

Rheological Properties of SBR Polymers by Capillary Extrusion

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Synopsis

A modification of the piston head of the Instron rheometer has enabled its use in studying rheological properties of SBR elastomers over a shear rate range of 30–2500 sec.^{-1} . In place of the usual piston head, a Teflon plug with a cavitated bottom was used. This eliminates leakage between the piston and barrel and results in uniform force traces that can be extrapolated to zero barrel length to yield the total force of extrusion. Hence, it gives a practical means to study, on sound theoretical basis, the rheological properties which are all important in the prediction of factory processing behavior and factors which influence it. Extrusions of SBR 1712 and 1712-HAF compound were made through capillaries having 180° entrance angles, diameters of 0.033, 0.043, 0.052, and 0.070 in. and length/diameter ratios near 1, 2, 4, 6, 8, and 10 at temperatures of 80, 90, 110, and 130° C. and crosshead speeds of 1/2, 1, 2, and 5 in./min. Linear fits were found between length/diameter (L/D) ratio and the force of extrusion (at zero barrel length). The slopes of these lines give values of true shear stress which fit one relationship to Newtonian shear rates at each of the four temperatures independent of die dimensions. Plots of log true shear stress versus log true shear rate show curvilinear behavior for clear SBR 1712 elastomer over the entire shear rate range of 45–3900 sec.^{-1} at all four temperatures. The same plots for the HAF compound of SBR 1712 showed curvilinear behavior below shear rates of 100 sec.^{-1} and linear behavior above with a power law exponent of 6.1. There is a great difference in slopes between lower and higher shear rates at all four temperatures. This indicates that extrapolation from low shear rate instruments cannot be made to predict behavior at higher rates common to factory equipment. This observation holds for both clear SBR 1712 elastomer and its HAF compound. True shear stresses at corresponding true shear rates (and therefore viscosities) were considerably higher for the compound than for the clear elastomer, as was expected. However, the addition of black reduces the extent of deviation from Newtonian behavior. Even though uncorrected for recoverable shear strain, viscosities were calculated and used to calculate activation energies according to the Arrhenius equation. Straight lines were obtained covering temperatures at 90, 110, and 130° C. at all shear rates with activation energies of 1.5 kcal./mole of both the clear elastomer and its compound. Log viscosity at 80° C. in all cases was above the straight lines through the log viscosities at the other three temperatures. This indicates a higher activation energy at temperatures below 90° C. Addition of black apparently does not affect substantially the identity of the rheological unit. Extrusion die swell was found to decrease with increasing temperature and increasing L/D ratio at all rates of shear. At a given temperature it increases with increasing rate of shear. Swell was anisotropic for the clear elastomer but not for the compound.

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INTRODUCTION

The last decade has seen an ever tightening demand on the processing qualities of SBR elastomers. This demand has given new stimulus to finding effective methods of measuring processability and basic flow properties. A Banbury processability index which predicts behavior in factory equipment was described recently by Einhorn.¹ In this paper a capillary extrusion test which spans a shear rate range of 30–25,000 sec.⁻¹ and includes those usually observed in both low and high speed factory equipment, is described. Prediction of properties from the common disk type viscometers whose shear rates are limited to ranges below 50 sec. is completely inadequate. The usual lack of linearity between shear stress and shear rate, even on logarithmic scales, makes extrapolation to the high shear rate region impossible.

Capillary extrusion experiments long have been used to characterize the rheology of liquids and more recently that of plastic melts but almost not at all that of elastomers. It is the lack of technique rather than theory that has been responsible for this omission.

Philippoff and Gaskins,² in a thorough review of capillary rheometry, showed that the capillary experiment is applicable to viscoelastic incompressible materials. They showed that, in addition to the force necessary to maintain flow through the capillary, there are two other contributing forces: that due to the so-called Couette correction arising from viscous gradients near the entrance to the capillary and that due to the energy stored as recoverable shear. Bagley^{3,4} has shown that this method is applicable to certain polyethylene melts. More recently, Metzger and Brodkey⁵ also showed that it is applicable to melts of a commercial low density polyethylene. A modification of the test method makes it applicable to SBR elastomers. This modification and results for SBR 1712 and 1712 compound with 50 parts HAF are presented in this paper.

Experimental Method

The basic rheometer used in this study was that supplied by the Instron Engineering Corporation and described by Merz and Colwell.⁶ It comprises of an electrically heated barrel and a piston coupled to a compression load weighing system. The latter is driven by the Instron tensile tester crosshead affording a wide range of constant displacement rates and a means of continuously recording the resulting extrusion forces. The barrel temperature may be accurately controlled at any desired level by means of a proportional band controller.

As supplied, the piston head is closely matched to slip fit into the barrel, has a pointed tip and is grooved to carry a Teflon O-ring. This sealing system apparently performs acceptably with negligible friction force in extrusion of plastic melts. However, repeated efforts in extruding elastomers resulted in excessive leakage past the piston tip and erratic force traces.

In order to eliminate the erratic force fluctuations the piston head was redesigned. The end was squared off and a Teflon TFE plug inserted between it and the sample. The bottom of this plug is cavitated by a 15° cone. The result of this cone cavity is to create a small horizontal component of force which keeps the knife edged bottom circumference tight against the barrel. This prohibits leakage past the piston. The plug and resultant force traces for SBR 1712 elastomer are shown in Figure 1.

It was found necessary to compensate for the difference in coefficients of expansion between Teflon and stainless steel from which the barrel is constructed. To accomplish this simply, plugs of different sizes were made.

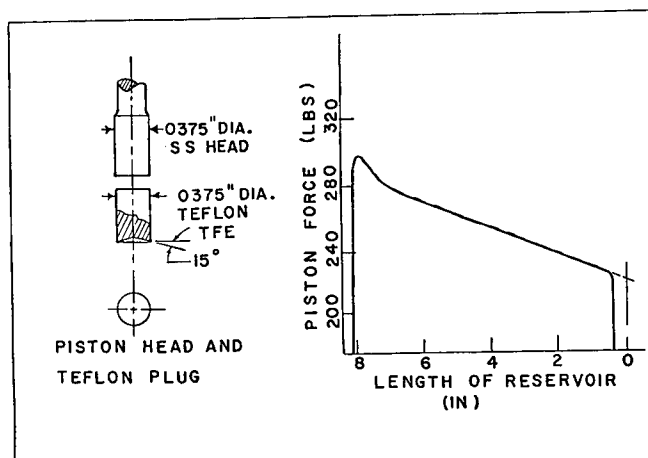


Fig. 1. Teflon plug and an SBR 1712 clear elastomer force trace. The force trace is with a die of 0.033 in. diameter having an L/D ratio of 0.903 at 110°C . and at a cross-head speed of 0.5 in./min.

The barrel diameter was 0.375 in. and plugs of 0.375, 0.376, and 0.377 in. diameter were made for use at 130, 90–110, and 80°C ., respectively. The dimensions of these were watched carefully, and when permanent deformation resulted in a change of 0.001 in. new plugs were used.

It was found essential to leave the plug unattached from the piston head and discharge it through the bottom of the barrel after each extrusion. When attached to the piston head the vacuum created on retraction caused the knife edged bottom circumference to deform. Even if the die is removed each time, the remaining elastomer plug is sufficient to hold a damaging vacuum. Removal of the die and holder after each experiment is usually necessary to change die size and has the added advantage of permitting discharge of the sample remainder. Thus, this procedure of discharging the plug is not a handicap but an advantage. Temperature equilibration of the plug after assembly for the next test was found much more rapid than that needed for the sample itself.

Treatment of Data

The Philippoff-Gaskins equation relating the total extrusion pressure (P_T) to the Couette correction n and the recoverable shear S_R is

$$P_T = 4\tau_{TW}[(L/D) + (n/2) + (S_R/4)] + m\rho v^2 \quad (1)$$

where τ_{TW} is the true shear stress at the wall of the capillary, L and D are length and diameter, respectively, of the capillary, $m\rho v^2$ is the kinetic energy correction (in which m is a constant, ρ is the density, and v the velocity). In addition to the P_T of eq. (1) there is also a pressure drop due to the plug flow of the sample in the barrel. This pressure component

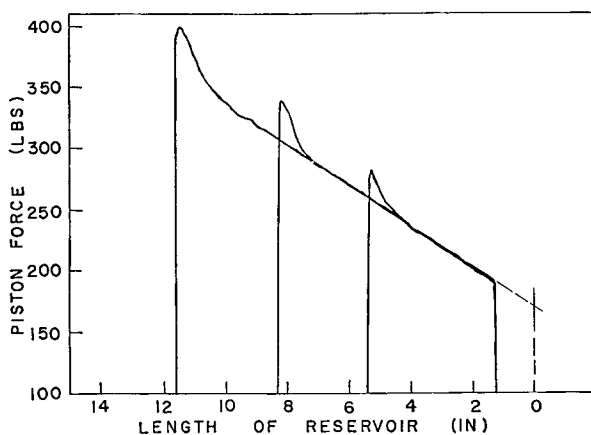


Fig. 2. Effect of sample size on force trace. Traces are from three separate tests with samples of 13.1, 8.8, and 5.7 g. of clear SBR 1712 elastomer. They were superimposed at the correct positions to have zero barrel length at the same point. Note that extrapolated force is independent of sample size. Die diameter 0.070 in., L/D of 6.000, 110°C ., crosshead speed 5 in./min.

is linearly proportional to the barrel length and is responsible for the linearly decreasing force trace shown in Figure 1. In addition, it is necessary to include a term for the friction force between the Teflon plug and the barrel. Due to the lubricative nature of Teflon this drag is essentially independent of total pressure above a nominal level and can be added as a constant to eq. (1). Since the force traces are linear they can be extrapolated to zero barrel length, thus eliminating the need to consider the sample reservoir height. This technique is shown in Figure 2, in which the traces for three different sized samples of SBR 1712 elastomer were superimposed on each other. The excellent reproducibility regardless of sample size substantiates this technique.

Examination of eq. (1) shows that a linear relationship exists between P_T and L/D . The straight line intersects the P_T axis at a value:

$$P_T(\text{at } L/D = 0) = 4\tau_{TW}[(n/2) + (S_R/4)] + m\rho v^2 + P_{hd} \quad (2)$$

(where P_{hd} is the drag due to the Teflon plug), and the slope is $4\tau_{TW}$.

Thus an experiment with several L/D ratios and constant D yields a method for calculating τ_{TW} , the true shear stress at the wall of the capillary.

Rabinowitch⁷ developed the relationship of eq. (3) below enabling the computation of $\dot{\gamma}_{TW}$, the true shear rate at the wall of the capillary.

$$\dot{\gamma}_{TW} = \dot{\gamma}_{NW}[(3/4) + (b/4)] \quad (3)$$

Here $\dot{\gamma}_{NW}$ is the shear rate from the expression for Newtonian liquids and is only a reference quantity.

$$\dot{\gamma}_{NW} = 32Q_3/\pi d \quad (4)$$

Also

$$b = d(\log \dot{\gamma}_{NW})/d(\log \tau_{TW}) \quad (5)$$

τ_{TW} can be calculated as explained above, and $\dot{\gamma}_{NW}$ can be calculated from eq. (5). A plot of $\log \dot{\gamma}_{NW}$ versus $\log \tau_{TW}$ supplies values of b for computation of $\dot{\gamma}_{TW}$ by eq. (3). Hence, it is possible from capillary experiments to obtain the basic shear stress–shear rate curves for any incompressible fluid including elastomers.

Computation of viscosity from the expression

$$\eta = \tau_{TW}/\dot{\gamma}_{TW} \quad (6)$$

also can be accomplished. Actually, this expression needs correction when the recoverable shear strain is of significant magnitude. Jobling and Roberts⁸ pointed out that under this condition the direction of the shear stress ellipsoid differs from that of the shear strain which remains fixed with the geometry of the capillary. The correction is given by

$$\eta_{\text{corr.}} = \eta[1 + (S_R^2/4)]^{1/2} \quad (7)$$

Since no means were devised to isolate P_{hd} , calculation of S_R in the present work was not possible. This will be the subject of a future refinement. Values of η from eq. (6), though not exact, will be used.

Experimental SBR 1712 and HAF Compound

Four series of dies having diameters of 0.033, 0.043, 0.052, and 0.070 in. and L/D ratios near 1, 2, 4, 6, 8, and 10 were fabricated from 420 stainless steel. The diameters and lengths were determined accurately by measurement with a cathetometer and depth gages of suitable accuracy. An entrance angle of 180° (i.e., flat face) was used for all dies. Test extrusions of SBR 1712 clear elastomer and compound (with 50 parts of HAF black) were run at crosshead speeds of $1/2$, 1, 2, and 5 in./min. at temperatures of 80, 90, 110, and 130°C . Newtonian shear rates calculated from eq. (4) corresponding to these speeds are shown in Table I.

The clear polymer was masticated by 10 mill passes through a 6 in. by 13 in. laboratory mill at 0.007 in. separation and 140°F . Its Mooney viscosity (ML-4) after mastication was 36.0. SBR 1712 is a high molecular

TABLE I
Capillary Extrusion Properties of Clear SBR 1712 Elastomer

Capillary diameter, in.	Crosshead speed, in./min.	$\dot{\gamma}_{NW}$, sec. ⁻¹	True shear stress τ_{TW} at wall of capillary, mdynes/cm. ²			
			80°C.	90° C.	110° C.	130° C.
0.033	1/2	260.9	3.16	2.92	2.81	2.39
	1	521.7	3.38	3.09	2.77	2.55
	2	1043.5	3.52	3.21	2.87	2.65
	5	2608.7	3.66	3.25	2.94	2.74
0.043	1/2	117.9	2.75	2.55	2.28	2.04
	1	235.8	3.13	2.87	2.57	2.37
	2	471.6	3.33	3.02	2.74	2.53
	5	1179.6	3.55	3.22	2.84	2.67
0.052	1/2	66.7	2.28	2.13	1.88	1.64
	1	133.4	2.80	2.62	2.34	2.11
	2	266.7	3.18	2.93	2.62	2.40
	5	666.7	3.44	3.15	2.79	2.59
0.070	1/2	27.3	1.55	1.46	1.09	0.93
	1	54.7	2.15	2.03	1.69	1.49
	2	109.3	2.67	2.49	2.22	1.99
	5	273.3	3.19	2.93	2.62	2.41

weight styrene-butadiene elastomer having 22.5% bound styrene, polymerized at 5.0°C. and extended with 37.5 parts of highly aromatic oil.

The HAF compound was mixed in a B Banbury at 155 rpm for 2 min. after 1 min. of premastication of the polymer. Its compound Mooney viscosity (ML-4) was 58.5.

In each case the force traces were extrapolated to zero barrel length. A typical set of traces are shown in Figure 3. The extrapolated forces were

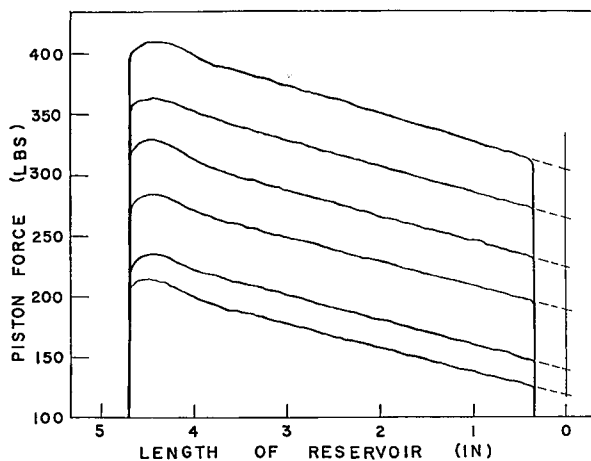


Fig. 3. Force traces for SBR 1712-HAF compound. Die diameter 0.043 in., 110°C., crosshead speed 2 in./min.; L/D ratios from top to bottom are 9.30, 7.44, 5.58, 3.72, 1.86, and 0.93. Sample size held constant for all six extrusions.

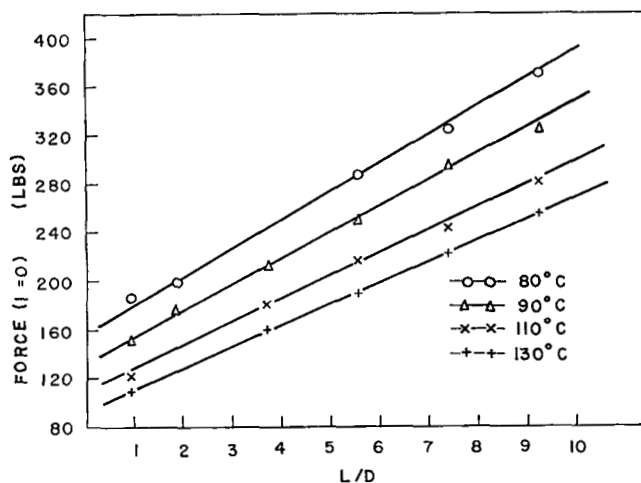


Fig. 4. Relationship of extrusion force to L/D ratio for clear SBR 1712 elastomer. Die diameter 0.043 in.; crosshead speed 5 in./min. Note increasing slope at lower temperatures indicating higher shear stress.

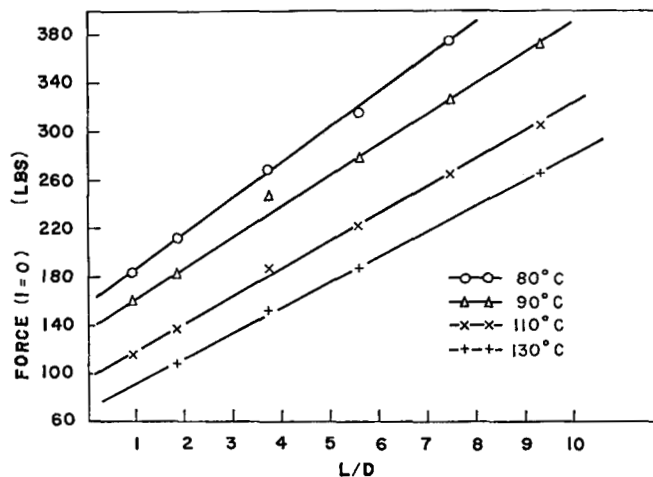


Fig. 5. Relationship of extrusion force to L/D ratio for SBR 1712-HAF compound. Die diameter 0.043 in., crosshead speed 2 in./min.

plotted against L/D which resulted in straight lines as predicted in eq. (3). Typical plots for the clear elastomer are shown in Figure 4 and for the compound in Figure 5. The shear stress τ_{TW} was calculated from the slopes of these lines.

Plots of $\log \tau_{TW}$ versus $\log \dot{\gamma}_{NW}$ are shown in Figure 6 for the clear elastomer and in Figure 7 for the compound. The data for these figures are listed in Tables I and II. The clear elastomer shows no linearity at any of the four temperatures, unlike much published data for plastic melts. However, the compound shows linearity above shear rates ($\dot{\gamma}_{NW}$) of approximately 100 sec.^{-1} ($\log \dot{\gamma}_{NW} = 2.00$).

As predicted by theory, at each of the four temperatures studied, a single shear stress–shear rate curve includes points obtained from all dies regardless of dimensions. This is true for both the clear elastomer and the compound. This is believed to be the first detailed demonstration that

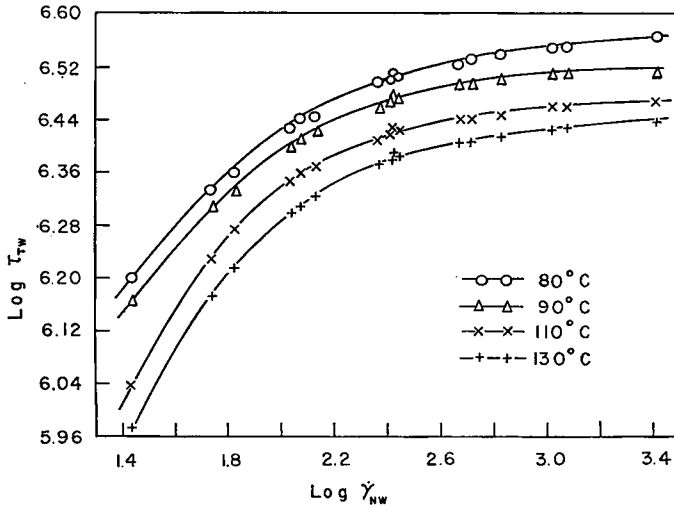


Fig. 6. $\text{Log } \tau_{TW}$ - $\text{log } \dot{\gamma}_{NW}$ relationships for clear SBR 1712 elastomer. In vertical planes from left to right are the following die diameter (in.)-crosshead speed (in./min.) combinations: 0.070 and $1/2$; 0.070 and 1; 0.050 and $1/2$; 0.070 and 2; 0.043 and $1/2$; 0.052 and 1; 0.043 and 1; 0.033 and $1/2$; 0.033 and 2; 0.070 and 5; 0.043 and 2; 0.033 and 1; 0.052 and 5; 0.033 and 2; 0.043 and 5; 0.033 and 5. Note that the relationship at each temperature is independent of die dimensions or crosshead speed. Note also curvilinear behavior over entire range.

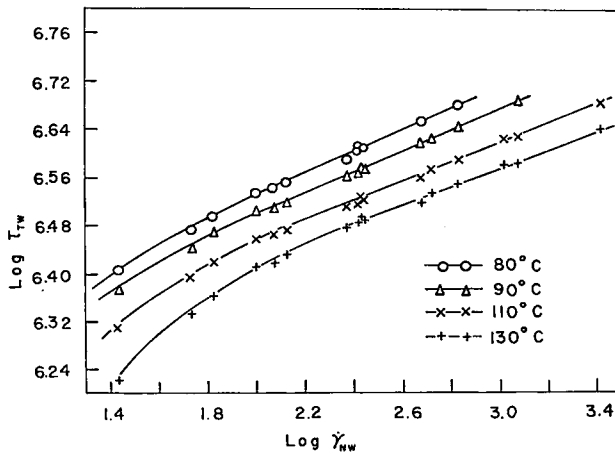


Fig. 7. $\text{Log } \tau_{TW}$ - $\text{log } \dot{\gamma}_{NW}$ relationships for SBR 1712-HAF compound. From left to right die diameter and crosshead speed combinations as in Fig. 6. Again note independence of relationships on die dimensions and crosshead speeds. Linear behavior is seen above shear rates of 100 sec.^{-1} .

TABLE II
Extrusion Properties of SBR 1712 Compound with 50 Parts HAF Black (B Banbury Mixed at 155 rpm)

Capillary diameter, in.	Crosshead speed, in./min.	True shear stress τ_{TW} at wall of capillary, dynes/cm. ²			
		80° C.	90° C.	110° C.	130° C.
0.033	1/2	4.02	3.70	3.28	3.05
	1	—	4.18	3.74	3.42
	2	—	—	4.19	3.79
	5	—	—	4.83	4.37
0.043	1/2	3.48	3.23	2.91	2.62
	1	3.95	3.63	3.25	3.00
	2	4.47	4.11	3.61	3.28
	5	—	4.82	4.24	3.80
0.052	1/2	3.13	2.93	2.61	2.30
	1	3.55	3.28	2.96	2.69
	2	4.03	3.71	3.32	3.06
	5	4.77	4.38	3.85	3.52
0.070	1/2	2.54	2.36	2.03	1.66
	1	2.96	2.52	2.48	2.15
	2	3.43	3.16	2.86	2.58
	5	4.03	3.73	3.34	3.07

this principle is valid for elastomers over a range of temperatures. McCabe and Mueller⁹ reported some studies with Neoprene W but of insufficient breadth to treat in this manner. They did not report a barrel pressure drop.

The slopes of the curves of Figures 6 and 7 were calculated at uniform intervals of $\log \dot{\gamma}_{NW}$ and correction factors computed according to eq. (3). These factors and the corrected shear rates $\dot{\gamma}_{TW}$ are shown in Table III for the clear elastomer and the compound. The greater deviation from Newtonian behavior by the clear polymer is seen in the almost tenfold change (1+ to 9+) of the correction factor at all four temperatures as $\dot{\gamma}_{NW}$ changes from 39.8 sec.⁻¹ to 2511.9 sec.⁻¹ compared to a twofold change (1.4+ to 2.4) for the compound. Thus, among other effects of addition of carbon black, there is the reduction of deviation from Newtonian flow.

The $\log \tau_{TW} - \log \dot{\gamma}_{TW}$ curves for the clear elastomer are shown in Figure 8. No linearity exists over the entire shear rate range at all four temperatures. The corresponding plots for the compounds are not shown but were curvilinear up to shear rates of just over 100 sec.⁻¹ and linear above. The linear portions could be described by a power law having an exponent of 6.1 independent of temperature.

At shear rates below 100 sec.⁻¹, both compound and clear elastomer have curves of rapidly changing slopes. This observation is important since most rotational viscometers used to test elastomers are limited to these lower rates. Therefore, tests from them would not predict behavior at the higher rates of factory equipment conditions (100–1000 sec.⁻¹).

TABLE III
 Extrusion Properties of SBR 1712

Temp., °C.	Log $\dot{\gamma}_{NW}$	$\dot{\gamma}_{NW}$, sec. ⁻¹	$(b/4) + (3/4)$		$\dot{\gamma}_{TW}$, sec. ⁻¹		τ_{TW} , Mdynes/cm. ²	
			Clear	Cpd.	Clear	Cpd.	Clear	Cpd.
80	1.50	31.6	—	1.71	—	54.1	—	2.56
	1.60	39.8	1.29	1.84	51.5	73.1	1.78	2.79
	1.80	63.1	1.41	1.94	88.8	122.4	2.16	3.08
	2.00	100.0	1.64	2.07	164.3	206.6	2.62	3.38
	2.20	158.5	2.14	2.16	339.0	341.7	2.92	3.69
	2.40	251.2	2.54	2.16	637.0	541.6	3.15	4.00
	2.60	398.1	3.88	2.16	1542.0	858.3	3.31	4.34
	2.80	631.0	4.92	2.16	3102.6	1360.4	3.44	4.71
	3.00	1000.0	5.75	2.16	5750.0	2156.0	3.54	5.12
	3.20	1584.9	7.00		11094		3.61	
3.40	2511.9	9.08		22186		3.88		
90	1.50		—	1.64	—	52.0	—	2.36
	1.60		1.32	1.68	52.5	66.7	1.73	2.59
	1.80		1.41	2.00	88.8	126.2	2.11	2.88
	2.00		1.64	2.20	Others	219.5	2.49	3.13
	2.20		2.14	2.20	same	347.5	2.72	3.40
	2.40		2.54	2.20	as	551.4	2.90	3.67
	2.60		3.88	2.20	above	873.8	3.04	3.98
	2.80		4.92	2.20		1385	3.15	4.32
	3.00		5.75	2.20		2195	3.21	4.64
	3.20		7.00				3.24	
3.40		9.08				3.25		
110	1.50			1.53	—	48.4		2.04
	1.60		1.16	1.56	46.1	62.0	1.42	2.28
	1.80		1.31	1.84	82.9	115.9	1.83	2.58
	2.00		1.64	2.25	Others	224.9	2.17	2.83
	2.20		2.14	2.25	same	356.5	2.42	3.05
	2.40		2.54	2.25	as	564.9	2.59	3.30
	2.60		3.88	2.25	above	895.3	2.72	3.56
	2.80		4.92	2.25		1419	2.80	3.84
	3.00		5.75	2.25		2249	2.85	4.15
	3.20		7.00	2.25			2.90	
3.40		9.08				2.92		
130	1.50			1.41		44.5		1.69
	1.60		1.11	1.45	44.3	57.6	1.23	1.97
	1.80		1.12	1.56	70.6	98.3	1.61	2.26
	2.00		1.49	1.94	148.5	194.0	1.95	2.54
	2.20		2.14	2.16	Others	343.0	2.20	2.78
	2.40		2.54	2.40	same	602.4	2.30	3.03
	2.60		3.88	2.40	as	954.6	2.50	3.25
	2.80		4.92	2.40	above	1513	2.58	3.48
	3.00		5.75	2.40		2398	2.66	3.73
	3.20		7.00				2.71	
3.40		9.08				2.74		

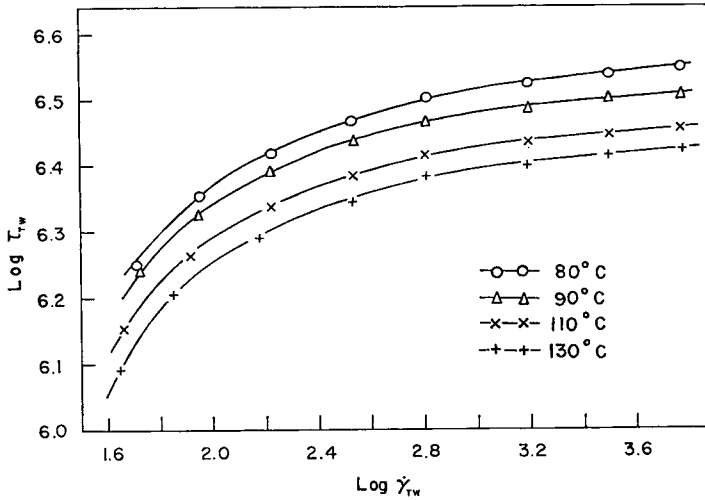


Fig. 8. Log τ_{TW} -log $\dot{\gamma}_{TW}$ curves for clear SBR 1712 elastomer. Note that no linearity exists at any of the four temperatures.

An equation by Powell and Eyring¹⁰ provides a modified hyperbolic sine law which, no doubt, could be made to fit the clear elastomer curves of Figure 8. However, this would not add to the present discussion and is planned as the subject of a future paper.

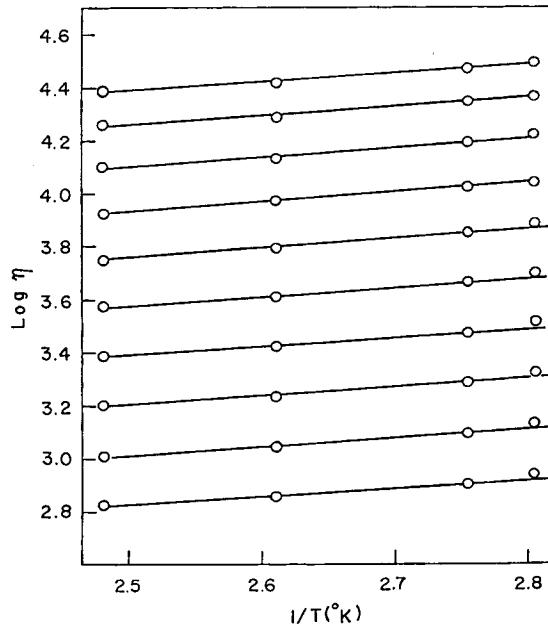


Fig. 9. Arrhenius plots for clear SBR 1712 elastomer. From top to bottom log shear rates $\dot{\gamma}_{TW}$ are: 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, and 3.4. From left to right, temperatures are: 130, 110, 90, and 80°C. Note that 80°C. points are above the lines, indicating higher activation energies for temperatures below 90°C.

Viscosities and Activation Energies

Viscosities computed according to eq. (6) are not shown but were computed at equal intervals of $\log \dot{\gamma}_{TW}$. The logarithm values were then plotted against the reciprocal absolute temperature to test for an Arrhenius fit. The plot for clear SBR 1712 elastomer is shown in Figure 9. A similar plot (not shown) was obtained for the HAF compound. Straight-line fits at all $\dot{\gamma}_{TW}$ levels were obtained for the points corresponding to temperatures of 90, 110, and 130°C. Activation energies, shown in Table IV, were essentially the same for both polymer and compound at 1.5 kcal./mole. The 80°C. points were all above the lines indicating a higher activation energy for this temperature region.

It is recognized here that if the proper correction were applied the above activation energies would be somewhat higher. Furthermore a greater correction would be applied to the clear elastomer viscosities than to the compound due to higher recoverable shear strain. However, even so, it is interesting that one could postulate almost the same basic process of flow for the compound as for the clear elastomer.

TABLE IV
Viscosities and Activation Energies at Various Rates of Shear $\dot{\gamma}_{TW}$

Log $\dot{\gamma}_{TW}$	$\dot{\gamma}$, sec. ⁻¹	Activation energies, kcal./mole	
		Clear SBR 1712	SBR 1712 cpd.
1.8	63.1	1.4	1.6
2.0	100.0	1.4	1.6
2.2	158.5	1.5	1.8
2.4	251.2	1.4	1.5
2.6	398.1	1.5	1.5
2.8	631.0	1.5	1.4
3.0	1000	1.6	1.3
3.2	1585	1.6	1.7
3.4	2512	1.5	—
3.6	3981	1.5	—

Extrusion Die Swell

It is known that, as L/D increases, extrusions become smoother and show less shrinkage. In association with an experiment of the scope described here, an excellent opportunity existed to examine the extrudates. Three 20 cm. lengths of extrudate at most test conditions were cut and weighed for calculation of average cross-sectional area and percentage increase over the area of the extrusion die. Increase of L/D at constant shear rate does cause a rapid decrease in die swell. Further, as shear rate is increased at constant temperature, die swell increases at all L/D ratios. This is shown photographically in Figure 10 for clear elastomer and in Figure 11 for the compound. The numbers beside each extrudate are die swells in per cent. At constant shear rate die swell decreases as tempera-

EFFECT OF TEMPERATURE ON DIE SWELL
DIE DIA.-0.043" & SHEAR RATE 472 SEC⁻¹

L/D	TEMPERATURE-(°C)			
	80	90	110	130
1	348	228	191	173
2	295	169	140	131
4	216	132	108	103
6	193	117	95	89
8	179	109	90	85
10	163	106	88	83

Fig. 10. Effect of shear rate on die swell of clear SBR 1712 elastomer. Numbers beside each extrudate are die swells in per cent. Note that die swell decreases as L/D increases at all shear rates and die swell increases as shear rate increases.

EFFECT OF SHEAR RATE ON DIE SWELL OF
SBR 1712-HAF COMPOUND
DIE DIA. 0.043", TEMP - 110° C

L/D	SHEAR RATE SEC ⁻¹			
	118	236	472	1179
1	110	111	112	116
2	91	91	92	95
6	65	65	68	70
8	61	61	62	66
10	59	60	61	65

Fig. 11. Effect of shear rate on die swell of SBR 1712-HAF compound. Note the same trends as in the clear elastomer but of much reduced magnitude.

ture increases at all L/D ratios. This is shown photographically in Figures 12 and 13 for the clear elastomer and compound, respectively. All compound extrudates had smooth surfaces, indicating isotropic recovery. All clear polymers extrudates are rippled and irregular, indicating anisotropic recovery.

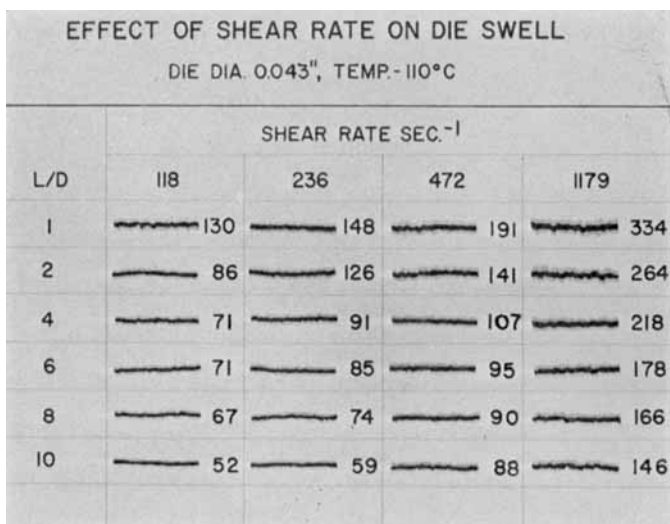


Fig. 12. Effect of temperatures on die swell of clear SBR 1712 elastomer. At all L/D values, die swell decreases as temperature increases.

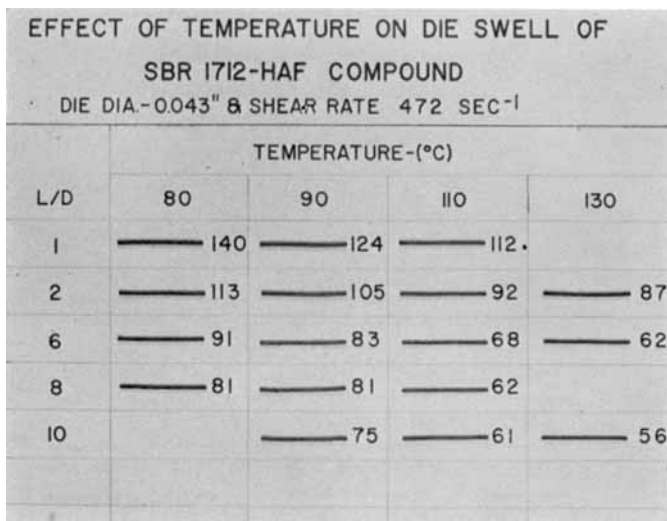


Fig. 13. Effect of temperature on die swell of SBR 1712-HAF compound. Note the same trends as for the clear elastomer but of reduced magnitude.

Conclusions

It has been shown that use of a Teflon plug with a cone cavitated bottom as the piston head permits employment of the Instron capillary rheometer to study the rheological properties of SBR elastomers. By using this technique, dies of various diameters and L/D ratios, and four volume rate speeds of extrusion, the following conclusions were observed to hold for

temperatures of 80, 90, 110, and 130°C. for both SBR 1712 clear elastomer and its 50 parts HAF compound.

(1) The force of extrusion is linearly proportional to the L/D ratio. The slopes of these lines give the true shear stress

(2) The true shear stress relates to Newtonian shear rate by a single relationship at each temperature independent of die dimensions or volume rate. This was found true for both clear SBR 1712 elastomer and its HAF compound.

(3) Corrected log shear stress–log shear rate curves showed no linearity for the clear polymer at any of the four temperatures in the shear rate range of 50–22,000 sec.^{-1} . For the compound, linear behavior was observed above shear rates of 100 sec.^{-1} ($\log \dot{\gamma}_{TW} = 2.00$) giving a power law exponent of 6.1.

(4) There is a great difference in slopes between lower and higher shear rates at all four temperatures for both clear elastomer and compound. This makes impossible the accurate prediction of properties by extrapolation from results at low rates common to most disk-type viscometers.

(5) The incorporation of carbon black increases viscosity but reduces deviation from Newtonian flow.

(6) Activation energies calculated from Arrhenius fits were 1.5 kcal./mole for both clear elastomer and compound independent of shear rate. This indicated retention of the identity of the rheological unit through the compounding step.

(7) Extrusion die swell was found to (a) increase with increasing shear rate at all four temperatures, (b) decrease with increasing L/D ratio at any rate and temperatures, and (c) decrease with increasing temperature at all L/D ratios and shear rates. The magnitude of the trends were much smaller for the compound than for the clear elastomer. Swell was anisotropic for the clear elastomer and isotropic for the compound.

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Résumé

En modifiant la tête du piston du rhéomètre de l'Instron, on a pu étudier les propriétés rhéologiques du caoutchouc SBR à une vitesse de cisaillement variant de 30 sec^{-1} à 2.500 sec^{-1} . En lieu et place de la tête de piston traditionnelle on a utilisé un bouchon de Téflon à base évidée. Par ce procédé on élimine toute fuite entre le piston et le cylindre et l'on peut obtenir un enregistrement continu de la force que l'on peut extrapoler à la

longueur 0 du cylindre afin d'obtenir la force totale d'extrusion. Par conséquent on obtient un moyen pratique pour étudier sur une base théorique sûre les propriétés rhéologiques qui sont de la plus grande importance lorsqu'on veut prédire le comportement lors du traitement industriel et étudier les facteurs qui l'influencent. On a extrudé le SBR 1712 et le produit 1712-HAF à travers des capillaires ayant des angles d'entrée de 180° et de diamètres respectivement de .033 pouce .043 pouce .052 et .70 pouce et de rapport diamètre-longueur 1,2,4,6,8 et 10; les températures d'extrusion étaient respectivement de 80,90,110 et 130° ; les vitesses de la tête modèle du diamètre étaient de $\frac{1}{2}$, 1, 2, et 5 pouces/min. On a trouvé des relations linéaires entre le rapport longueur sur diamètre et la force d'extrusion (rapportée à la longueur 0 du cylindre). A partir de la pente de ces droites on peut obtenir la valeur de la force de cisaillement qui satisfait à la relation de Newton lorsqu'on la rapporte aux vitesses de cisaillement. Ceci pour chacune des 4 températures étudiées et sans dépendance des dimensions de la filière. Lorsqu'on porte la force de cisaillement vraie en fonction de la vitesse de cisaillement vraie, on obtient un graphique qui montre que le caoutchouc SBR 1712 transparent a un comportement curviligne quand la vitesse de cisaillement varie de 45 sec^{-1} à 3900 sec^{-1} . Ceci est vrai aux températures de 80,90,110 et 130° . Les mêmes graphiques pour le composé HAF du caoutchouc SBR 1712 montrent un comportement curviligne à des vitesses de cisaillement supérieur, la pente étant de 6,1. La pente varie fortement lorsqu'on compare les résultats obtenus aux hautes et basses vitesses de cisaillement aux 4 températures étudiées. Ceci montre clairement que l'on ne peut pas extrapoler les résultats obtenus lors des mesures à basses vitesses de cisaillement pour prédire le comportement aux vitesses de cisaillement élevées telles qu'on les rencontre dans les machines industrielles. Cette remarque est valable à la fois pour le caoutchouc SBR 1712 et son composé HAF. Les forces de cisaillement vraie à vitesse de cisaillement correspondant (et par conséquent les viscosités) étaient notablement plus grandes pour le dérivé HAF que pour le caoutchouc transparent, ceci en conformité avec les prévisions. Cependant l'addition de noir animal réduit notablement l'écart par rapport au comportement Newtonien. On a utilisé les viscosités en négligeant la correction due à une déformation de cisaillement élastique pour calculer les énergies d'activation par l'équation d'Arrhénius. On a obtenu des droites couvrant les températures de 90, 110, 130° à toutes les vitesses de cisaillement, ce qui a permis de calculer des énergies d'activation de 1.5 kg-calories par mole pour le caoutchouc transparent et son dérivé. Le logarithme de la viscosité la température de 80° était toujours au-dessus de la droite reliant le logarithme des viscosités aux 3 autres températures. Ceci montre que l'énergie d'activation augmente lorsque la température est inférieure à 90° . L'addition du noir animal n'affecte pas sensiblement le caractère de la rhéologie. On a trouvé que le gonflement à la sortie de la filière diminuait avec l'élévation de la température et l'augmentation du rapport longueur/diamètre; ceci à toutes les vitesses de cisaillement étudiées. A une température donnée, il augmente avec la vitesse de cisaillement. Le gonflement est anisotrope pour le caoutchouc transparent mais non pas pour son dérivé.

Zusammenfassung

Eine Modifizierung des Kolbenkopfes des Instronrheometers ermöglichte seine Verwendung zur Untersuchung der rheologischen Eigenschaften von SBR-Elastomeren über einem Schubgeschwindigkeitsbereich von 30 sek^{-1} bis 2500 sek^{-1} . An Stelle des üblichen Kolbenkopfes wurde ein Teflonpfropfen mit hohlem Boden verwendet. Dadurch werden Undichtigkeiten zwischen Kolben und Zylinder vermieden und gleichmässige Kraftaufzeichnung erreicht, was eine Ermittlung der gesamten Extrusionskraft durch Extrapolation auf die Zylinderlänge Null ermöglicht. Auf einer gesunden theoretischen Grundlage erhält man so eine praktische Möglichkeit zur Untersuchung der rheologischen Eigenschaften, die alle für die Beurteilung des Verhaltens unter den technischen Verarbeitungsbedingungen und der dafür wichtigen Faktoren von Bedeutung sind. Die Extrusion von SBR 1712 und der 1712-HAF-Mischung durch Kapillaren mit

einem Eintrittswinkel von 180° , einem Durchmesser von 0,33 in., 0,043 in., 0,052 in. und 0,070 in. und einem Verhältnis Länge zu Durchmesser von 1, 2, 4, 6, 8 und 10 wurde bei Temperaturen von 80°C , 90°C , 110°C und 130°C und einer Kreuzkopfgeschwindigkeit von $1/2$, 1, 2 und 5 in./min durchgeführt. Zwischen dem Verhältnis Länge zu Durchmesser und der Extrusionskraft (bei Zylinderlänge Null) bestand eine lineare Beziehung. Die Neigung dieser Geraden liefert Werte für die wahre Schubspannung welche unabhängig von den Stempeldimensionen bei jeder der vier Temperaturen eine bestimmte Abhängigkeit von der Newton'schen Schubgeschwindigkeit zeigen. Im doppellogarithmischen Diagramm bildet die Abhängigkeit der wahren Schubspannung von der wahren Schubgeschwindigkeit für klares SBR-1712-Elastomeres über den gesamten Schubgeschwindigkeitsbereich von 45 sek^{-1} bis 3900 sek^{-1} bei den vier Temperaturen 80°C , 90°C , 110°C und 130°C eine gekrümmte Linie. Das entsprechende Diagramm für die HAF-Mischung von SBR-1712 zeigte die gekrümmte Abhängigkeit unterhalb von Schubgeschwindigkeiten von 100 sek^{-1} und oberhalb dieses Wertes lineares Verhalten entsprechend einem Exponenten von 6,1. Bei allen vier Temperaturen besteht ein grosser Unterschied in der Neigung zwischen niedrigen und hohen Schubgeschwindigkeiten. Das beweist, dass eine Extrapolation der Messungen an Instrumenten mit niedriger Schubgeschwindigkeit auf die unter technischen Bedingungen üblichen höheren Geschwindigkeiten nicht möglich ist, und zwar sowohl beim klaren SBR-1712-Elastomeren als auch bei seiner HAF-Mischung. Die wahre Schubspannung bei einer entsprechenden wahren Schubgeschwindigkeit (also die Viskosität) war wie zu erwarten bei der Mischung bedeutend höher als beim klaren Elastomeren. Hingegen setzt der Zusatz von Russ das Ausmass des Abweichens vom Newton'schen Verhalten herab. Die Viskosität wurde ohne Korrektur für Verformungserholung errechnet und daraus die Aktivierungsenergie nach der Arrheniusgleichung bestimmt. Bei Temperaturen von 90°C , 110°C , und 130°C wurden bei allen Schubgeschwindigkeiten für das klare Elastomere und seine Mischung gerade Linien entsprechend einer Aktivierungsenergie von 1,5 kcal pro Mol erhalten. Der Logarithmus der Viskosität bei 80°C lag in allen Fällen oberhalb der durch die Viskositätslogarithmen bei den anderen drei Temperaturen gehenden Geraden. Das spricht für eine höhere Aktivierungsenergie bei Temperaturen unterhalb 90°C . Zusatz von Russ hat offenbar keinen wesentlichen Einfluss auf die Identität der rheologischen Einheit. Die Extrusionsschwellung nahm bei allen Schubgeschwindigkeiten mit steigender Temperatur und steigendem Quotienten L/D ab. Bei gegebener Temperatur steigt sie mit zunehmender Schubgeschwindigkeit an. Beim klaren Elastomeren war die Schwellung anisotrop, nicht aber bei der Mischung.

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