Viscous Behavior of Some Liquid Rubber Resins

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Synopsis

The flow behavior of several low molecular weight polymers has been studied as a function of shear rate and temperature. These polymers, which had terminating hydroxyl or bromine groups, included homopolymers of polybutadiene and acrylonitrile–butadiene and styrene–butadiene copolymers. Viscosity was measured as a function of shear rate for the temperature range 25°–35°C, and the limiting zero shear viscosities were obtained for the range 25°–60°C. A cone plate viscometer was employed to measure the effect of shear rate on viscosity, and a Brookfield viscometer was used to verify the zero-shear rate values. A tendency of the fluid to flow out of the cone-plate gap was observed for some of the materials studied. From the viscosity data, characteristic times were estimated, and the data were compared with two constitutive equations. A modified Arrhenius equation was fitted to the zero-shear viscosity data. In the case of one material, it was possible to test the Nakajima relationship between viscosity and molecular weight distribution. The dependence of material parameters on temperature is discussed in detail.

INTRODUCTION

Low molecular weight polybutadiene liquid resins form a unique class of polymer melts. They are usually referred to as rubber liquids, since they are in the melt state at room temperature. The hydroxyl-terminated polybutadiene resin is a recent addition to the urethane field and offers many advantages for producing products such as castable, moldable, and millable elastomers, foams, adhesives, etc. Copolymerization of styrene and acrylonitrile with the polybutadiene backbone permits the production of tailored polymers that will meet specific requirements. Bromine-terminated polybutadiene liquid resins take advantage of the fact that the bromine group may react with amines to yield elastomers that have desirable properties.

The rheological properties associated with these low molecular weight polymer resins are of importance for their processing. Moreover, rheological characterization provides information of value in elucidating the structure and molecular characteristics of these relatively low molecular weight polymers.

The most fundamental material parameter is the zero-shear viscosity. Characteristic times also play an important role in the formulation of constitutive equations.[1,2] Bueche[3] and Bueche and Harding[4] have proposed a

characteristic time which may be used to estimate the molecular weight of a polymer from simple shear experiments. Recent published results have indicated that there is a direct relationship between the viscosity–shear rate curve and the molecular weight distribution (MWD) of a polydisperse polymer. The results obtained in this study have been analyzed in the light of these ideas.

The effect of temperature on η_0 has been extensively studied, and a number of correlations have been suggested. However, the effect of temperature on characteristic times has been studied to a lesser extent, for example, by Cross.[7]

The objectives of this work were: (1) to characterize the materials rheologically, with special emphasis on viscous behavior; (2) to interpret material constants such as zero-shear viscosity and characteristic time in terms of molecular theories of viscous flow; (3) to determine the temperature dependence of the material constants; (4) to study the effect of endgroups and copolymerization; and (5) to compare the results of the above with other studies on similar materials.

MATERIALS

Polybutadiene liquid resins are low molecular weight polymers which are in the liquid state at room temperature. Such polymers have a molecular weight of the order of 10,000 or less. *Cis*- and *trans*-polybutadiene form the backbone structure, and terminating groups of hydroxyl or bromine serve as ending active sites. Some of the hydroxyl-terminated polymers of this study were based on copolymers of butadiene with styrene and acrylonitrile.

TABLE I
Material Properties[a]

	Resin 1	Resin 2	Resin 3	Resin 4	Resin 5
Manufacturer's code number	XPRD-C-162	XPRD-B-241	R-15M	CS-15	CN-15
Code number used in presentation of data	C-162	B-241	R-15M	CS-15	CN-15
Butadiene, wt-%	98	100	100	75	85
Styrene, wt-%	—	—	—	25	—
Acrylonitrile, wt-%	—	—	—	—	15
Nonpolymeric additives, wt-%	2	—	—	—	—
Terminating groups	Br	Br	OH	OH	OH
Hydroxyl content, meq/g	—	—	0.75	0.75	0.7

[a] Materials 1 and 2 were supplied by Polymer Corporation Ltd., Sarnia, Ontario, Canada. Materials 3, 4, and 5 were supplied by Sinclair Petrochemicals Inc., New York, N. Y.

To make a useful rubber network with such materials, it is necessary during cure to increase their molecular weight. This is made possible by the active sites at the ends of the polybutadiene chains which, by means of a chain extension mechanism, lead to the formation of an end-free network as shown by Dolezal and co-workers.[5]

Five different polybutadiene liquid resins were studied. Their physical properties, as obtained from Dolezal et al.[5] and Sinclair Petrochemical,[6] are shown in Table I. For polymer B-241, an analysis of the molecular weight distribution by gel permeation chromatography (GPC) was supplied by the manufacturer, and the results are shown in Table II.

TABLE II
Polymer B-241, Molecular Weight Distribution Data[a]

Wt fraction, %	Mol wt
0.02	203,000
0.07	156,000
0.19	119,000
0.48	91,000
1.15	70,000
2.25	53,600
4.23	41,100
5.96	31,500
7.87	24,100
9.14	18,500
10.08	14,200
10.36	10,850
10.21	8,300
9.56	6,400
8.30	4,900
6.99	3,800
5.25	2,860
3.78	2,190
2.11	1,680
1.22	1,290
0.53	990
0.21	760
0.04	580

[a] $\bar{M}_n = 6,300$, $\bar{M}_w = 15,300$; $\bar{M}_z = 31,300$.

EQUIPMENT

In the present work, a Ferranti-Shirley cone-and-plate viscometer was used to carry out rheological measurements. Detailed description of this instrument and analytical methods of handling experimental data are available in the literature.[7] The choice of this equipment was governed mainly by its ability to operate at low and high shear rates with good control over temperature. The use of a capillary rheometer was ruled out because temperature control with commercial capillary instruments is not satisfactory in the desirable temperature range for this study ($25°$–$35°C$).

By means of an "on-off" relay control and a constant-temperature circulating bath, the temperature was maintained within ±0.5°C of the desired value.   Two sets of gears and three different cones were used in the viscosity measurements.   The geometry of these cones is given in Table III. Newtonian fluids of known viscosity were used to obtain a calibration constant for each of the cones at each of the shear rates employed.

TABLE III
Geometry of Cones

Cone	Radius, cm	Apex angle θ, rad
Large	3.5	0.006026
Medium	2	0.006010
Small	1	0.0056588

A Brookfield bob-and-cup viscometer was used to verify the limiting zero-shear viscosity, η_0, which was obtained by extrapolating the cone-and-plate results.   A special jacketed sample chamber assembly was used, which allowed control over the temperature of the fluid within ±0.5°C.   Spindles of two sizes were used because of the wide variation of viscosity over the range of temperatures studied.   The spindles were chosen so as to ensure accurate viscosity measurements in the range of 50–1000 poises.   The apparatus was calibrated using Newtonian fluids.   The Brookfield viscometer was used to obtain limiting zero-shear viscosities for fluids B-241, R-15M, CS-15, and CN-15 at temperatures of 25°, 30°, 35°, 40°, 50°, and 60°C.

In general, viscosity measurements were reproducible to within ±5 poises.

EXPERIMENTAL OBSERVATIONS

At intermediate and high shear rates, marked "shear thinning" can be seen in the two polymers B-241 and C-162 (Figs. 1 and 2).   The other three polymers, CN-15, CS-15, and R-15M, also show a decrease in viscosity with increase of shear rates, as shown in Figures 3 to 5, but the decrease in viscosity is fairly moderate.

To make a comparison between the polymers studied n the present work and those studied by Boyce et al.,[8] a graph of viscosity versus shear rate was made, using the results obtained at 25°C.   Polymers B-1 and A-1 from Boyce's experimental results were chosen for comparison.   B-1 is a random carboxyl-grafted polybutadiene with molecular weight $\bar{M}_w$ = 6360 and $\bar{M}_w/\bar{M}_n$ = 2.35.   Polymer A-1 is polybutadiene having a molecular weight of $\bar{M}_w$ = 8460 and $\bar{M}_w/\bar{M}_n$ = 1.29.   In Figure 6, polymers B-241 and C-162 show the largest amount of shear thinning.   Polymers B-1 and CN-15 show moderate shear thinning of the same order of magnitude, while polymers CS-15, R-15M, and A-1 indicate very slight shear thinning.

Boyce et al.[8] noted in their study that both molecular weight and molecular weight distribution have a marked influence on the flow properties of

these polymers.   The effect of branching and molecular structure was found
to be of second order.   The high value of the ratio $\bar{M}_w/\bar{M}_n$ leads to the early
appearance of pseudoplasticity and the broadly sloping fall-off viscosity in
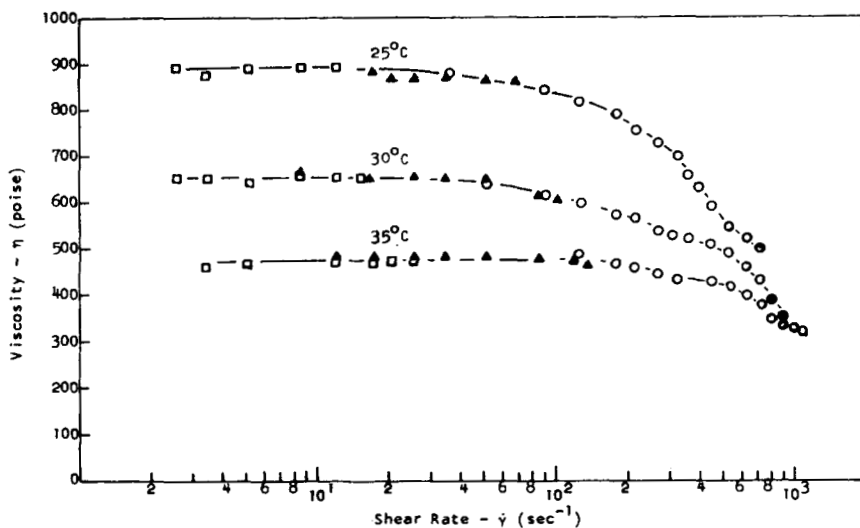the shear thinning region.   They also noted that the narrow distribution

Fig. 1. Polymer B-241, plot of η vs. $\dot{\gamma}$:   ($\square$) large cone; ($\blacktriangle$) medium cone; ($\bigcirc$) small cone.
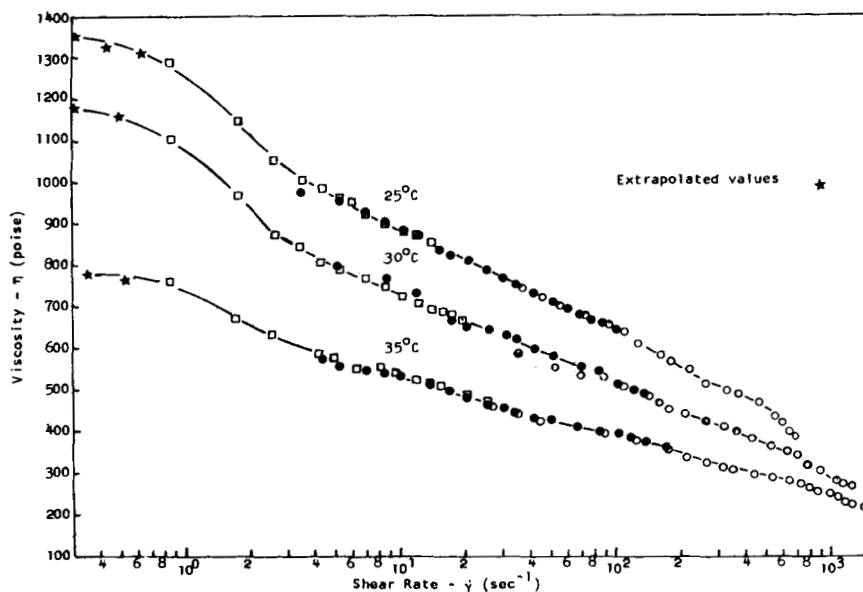
Fig. 2. Polymer C-162, plot of η vs. $\dot{\gamma}$:   ($\square$) large cone; ($\blacktriangle$) medium cone; ($\bigcirc$) small cone; ($\star$) extrapolated values.

polymers like A-1 show a steep fall-off viscosity in the shear thinning region similar to the steep curve predicted for a monodisperse polymer by Bueche and Harding.[4]   This was also shown by Rudd[9] and Ballman[10] for high molecular weight polystyrene.   The shape of the viscosity fall-off for the polymers CN-15 and R-15M is very similar to the narrow MWD polymers
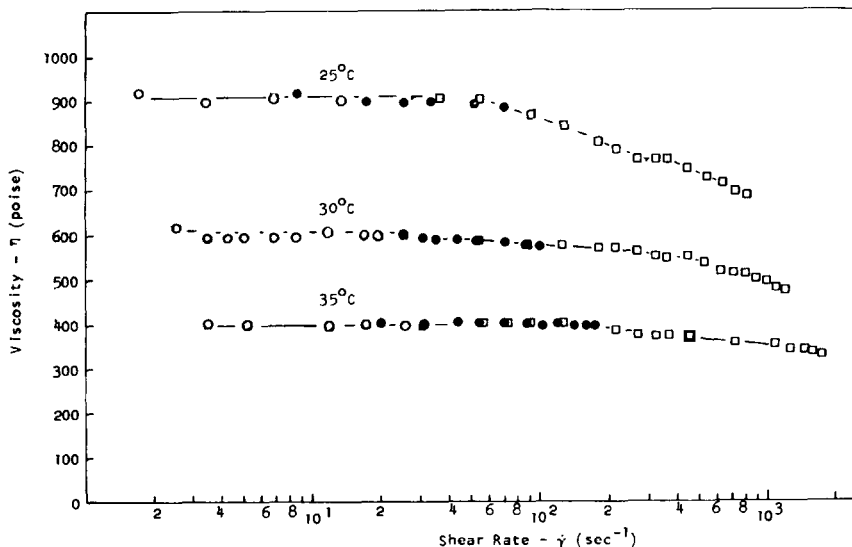

Fig. 3. Polymer CN-15, plot of η vs. $\dot{\gamma}$:   (O) large cone;   (▲) medium cone;   (□) small cone.
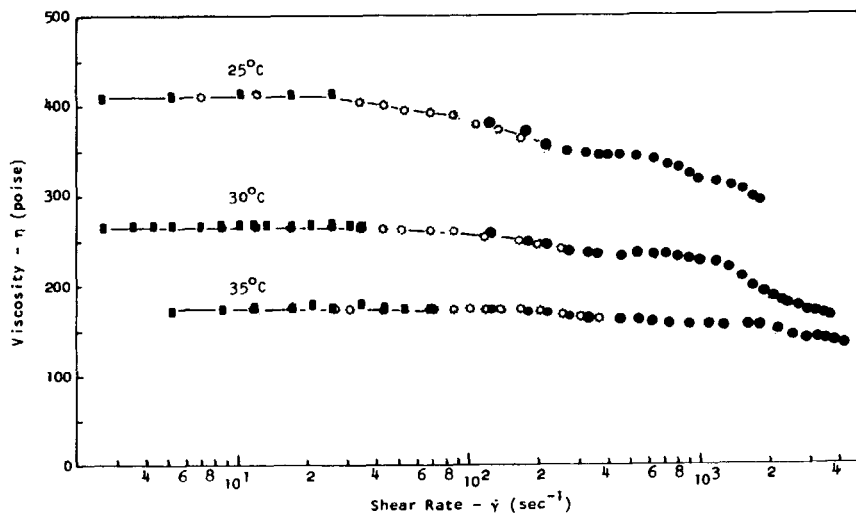

Fig. 4. Polymer CS-15, plot of η vs. $\dot{\gamma}$:   (■) large cone;   (O) medium cone;   (●) small cone.

studied by Boyce, and the viscosity fall-off of B-241 is very similar to the broader MWD polymers.

A close examination of Figure 6 reveals inflection points in the viscosity–shear rate curves for polymers CN-15, B-1, R-15M, and CS-15.   These inflection points all fall in the range of shear rates between 250 and 800 sec^{-1} at 25°C.   With an increase in temperature, the inflection points occur at higher shear rates, as can be seen in Figures 3 to 5 and in the work of Boyce et al.[8]
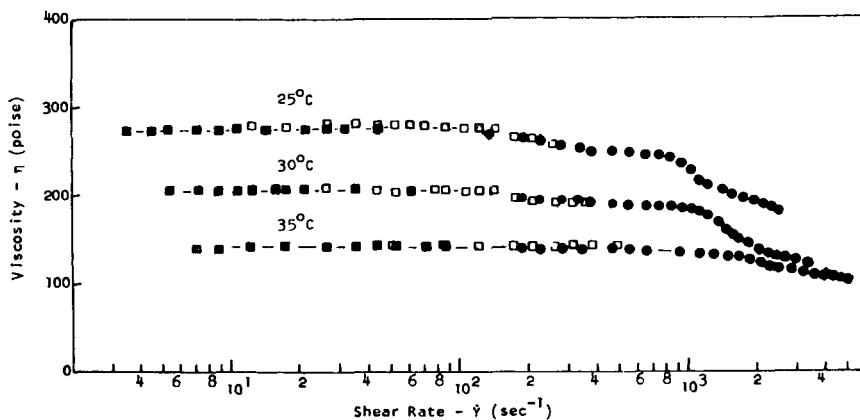

Fig. 5. Polymer R-15M, plot of η vs. $\dot{\gamma}$:   (■) large cone;   (□) medium cone;   (●) small cone.
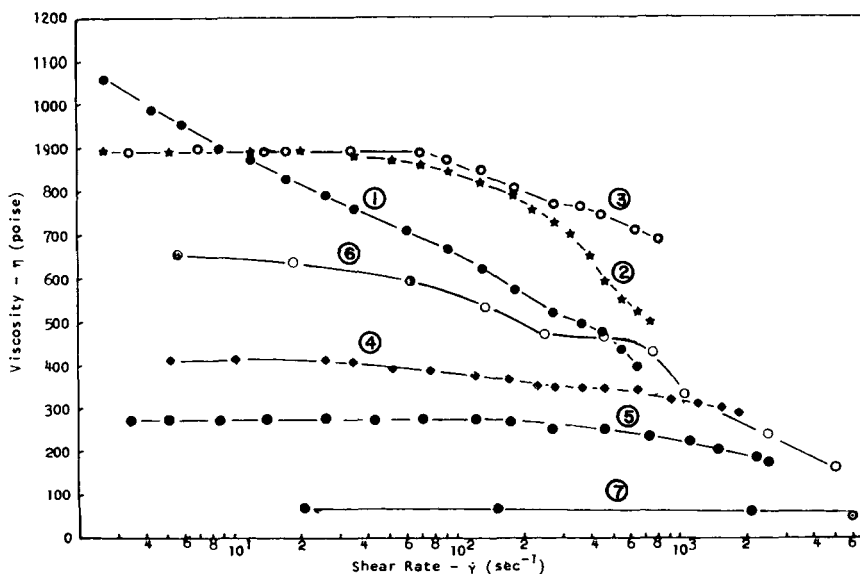

Fig. 6. Comparative plot of η vs. $\dot{\gamma}$ at 25°C for various polymers: (1) C-162;   (2) B-241;   (3) CN-15;   (4) CS-15;   (5) R-15M;   (6) B-1;   (7) A-1.

It should be noted that all the polymers studied exhibited pseudoplasticity even though their molecular weights were in the region of 5600, which has been suggested to be the entanglement molecular weight, M_c, by Kraus and Gruver.[11,12] There is no indication of a shift to Newtonian behavior as is often observed in the range of M_c. Regarding this point, it is of interest that Cross[13] has recently reported η_0 data which failed to show a discontinuity at M_c when plotted as a function of molecular weight.

At high shear rates, some of the polymers exhibited a sudden decrease in the measured stress at all the temperatures studied. This phenomenon has been observed by other investigators in cone-and-plate flow, and Hutton,[14] Pearson,[15] and Lenk[16] have suggested that it is a result of separation of the fluid between the cone and plate which starts at the periphery of the cone and grows radially inward. The above investigators have suggested that the tendency of the fluid to climb out of the gap is associated with normal stress differences, and Hutton[17] has proposed an explanation based on the concept of "fracture" due to "stored elastic energy."

When the small cone was employed at high shear rates, it was found that all the fluids began to climb on the outside periphery of the cone. At higher shear rates, three of the polymers, C-162, B-241, and R-15M, showed a sudden decrease in the torque reading resulting in violent fluctuations of the needle on the indicator unit.

To study the above phenomenon, several experiments were carried out:

1. The fluids were tested in an Instron capillary rheometer at shear rates exceeding those measured in the cone-and-plate viscometer. There was no indication of flow instability at any shear rate measured.

2. An excess of fluid was placed on the plate, and it was observed that the sudden decrease in the stress occurred at higher shear rates for the same fluid.

3. A Newtonian fluid of the same order of viscosity showed no instability at even higher shear rates.

4. Recordings of the shear rate versus the torque at constant acceleration were made using the small cone, and these showed a large decrease in the stress at a certain shear rate. Moreover, it was found that as the temperature increased, the occurrence of this "instability" point was shifted to higher shear rates. As the cone decelerated, a recovery of the stress was obtained at low shear rates.

It has already been noted that separation takes place in the polymers which have a linear structure, whereas the branched polymers like CN-15 and CS-15 do not exhibit any separation up to the maximum shear stress attainable. A possible explanation of this difference is as follows. The compact size of a branched polymer, when compared with a linear polymer of the same molecular weight, will result in a better transfer of stresses throughout the polymer chains. Accordingly, branched polymer melts tend to exhibit less elasticity and smaller normal stress differences than linear polymers of the same molecular weight. As a result, the tendency for

separation which has been associated with normal stress differences will be
reduced with branched polymer melts.

ZERO-SHEAR VISCOSITY AS A FUNCTION
OF TEMPERATURE

The study of the limiting zero-shear viscosity, η_0, for the polymers B-241,
R-15M, CS-15, and CN-15 was carried out in the range of 25°–60°C, which
is well above the glass transition temperature for polybutadiene polymers.

One fluid that seems to stand completely apart is C-162. It contains
small quantities of nonpolymeric ingredients, which apparently influence its
properties to such an extent that its viscosity continued to show a signifi-
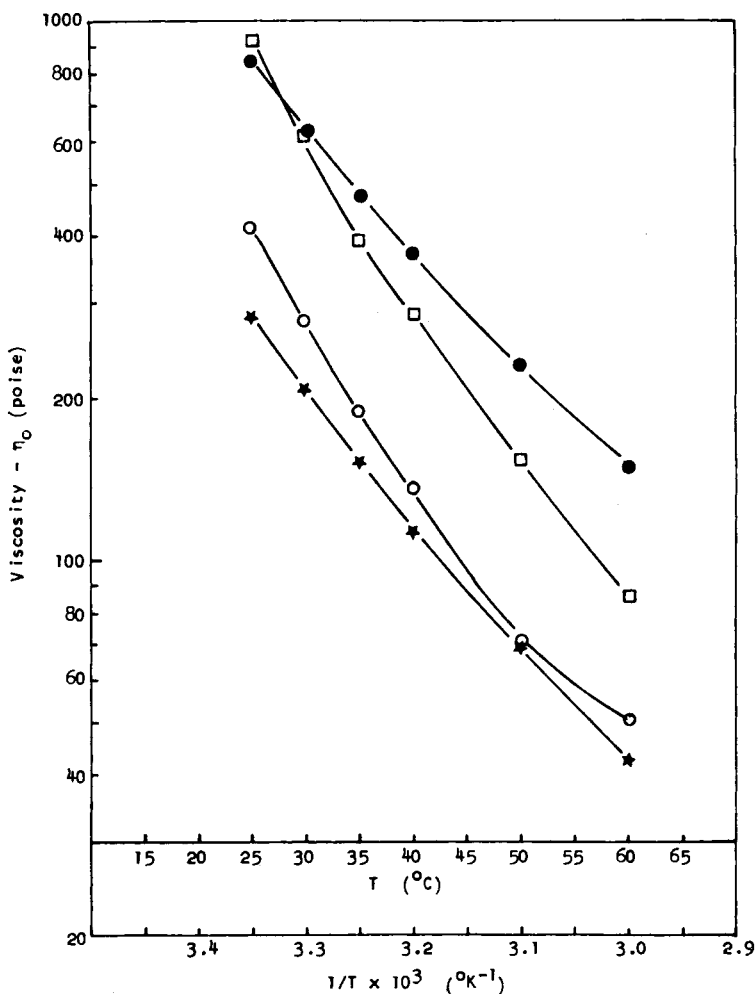cant increase as shear rate decreased even at shear rates equal to 0.87 sec^{-1}.

Fig. 7   Plot of η_0 vs. $1/T$:   (□) CN-15;   (●) B-241;   (○) CS-15;   (★) R-15M.

Therefore, an estimation of η_0 was made by means of an extrapolation based on a series expansion of the fluidity, as given by Reiner:[18]

$$\frac{1}{\eta} = \frac{1}{\eta_0} + \sum_{n=1}^{\infty} a_{2n} \cdot \tau^{2n}. \tag{1}$$

To estimate η_0, only the first term of the series is taken, and eq. (1) becomes

$$\frac{1}{\eta} = \frac{1}{\eta_0} + \beta\tau^2. \tag{2}$$

Extrapolation to $\tau = 0$ on a graph of $1/\eta$ versus τ^2 yields η_0 at each temperature studied. The values estimated for η_0 by this procedure for C-162 are 1425, 1175, and 787 poises at 25°, 30°, and 35°C, respectively. The extrapolated values in Figure 2 show the viscosity dependence on low shear rates. Other methods of extrapolation have been used to evaluate the limiting zero-shear viscosity.[19,20] However, in a large number of works, extrapolation is made by plotting a graph of $1/\eta$ versus τ, which is not in agreement with eq. (1) and violates the condition of isotropy, i.e., the requirement that η be an even function of τ.

When the data for the limiting zero-shear viscosity were plotted in the form of log η_0 versus the reciprocal of the absolute temperature, $1/T$, the resulting curves were not linear, as shown in Figure 7. For polymers R-15M and B-241, the decrease in viscosity with temperature was somewhat smaller than with polymers CS-15 and CN-15. The apparent decrease of activation energy with an increase in temperature has also been reported by Boyce et al.[8] for low molecular weight polymers and copolymers of butadiene.

The use of a modified type of Arrhenius equation was suggested by Lenk,[16] Berry and Fox,[21] and others[22−26] to show the dependence of viscosity on temperature and to allow extrapolation of η_0 to temperatures outside the range of experimental data. In this work, a modified Arrhenius equation with an adjustable parameter, T_R, corresponding to a reference temperature was employed:

$$\eta_0 = A \exp\left[\frac{E}{R(T - T_R)}\right]. \tag{3}$$

The validity of eq. (3) is demonstrated in Figure 8.

With the decrease in temperature, the viscosity will increase exponentially and will approach infinity as $T \to T_R$. Berry and Fox[21] have shown that, for low molecular weight polymers, the glass transition temperature, T_g, is close to the reference temperature, T_R, such that $T_g - T_R \approx 0$. This appears to be true for polymer B-241, where T_R coincides with the experimental value of $T_g = 188°K$ as given by Dolezal et al.[5] The value of $T_R = 196°K$, obtained for CN-15, seems to be in good agreement with the experimental value of T_g given by Boyce et al.[8] for butadiene–acrylonitrile copolymers.
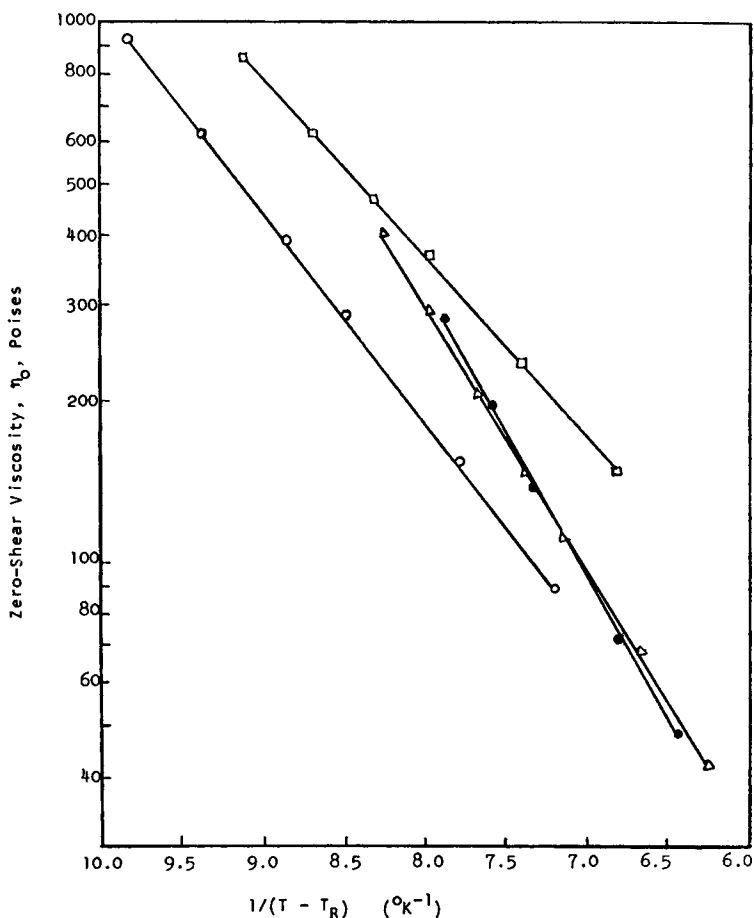
Fig. 8. Plot of η_0 vs. $1/(T - T_R)$: ($\square$) B-241, $T_R = 188°$K; ($\bigcirc$) CN-15, $T_R = 196°$K; ($\triangle$) CS-15, $T_R = 177°$K; ($\bullet$) R-15M, $T_R = 173°$K.

A CHARACTERISTIC TIME

A "phenomenological" characteristic time, not dependent for its definition on any molecular theory or empirical constitutive equation, has been suggested by Dealy[2] as a basic material constant. It is defined in terms of a series expansion of the apparent viscosity as a function of the second invariant of the rate-of-strain tensor. In terms of the shear rate in a viscometric flow experiment,

$$\eta/\eta_0 = 1 - \lambda_1^2 \dot{\gamma}^2 + \dots \tag{4}$$

The characteristic time, λ_1, can be estimated from experimental data obtained at a shear rate for which η/η_0 is near unity:

$$\lambda_1 \approx \frac{(1 - N)^{1/2}}{\dot{\gamma}_N} \tag{5}$$

TABLE IV
Values of λ_1 Estimated by Use of Eq. (5)

Temp.		CN-15	CS-15	R-15M	B-241	C-162
25°C	$\dot{\gamma}_N$, sec^{-1}	86	72	157	70	0.9
	λ_1, sec	2.6×10^{-3}	3.1×10^{-3}	1.4×10^{-3}	3.2×10^{-3}	3.5×10^{-1}
30°C	$\dot{\gamma}_N$, sec^{-1}	110	120	220	90	1.2
	λ_1, sec	2.0×10^{-3}	1.9×10^{-3}	1.0×10^{-3}	2.5×10^{-3}	2.6×10^{-1}
35°C	$\dot{\gamma}_N$, sec^{-1}	220	200	320	250	1.5
	λ_1, sec	1.0×10^{-3}	1.1×10^{-3}	0.7×10^{-3}	0.9×10^{-3}	2.1×10^{-1}
	$N = \eta/\eta_0$	0.95	0.95	0.95	0.95	0.90

where $N = \eta/\eta_0$ at $\dot{\gamma} = \dot{\gamma}_N$, and N is close to 1. Using the viscosity-shear rate data in Figures 1 to 5, the value of λ_1 at each of the measured temperatures was estimated. For the polymers B-241, R-15M, CS-15, and CN-15, a value of $N = 0.95$ was used to estimate λ_1, but a value of $N = 0.90$ had to be used for polymer C-162. The values of $\dot{\gamma}_N$ were obtained from viscosity-shear rate graphs and are given in Table IV, with the corresponding values of λ_1 calculated from eq. (5). The estimated values of λ_1 for polymers B-241, R-15M, CS-15, and CN-15 have a magnitude of about 10^{-3} sec. In comparison, polymer C-162, which is similar to B-241 except that it contains some nonpolymeric additives, has a characteristic time of the order of 10^{-1} sec.

SUPERPOSITION

It is of particular practical importance to know if there are ways of presenting viscosity data which can bring onto one curve data for a particular material for a variety of temperatures. Of even greater value would be a plot on which data for an entire class of materials (at various temperatures) fall on one curve. Vinogradov and Malkin[27-29] have published data which indicate that this latter, more comprehensive superposition can be achieved by plotting η/η_0 versus $\dot{\gamma}\eta_0$. On the other hand, a number of investigators[1-3] have found that superposition is achieved by plotting η/η_0 versus $\dot{\gamma}\lambda$, where λ is some relaxation time. In our work, satisfactory temperature superposition of the data was achieved by plotting η/η_0 versus $\dot{\gamma}\lambda_1$ for any one of the materials studied. However, although a plot of η/η_0 versus $\dot{\gamma}\lambda_1$ is found to superpose data for different materials at shear rates below $\dot{\gamma}_N$, a comprehensive superposition at somewhat higher shear rates was not obtained by this procedure. Neither was it possible to achieve such a comprehensive superposition by plotting η/η_0 versus $\dot{\gamma}\eta_0$.

CONSTITUTIVE EQUATIONS

Bueche,[3] employing molecular theories, derived a theoretical equation for the dependence of the viscosity of monodisperse polymer melts on the shear rate:

$$\frac{\eta}{\eta_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{(\dot{\gamma}\lambda_2)^2}{n^2(n^4 + \dot{\gamma}^2\lambda_2^2)} \left(2 - \frac{(\dot{\gamma}\lambda)^2}{n^4 + \dot{\gamma}^2\lambda_2^2}\right) \tag{6}$$

where λ_2 is defined as

$$\lambda_2 = \frac{12 \cdot \eta_0 M}{\pi^2 \rho R T}. \tag{7}$$

However, when Bueche and Harding[4] carried out experiments to test this theoretical equation, they found that the data were more consistently and simply correlated by the following empirical equation:

$$\frac{\eta}{\eta_0} = \frac{1}{1 + 0.6(\dot{\gamma}\lambda_2)^{0.75}} \tag{8}$$
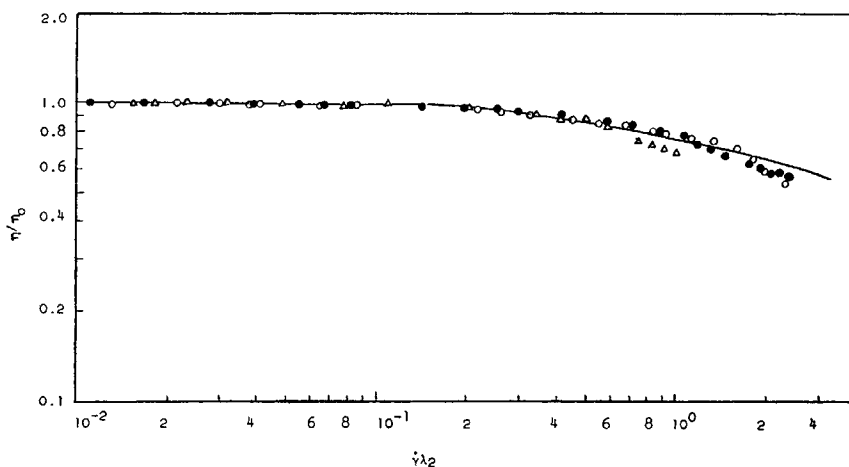
Fig. 9. Polymer B-241, Bueche-Harding standard curve: (●) 25°C;   (O) 30°C;   (Δ) 35°C.
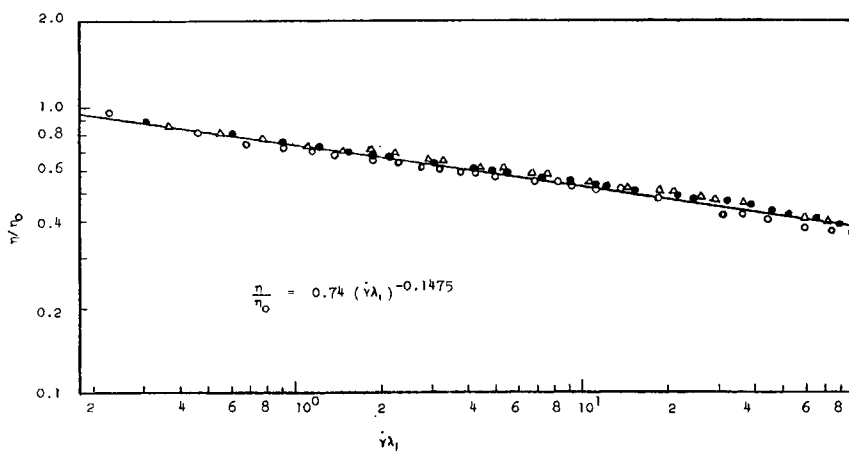

Fig. 10. Polymer C-162; power law curve: (●) 25°C;   (O) 30°C;   (Δ) 35°C.

The experimental results for four of the materials studied were fitted to eq. (8), and values of λ_2 were determined from this procedure.   Figure 9 gives a comparison of the data for material B-241 with eq. (8), with λ_2 chosen to give the best fit.   Good temperature superposability was achieved by this procedure.   Similar results were obtained for the other materials studied, with one exception.   In the case of polymer C-162, no fit was possible, but the data appeared to follow closely a power law model:

$$\frac{\eta}{\eta_0} = k(\dot{\gamma}\lambda_1)^m \tag{9}$$

where k and m are empirical constants.   This is shown in Figure 10.   Ball-

man[10] has also reported that polymer blends cannot be described by eq. (8). Although eqs. (8) and (9) are only empirical representations of the viscosity-shear rate data, they are useful for the prediction of viscosity-shear rate dependence in the experimental range to within $\pm 15\%$.

The superposition of experimental data employing both $\dot{\gamma}\lambda_1$ and $\dot{\gamma}\lambda_2$ implies that the ratio λ_1/λ_2 is independent of temperature for each material. Values of λ_1/λ_2 are given in Table V.

TABLE V
Calculation of λ_1/λ_2 and M

	B-241	R-15M	CS-15	CN-15
λ_1 at 25°C, sec	3.2×10^{-3}	1.4×10^{-3}	3.1×10^{-3}	2.6×10^{-3}
λ_2 at 25°C, sec	1.3×10^{-3}	0.4×10^{-3}	0.6×10^{-3}	0.8×10^{-3}
λ_1/λ_2	2.5	3.5	5	3.2
density ρ at (room temp.), g/cc	0.925	0.902	0.933	0.932
η_0 at 25°C, poises	890	283	410	920
$M = \dfrac{\pi^2 \rho R T \lambda_2}{12\eta_0}$	27,000	26,500	29,200	16,700

Having evaluated λ_2, it is possible to calculate a molecular weight using eq. (7):

$$M = \frac{\pi^2 \rho R T \lambda_2}{12\eta_0}. \tag{10}$$

The values of M calculated in this way, which are given in Table V for the polymers B-241, R-15M, CS-15, and CN-15, indicate that these polymers have low molecular weights of the same order of magnitude. However, since eq. (10) comes out of a theory of monodisperse systems, the meaning of these calculated values of M for polydisperse systems is not immediately clear. Many investigators have suggested that M in eq. (10) is very nearly the weight-average molecular weight, $\bar{M}_w$. A number of studies in recent years have indicated that $M = (\bar{M}_w)^d$, but there has been no agreement among investigators as to the value of d. This parameter was found to be smaller than unity by Brodnyan et al.[30] and larger than unity by Stratton.[31] In the present work, a value of $M = 27{,}000$ for polymer B-241 is larger than the manufacturer's value of $\bar{M}_w$ (15,300) and smaller than $\bar{M}_z$ (31,300). As for the other polymers studied, no conclusions can be drawn because their molecular weight distributions (MWD) were not available.

PREDICTION OF THE VISCOSITY CURVE FROM MWD

A number of investigators,[11,31,32] have shown that the relationship between η/η_0 and $\dot{\gamma}/\dot{\gamma}_0$, where $\dot{\gamma}_0$ is some characteristic shear rate, is closely related to the molecular weight distribution. Nakajima[33] has suggested a rather simple and direct empirical relation to predict the viscosity-shear
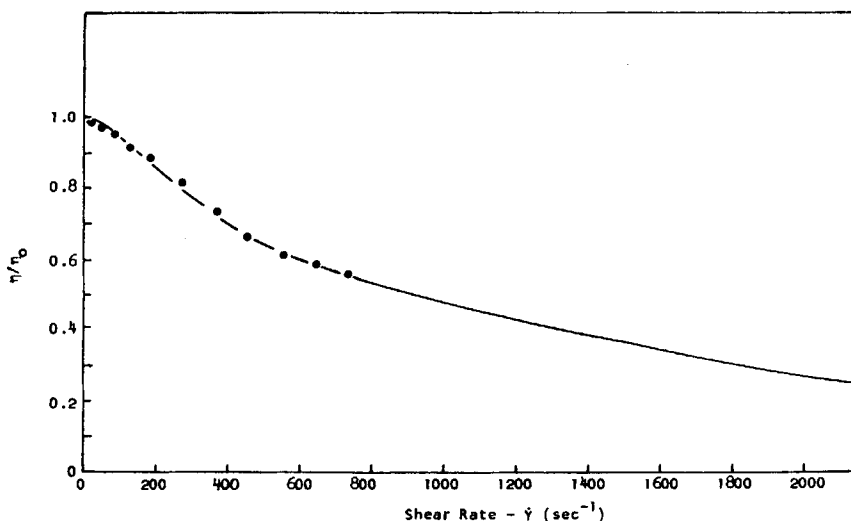
Fig. 11. Polymer B-241 at 25°C, comparison between Nakajima's theory and experimental results: (—) Nakajima's theory; (●) experimental.

rate dependence from MWD data.   A test of this theory is made by taking the MWD data for polymer B-241 given in Table II.

In his correlation, Nakajima proposed the following empirical relation:

$$\dot{\gamma}_N = (K/M_{iN})^\alpha \tag{11}$$

$$N = \eta/\eta_0 = \Sigma w_i. \tag{12}$$

To estimate values for the material parameters K and α, two molecular weights were chosen from Table II.   The corresponding cumulative weight fraction, Σw_i, were then calculated, and, using eq. (12) together with Figure 2, it was possible to obtain the corresponding values of $\dot{\gamma}_N$ and apply them in eq. (11) to determine K and α.   Using the values so determined, eq. (12) becomes

$$\dot{\gamma}_N = (1.03 \times 10^6/M_{iN})^{1.51} \tag{13}$$

From the above equations, it is now possible to obtain the viscosity-shear rate dependence using MWD data from Table II.   In Figure 11, a plot of η/η_0 versus $\dot{\gamma}$ at 25°C shows good agreement between the experimental results and the predicted line using eqs. (11) and (12).   The deviation between the experimental results and the theoretical line does not exceed 3%–4%.   It is important to note that one can also apply eqs. (11) and (12) to calculate MWD from viscosity-shear rate data.   However, special mathematical techniques are needed, as has been shown by Nakajima.[33,34]

CONCLUSIONS

The above studies show that liquid rubber resins are sensitive to both shear rate and temperature, showing significant shear thinning and a sub-

stantial decrease in viscosity with a small increase in temperature.   The dependence of the zero-shear viscosity on temperature may be described by a modified Arrhenius equation with an adjustable parameter, T_R, which appears to be very close to the glass transition temperature.   Satisfactory superposition is obtained by plotting η/η_0 for all temperatures versus $\dot{\gamma}\lambda_1$ for each material, where λ_1 is a characteristic time based on the fluid's initial departure from Newtonian behavior.   However, it was not possible to obtain a comprehensive superposition of the data for all materials on one plot. All the resins, except one which contained some additives, could be fitted adequately to the Bueche-Harding standard curve.   Finally, it was shown that Nakajima's empirical method for the prediction of viscosity-shear rate curves from MWD data yields excellent results, for at least one of the materials under study.

List of Symbols

k	constant in power law equation, eq. (9)
K	constant in Nakajima's equation, eq. (11)
m	power law exponent, eq. (9)
M	molecular weight in Bueche's theory, eq. (7)
M_c	entanglement molecular weight
M_{iN}	molecular weight corresponding to $\eta/\eta_0 = N$
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
$\bar{M}_z$	z-average molecular weight
N	a particular value of η/η_0
R	gas constant
T	absolute temperature
T_g	glass transition temperature
T_R	reference temperature
w_i	cumulative weight fraction corresponding to M_{iN}

Greek Symbols

α	Nakajima's exponent, eq. (11)
$\dot{\gamma}$	shear rate in viscometric flow
$\dot{\gamma}_0$	a characteristic shear rate
$\dot{\gamma}^{1}/_2$	shear rate corresponding to $\eta/\eta_0 = {}^1/_2$
$\dot{\gamma}_N$	shear rate corresponding to $\eta/\eta_0 = N$
η	apparent viscosity
η_0	limiting zero-shear viscosity
λ	some relaxation time
λ_1	characteristic time in eq. (4)
λ_2	Bueche's relaxation time
ρ	density
τ	shear stresses in viscometric flow

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