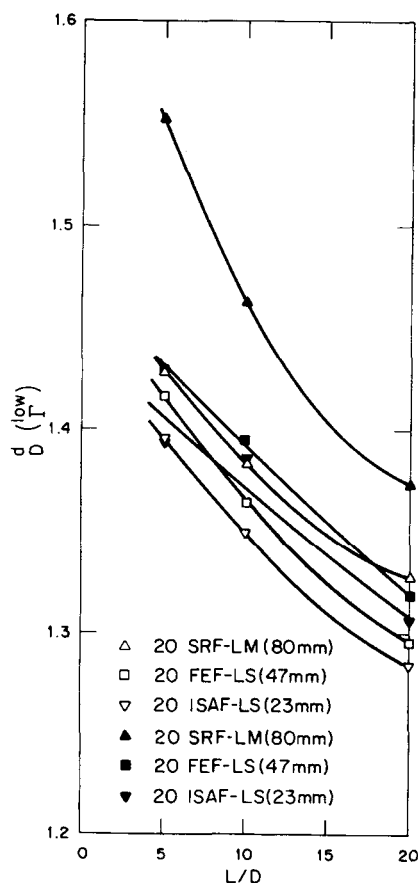


Fig. 10. Die swell of SBR (open symbols) and BR-1 (closed symbols) extrudates as a function of carbon black particle size at constant loading and structure.

shown in Figure 19. There is an enormous amount of scatter especially for the BR-2.

The extrudate character exhibited by the elastomers differs somewhat from that observed with molten plastics in which there is more extensive literature.^{24,33,40,41} There appear to be three regions of distortion, though each of the materials did not exhibit all of these regions. As the extrusion rate is increased through the range of smooth extrudates, a first region of distortion is encountered in which the extrudates exhibit a surface irregularity of either a ridged or cone-within-cone form. Further increases in extrusion rate result in a region of oscillating stresses, with the extrudate having surface irregularity during increasing stress and being grossly distorted during decreasing stress. At higher extrusion rates, the extrudates exhibit a third region of complete gross distortion.

Let us now look at the specific compounds in terms of these remarks. The unmastered styrene-butadiene copolymer exhibited grossly distorted

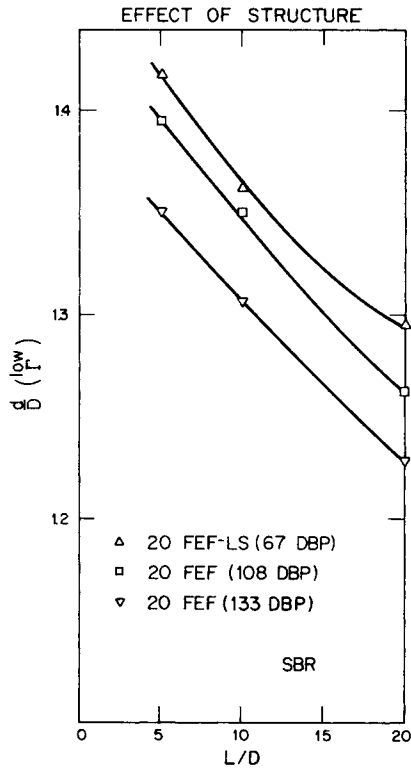


Fig. 11. Die swell of SBR compounds as a function of structure at constant loading and particle size. Structure is given in DBP adsorbed in cm^3 per 100 g rubber.

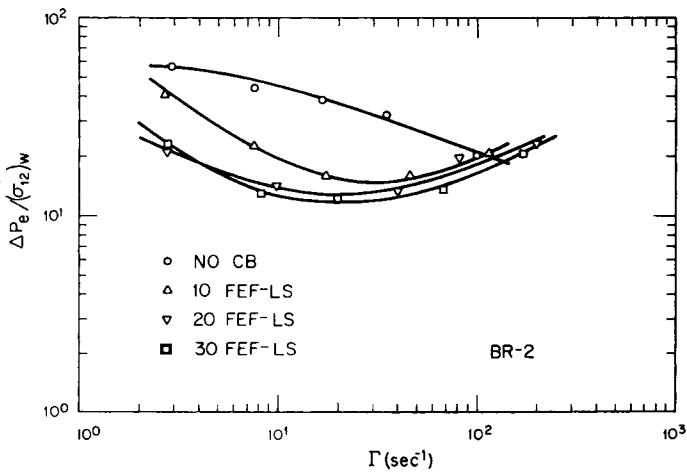


Fig. 12. Entrance pressure drop of BR-2 compounds as a function of carbon black loading (parts of black per 100 parts of rubber).

extrudates over the entire range of study. However, when the material was masticated or compounded with carbon black, surface irregularity (and not gross distortion) began appearing at the lower shear rates. The unmasticated polybutadiene extrudates exhibited surface irregularity,

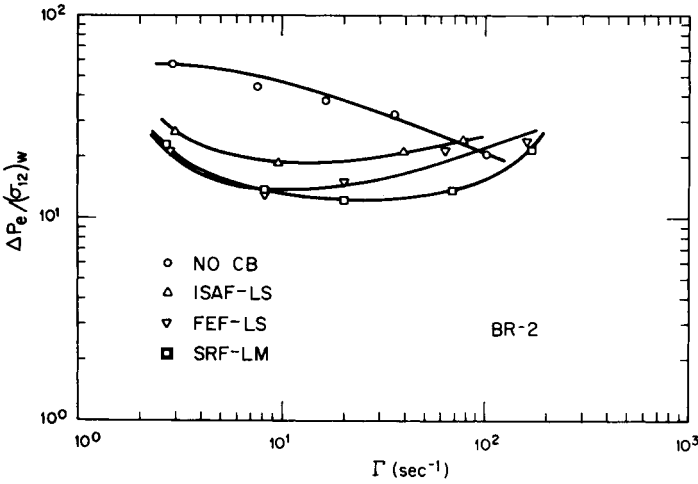


Fig. 13. Entrance pressure drop of BR-2 compounds as a function of carbon black particle size.

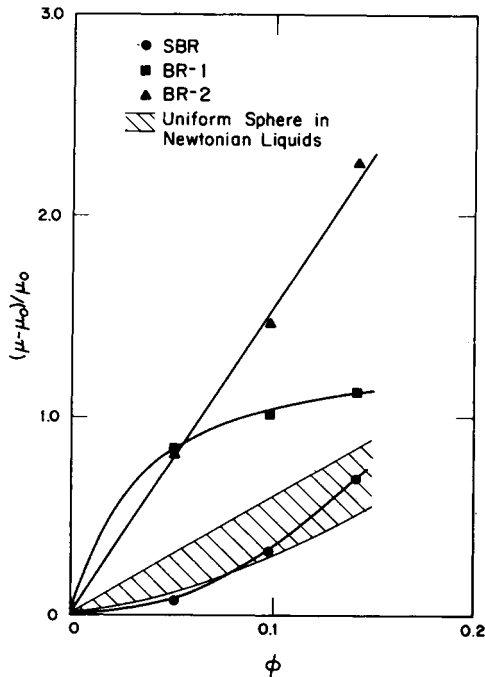


Fig. 14. Plot of $(\mu - \mu_0) / \mu_0$ vs. volume fraction ϕ of carbon black for SBR, BR-1, and BR-2 compounds. Shear rate is 10 sec⁻¹; μ_0 is for masticated polymer. Particle size and loading are constant.

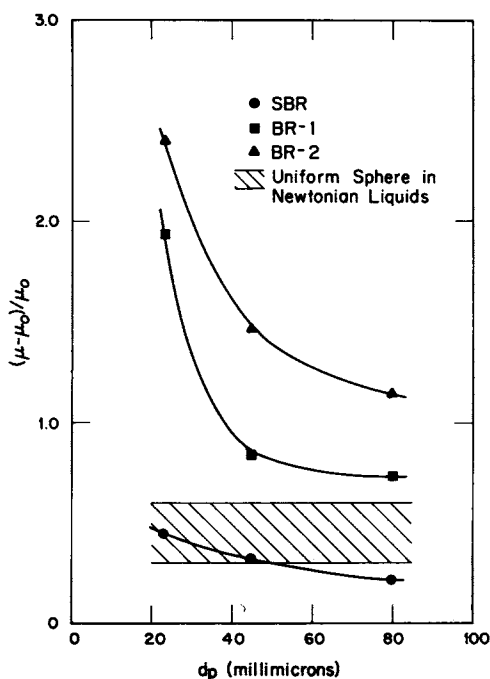


Fig. 15. Plot of $(\mu - \mu_0)/\mu_0$ vs. particle diameter d_p of the carbon black for SBR, BR-1, and BR-2 compounds. Shear rate is 10 sec^{-1} . Loading and structure are constant.

stress oscillations, and gross distortion. Mastication of the samples resulted in only grossly distorted extrudates, but the addition of carbon black brought the return of the behavior exhibited by the unmasticated samples with varying effects on the stress oscillations.

Let us now consider the probable sites of initiation of the instabilities leading to extrudate distortion. It is of interest to compare for discussion with recent reviews of Tordella⁴⁰ and White.⁴¹ We will first consider what we have called surface irregularity. This type of extrudate character is relatively insensitive to capillary length variations, and the surface irregularity may indeed be produced in the polybutadienes by forcing the material through the rheometer barrel without the use of a capillary. The material is observed to emerge from the barrel in a series of short spurts. The site of initiation for the surface irregularity would seem to be within the capillary (perhaps at the wall) or at the exit. We now turn to a discussion of grossly distorted extrudates. It is found that gross distortion is damped out with increasing L/D ratio (at the same extrusion rate). This would indicate that the gross distortion instability arises in the die entrance perhaps much in the manner of low-density polyethylene.^{33, 40, 41}

Entrance Pressure Drop

The very large magnitudes of capillary entrance pressure losses Δp_e for rubber and its compounds were first noted by Mooney¹⁴ during the World

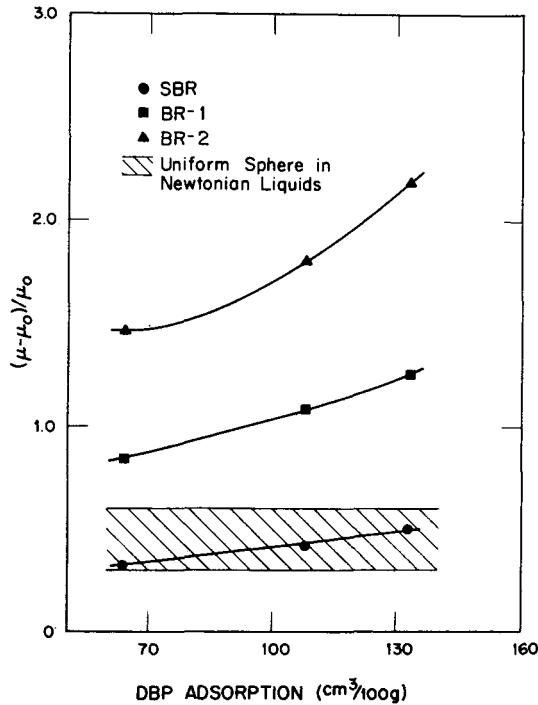


Fig. 16. Plot of $(\mu - \mu_0)/\mu_0$ vs. carbon black structure (DBP adsorption) for SBR, BR-1, and BR-2. Loading and particle size are constant.

War II GR-S Program. It was later rediscovered by Bagley³⁴ for polyethylene. Mooney associated large Δp_e with thixotropy. Philippoff and Gaskins³⁵ pointed out at a later date that they were associated rather with melt elasticity. It should be noted that the values of entrance pressure drop-to-shear stress ratio are of the same order of magnitude as those noted by Ballenger and White^{24,33,41} for polyethylene, polystyrene, and polypropylene melts. These authors indicate that the entrance pressure drop-to-shear stress ratio is a rough measure of relative elasticity.

Our capillary entrance pressure drop data are generally consistent with the view that addition of carbon black and black surface area is decreasing melt elasticity. The addition of glass beads to molten polymers has been shown to lead to decreased entrance pressure drops by Bagley.⁴²

THEORY OF RHEOLOGICAL PROPERTIES OF RUBBER COMPOUNDS

Carbon Black and Rheological Properties

It is well established that uncompounded elastomers are viscoelastic fluids and that the relationship between stress and deformation history in them may be represented by the theory of nonlinear viscoelasticity.⁴³⁻⁴⁵ Such a quantitative verification has not been carried out for rubber com-

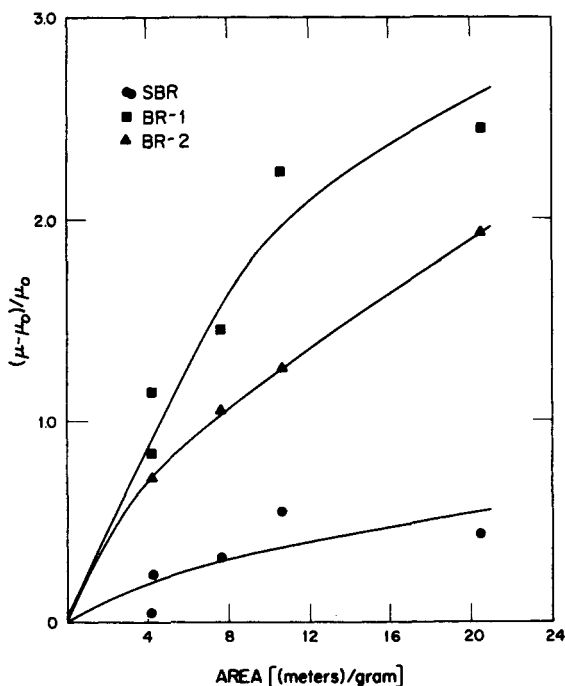


Fig. 17. Plot of $(\mu - \mu_0)/\mu_0$ vs. carbon black surface area (ϕ/d_p) for SBR, BR-1, and BR-2. Structure is constant.

pounds, but it would seem reasonable to say that (even considering Mullins effects²³) that nonlinear viscoelasticity is not a bad representation. Accepting this, we ask the question, "What is the influence of carbon black loading, particle diameter, and structure on the viscoelastic properties of the elastomer?" Certainly, from Figures 2-8, it may be seen that increasing carbon black surface area and increasing structure increase the shear viscosity. If we accept the view that die swell is an unconstrained recovery or recoil of the material from Poiseuille flow in a tube,⁴⁶ we see that increasing carbon black loading, surface area, and structure decreases elastic recovery. In unpublished experimental studies carried out by one of us (J.L.W.) a decade ago, it was found that increasing black loading and surface decreased the elastic recoil observed in a Mooney viscometer.¹⁷ A limited number of basic and well thought out experimental studies of the influence of solid fillers on the viscoelastic properties of amorphous uncrosslinked polymer systems exist,⁴⁷⁻⁴⁹ but these seem to offer little help to the central point at hand.

It would seem useful to attempt to see the implications of the above paragraph in terms of the actual functions occurring in the theory of viscoelastic fluids. Experimental studies by various researchers^{43, 44, 45, 50, 51} have shown that constitutive equations^{36, 50-52} of form

$$\sigma = -p\mathbf{I} + \int_0^\infty [m_1(z)\mathbf{c}^{-1} - m_2(z)\mathbf{c}]dz \quad (7)$$

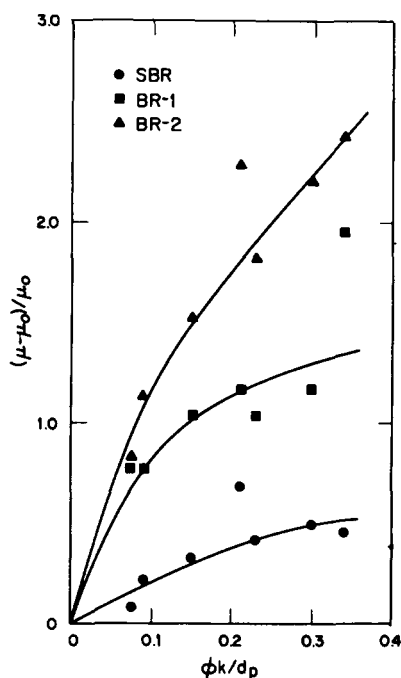


Fig. 18. Plot of $(\mu - \mu_0)/\mu_0$ vs. $k\phi/d_p$, where k is the structure in DBP adsorption.

represent the steady-state and transient-flow behavior of polymer solutions and melts in shear and extension. Here, δ is the stress tensor, p is the pressure, \mathbf{I} is the unit tensor, \mathbf{c}^{-1} is the Finger deformation tensor, \mathbf{c} is the Cauchy deformation tensor, and $m_1(z)$ and $m_2(z)$ are the relaxation modulus functions generally considered^{50,52} to be related by

$$m_2(z) = -\left(\frac{\epsilon/2}{1 + \epsilon/2}\right) m_1(z) \quad (8)$$

for a steady shearing flow, defined by $v_1 = \Gamma x_2$. The viscosity function μ for a fluid defined by eqs. (7) and (8) is

$$\mu = \int_0^\infty z[m_1(z) + m_2(z)]dz = \left[\frac{1}{1 + \epsilon/2}\right] \int_0^\infty z m_1(z) dz. \quad (9)$$

The constrained elastic recovery s from a simple shearing flow has the form^{53,54}

$$s = \frac{\sigma_{11} - \sigma_{22}}{2\sigma_{12}} = \frac{1}{2} \left[\frac{\int_0^\infty z^2 m_1(z) dz}{\int_0^\infty z m_1(z) dz} \right] \Gamma. \quad (10)$$

From eqs. (9) and (10), it would appear that the influence of carbon black surface and structure is to simultaneously increase the first moment and

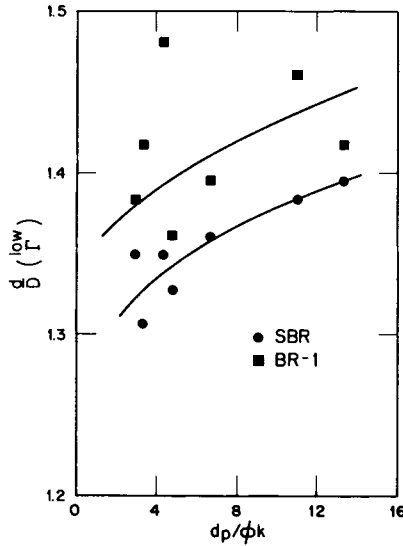


Fig. 19. Plot of die swell d/D vs. $d_p/k\phi k$ for SBR and BR-1 compounds.

decrease the second moment of $m_1(z)$. As $m_1(z)$ is a relaxation modulus which monotonically decreases from some initial finite value to zero, we must interpret this finding as meaning that carbon black increases the initial amplitude of $m_1(z)$ but decreases the period required for decay. The ideas expressed above may be in some sense made more specific if we note that $m_1(z)$ may be expressed as^{50,51}

$$\dot{m}_1(z) = \left(1 + \frac{\epsilon}{2}\right) \sum_i G_i e^{-t/\lambda_{ieff}} \tag{11a}$$

where λ_{ieff} is a function of deformation invariants. One form used of λ_{ieff} is

$$\lambda_{ieff} = \frac{\lambda_i}{1 + b_i \lambda_i^{2c} II_d^c} \tag{11b}$$

where II_d is the second invariant of the rate of deformation tensor and c is a constant exponent. Substitution of eq. (11) into eqs. (9) and (10) yields

$$\mu = \sum_i G_i \lambda_{ieff} \tag{12}$$

$$s = \left[\frac{\sum_i G_i \lambda_{ieff}^2}{\sum_i G_i \lambda_{ieff}} \right] \Gamma \sim \lambda_{meff} \Gamma. \tag{13}$$

It would seem that carbon black generally increases the G_i and decreases the maximum λ_{ieff} , i.e., λ_{meff} .

Mechanisms of Rubber-Black Interaction and Theories of Reinforcement

The physical basis for the filler reinforcement of elastomers has long attracted researchers; however, this effort has almost entirely emphasized vulcanizates. Some of this research has focused on the detailed nature of the interaction between rubber and carbon black, while other investigators have sought to develop models which explain the reinforcement phenomenon. Generally, two types of interactions exist between rubber and carbon black: adsorption and covalent bonding. It is well known that elastomers are adsorbed from solution onto carbon black^{1,55} and that the surface of carbon black acts as a free-radical acceptor and terminates free radicals created by mastication induced degradation.⁵⁶ Generally, if carbon black is milled into rubber, the rubber in the compound, though initially soluble, exhibits only limited solubility. The insoluble remainder, known as bound rubber,^{1,56,57} is probably a crosslinked rubber-black gel containing both adsorptive and covalent attachments.

Two analytical approaches have been developed to explain filler reinforcement. The first theory, which was adapted by Smallwood⁵⁸ and Guth^{39,59} from Einstein's theory of suspensions,⁶⁰ is based upon the increase in viscous dissipation or strain in the medium, considered continuous, which surrounds the embedded filler. However, comparison of this theory with experiment shows that this "hydrodynamic" approach is inadequate as it predicts a volume fraction rather than a surface area dependence of properties on black loading and also underestimating the magnitude of reinforcement. Guth^{39,59} argued that the anisotropy of the agglomerated particles led to the enhanced reinforcement and thus explain the "structure" but not the particle size effect. Wiegand⁶ and Smallwood⁵⁸ and later Medalia,⁶¹ Smit,²¹ and Pliskin and Tokita⁵⁷ argued that there is an immobile adsorbed layer of rubber around the black which acts to effectively increase the volume fraction of filler. Presuming such a hypothetical layer and Guth's shape factor, one may explain the influence of black on the small-strain modulus and Newtonian shear viscosity.

A second approach, which was adapted by Blanchard and Parkinson,⁶² A. M. Bueche,^{63,64} F. Bueche,⁶⁵ and Rigbi⁶⁶ from the theory of rubber elasticity,⁶⁷ involves consideration of the black as increasing the effective crosslink density in vulcanizates. According to this theory, a filled polymer contains two types of crosslinks—chemical crosslinks and crosslinks due to the interaction of polymer chains with the black surface. The modulus is proportional to this enhanced crosslink density.

Constitutive Equation for Reinforced Polymer Melts

Two approaches based upon the previous section suggest themselves to explain the nonlinear and viscoelastic rheological properties of carbon black-filled raw elastomers. The first approach is based on consideration of the "hydrodynamic interaction" of the carbon black in the deforming medium.

To rigorously work out this approach would require the solution of a complex boundary value problem, namely, the extension of the Einstein-Smallwood-Guth analysis to viscoelastic fluids. Radok and Tai,⁶⁸ Rigbi,⁶⁹ and Hashin⁷⁰ have made limited progress in this direction using the theory of linear viscoelasticity. It would seem from their results that the presence of fillers will change the details of the relaxation modulus function of the unfilled material.

Certainly linear viscoelasticity will not provide enough information to explain the flow behavior of compounds in the nonlinear range. As the deformations in the matrix surrounding the black particles are much greater and their rates more severe than the averaged behavior of the entire composite system, the deforming matrix material will be in the nonlinear range even under mild overall deformation conditions. One of the features of the behavior of $m_1(t)$ under severe deformation conditions is a decrease in λ_{ieff} ,^{32,50,71} see eq. (11c). We must couple this with the adsorbed rubber on the surface of the black, as viewed by Smit²¹ and Pliskin and Tokita.⁵⁷ A possible way of putting all of this together is

$$m_1(t, II_a) = m_{10}(t, n II_a) [1 + \alpha_1 f \phi_e + \alpha_2 f^2 \phi_e^2 + \dots] \quad (14)$$

where $m_{10}(t)$ is the modulus function of the unfilled polymer, ϕ_e is an effective volume fraction equal to the sum of that of the black and the occluded rubber, n is a number greater than unity which is an increasing function of ϕ_e , and f is an anisotropy factor. For spherical particles, f is unity and α_1 is 2.5 and α_2 is 14.1 or 12.6. The effective volume fraction ϕ_e may be expressed as

$$\phi_e = \phi + \left(\frac{6\phi}{d_p}\right)\Delta \quad (15)$$

where Δ is the thickness of the occluded layer, being 50–60 Å according to Pliskin and Tokita.⁵⁷ As d_p is of the order 230–800 Å, ϕ_e is approximately double ϕ . If we accept the Radok-Tai-Rigbi result for the influence of fillers on the detailed shape of the relaxation modulus function, $m_{10}(t)$ in eq. (14) should be replaced by some $\tilde{m}_{10}^*(t)$ different from $m_{10}(t)$.

The viscosity function is then, from eq. (9),

$$\mu = \frac{1}{1 + \epsilon/2} \left[\int_0^\infty z \tilde{m}_{10}^*(z, n II_a) dz \right] [1 + \alpha_1 f \phi_e + \alpha_2 f^2 \phi_e^2 + \dots] \quad (16)$$

and the recoverable strain is

$$s = \left[\frac{\int_0^\infty z^2 \tilde{m}_{10}^*(z, n II_a) dz}{\int_0^\infty z \tilde{m}_{10}^*(z, n II_a) dz} \right] \Gamma \sim \lambda_{meff}(n II_a) \Gamma. \quad (17)$$

This would seem in general agreement with observation. The viscosity increases with loading, decreasing particle diameter, and structure, while the elastic recovery and die swell decrease.

A second approach to the problem is possible. Yamamoto,⁷² Lodge,⁷³ and more recent researchers⁵¹ have described the flow of polymer melts in terms of deforming networks and argued that a modified form of the kinetic theory of rubber elasticity may be applied with temporary entanglements replacing permanent crosslinks. Following Lodge specifically, a constitutive equation of the form of eq. (7) may be applied with $m_2(z)$ equal to zero and

$$m_{10}(t) = kT \nu(t) \quad (18)$$

where $m_{10}(t)$ refers to an unfilled polymer, k is Boltzmann's constant, T is the temperature, and $\nu(t)$ is the density of entanglements. If one introduces carbon black, rubber-black attachments will act to increase the effective entanglement density. The number of rubber-black attachments formed per unit volume will be proportional to the black surface area per unit volume, i.e., ϕ/d_p , and we may write

$$\begin{aligned} m_1(t) &= kT(1 - \phi) \left[\nu(t) + \left(\frac{\phi}{d_p} \right) \beta(t) \right] \\ &= m_{10}(t) (1 - \phi) + kT \beta(t) \left[\frac{\phi(1 - \phi)}{d_p} \right]. \end{aligned} \quad (19)$$

Generally, the relaxation processes associated with rubber-black attachments will differ from those associated with entanglements between polymer chains. If we substitute eq. (19) into eqs. (9) and (10), we see that viscosity μ and recovery s have qualitatively the corrected dependence on filler loading and particle size if the relaxation processes involved in $\beta(t)$ are more rapid than those involved in $\nu(t)$.

Specifically,

$$\mu = \left[\int_0^\infty z m_{10}(z) dz \right] (1 - \phi) + k \left[\int_0^\infty z \beta(z) dz \right] \frac{\phi(1 - \phi)}{d_p} \quad (20)$$

$$s = \left[\frac{\int_0^\infty z^2 \left[m_{10}(z) + \frac{\phi}{d_p} kT \beta(z) \right] dz}{\int_0^\infty z \left[m_{10}(z) + \frac{\phi}{d_p} kT \beta(z) \right] dz} \right] \Gamma. \quad (21)$$

If $\beta(t)$ decays more rapidly than $m_{10}(t)$, we can predict from eqs. (20) and (21) an increasing viscosity and decreasing elastic recovery.

It would seem to us that of the two theories described, the first based upon continuum mechanical considerations of suspended particles in a viscoelastic continuum is the better.

CONCLUSIONS

An experimental study of the extrusion characteristics of synthetic rubber compounded with carbon black has been carried out. The character of

extrudate distortion is discussed. Increasing black loading, decreasing particle size, and increasing structure increase viscosity and decrease die swell and extrudate distortion—and thus presumably elastic memory. These results are interpreted in terms of nonlinear viscoelasticity theory. Two mechanistic theories are put forward to explain this behavior, one theory based on the idea of a suspension of particles in a viscoelastic fluid and the second based on the idea of the interaction of an entanglement network with carbon black surface.

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