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Rheological Analysis of Raw Elastomers with the Multispeed Mooney Shearing Disk Viscometer

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Synopsis

Mooney's shearing disk viscometer is one of the most important analytical research and process control instruments for elastomers. In this paper a new method is developed for computing the shear stress and shear rate of materials from data obtained on this instrument. In addition, the non-linear viscoelastic behavior of elastomers in the viscometer is analyzed with special emphasis upon normal stress effects. Experimental data for natural rubber, SBR, and polyisobutylene are discussed.

INTRODUCTION

Raw elastomers are well known to have rheological properties which differ significantly from the classical concepts of elastic solids and Newtonian fluids. When these materials are subjected to steady shearing deformations such as exist in calenders and extruders, nonclassical properties such as non-Newtonian viscosity, viscoelasticity, and thixotropy are of the utmost importance. If elastomers are to be processed under optimum conditions, knowledge of these rheological properties proves essential.

Though the industrial manufacture of rubber articles dates to the third decade of the nineteenth century,[1] it was not until the 1920's that quantitative methods of testing processability of uncured bulk rubber were developed. Investigations before this time, reviewed for instance by deVries,[2] consisted largely of dilute solution viscosity measurement and interpretation. The two important testing devices developed in these years were Marzetti's extrusion rheometer[3] and Williams' parallel plate compression plastometer.[4] In succeeding years rotational instruments were introduced by Mooney and others in which the torque necessary to maintain a steady shearing flow was measured.[5–8] These basic types of instruments remain today as the important methods of rheological analysis of raw elastomers.[9]

A major factor in choosing a type of rubber rheometer is its ability to separate out the various anomalous effects and to measure each individually. Extrusion and compression instruments are subject to severe handicaps in separating the non-Newtonian shear viscosity, viscoelastic memory, and thixotropic contributions. As first pointed out by Mooney and Black,[10] there are large end effects in the extrusion of elastomers, and corrections must be made before the standard procedures[11] may be applied to evaluate the apparent viscosity.* Thus, several time-consuming measurements will be required to obtain each viscosity value. In addition, thixotropic contributions cannot be separated out in this experiment. However, it remains the only procedure for measuring rheological properties of compounded elastomers at high rates of deformation. Compression plastomers are in a far worse position for analytical utility. In their analysis of steady extension of a viscoelastic fluid, Coleman and Noll[15] show that viscoelasticity contributes directly to the compression or extension viscosity. If we also consider the influence of thixotropy, the compression plastometer is seen to yield a hopeless garble of interrelated effects. Neither of the usually quoted studies of Peek[16] and Scott[17] consider either viscoelastic or thixotropic contributions.

Mooney was led into the development of rotational rheometers by the need separating out anomalous rheological effects.[18] Eventually, it was this researcher[7] who in 1936 published the first set of meaningful quantitative rheological data for a high molecular weight bulk elastomer. Of the various types of rotational instruments introduced, the most popular at present are Mooney's shearing disk viscometer[5] and the Piper Scott biconical viscometer.[8] Both instruments suffer from certain disadvantages in analytical interpretation of the torque–rotor velocity relationship. Edge effects exist in each and are probably more significant in the Mooney instrument. A further difficulty in the biconical instrument is the existence of secondary flows caused by the viscoelastic stresses[19,20] which have been observed experimentally in polymer solutions by Giesekus[21] and computed by Langlois.[22] In the remainder of this paper, we shall only consider the shearing disk viscometer.

The shearing disk viscometer, which consists of a knurled disk rotor inside of a cylindrical cavity, was originally developed for one-point viscosity measurements on raw rubber, but in succeeding years more extensive applications were devised. Weaver[23] first published in 1940 the application of a Mooney viscometer to measure scorch (vulcanization) rates. During World War II, the shearing disk viscometer was the standard instrument to control the quality of GR-S production and thus became the subject of several studies.[18,24–26] Taylor, Fielding, and Mooney[25] discuss the incorporation of an elastic recovery device to measure viscoelasticity and a continuous recorder to measure torque–time variation and through this to gain an insight into thixotropy. At this time, multispeed drives were introduced on the disk viscometer;[26] Mooney has derived a procedure to compute shear stress–shear rate data from such an instrument.[27] Mooney's method consists of application of integrating an empirical expression for the

* Philippoff and Gaskins[12] have pointed out that this end effect is caused by the contribution of the pressure driving force to the "elastic straining" of the polymer. The use of end effects as a measure of quantitative determination of nonlinear viscoelastic properties of molten plastics has been exploited by Bagley.[13] However, as a recent careful study by Einhorn and Turetzky[14] indicates, meaningful interpretation of end effects is a difficult problem.

viscosity throughout the instrument and determining the constants. A graphical technique was developed to rapidly compute the viscosity from torque–disk rotation rate data. Multispeed viscometer and elastic recoil measurements though have not been extensively used in maintaining process control in the rubber industry. As will be shown in the experimental part of this paper, single-point Mooney viscosities (ML-4) are often quite midsleading in their prediction of high shear rate viscosity. It should also be noted that on the basis of data which show the existence of slippage in elastomer processing[9,10,28] Mooney[27] has derived a method of evaluation of the slippage velocity in this instrument.

It is the purpose of this paper to refine and improve Mooney's analysis of the shearing disk viscometer especially in the light of modern continuum mechanics. A detailed study will be made of the kinematics of flow and stress variation throughout the instrument. Following this, a new method of deriving the non-Newtonian viscosity behavior will be developed and nonlinear viscoelastic effects analyzed. The work in these sections is similar in approach to existing studies of other instruments which are reviewed in Fredrickson's recent text.[29] In the final part of the paper, we give new experimental data obtained on raw elastomers and discuss its significance.

Kinematics and Stress Components

Mooney's procedure for analyzing flow in the disk viscometer makes use of the artifice of dividing the instrument into regions designated in Figure 1 as I, II, and III. In both region I, between the faces of the disk rotor and the platens, and region II, between the disk edge and the platens, the flow was presumed to be steady laminar shear. Flow in region III and related edge effects were not considered. These flow patterns may be specified in terms of acceleration tensors. We make use of a series of tensors which measure the rate and accelerations of distortions of a differential area element embedded in the fluid. These are defined by the iterative equations:[30]

$$\overset{(1)}{B}{}^{ij} = V_{,m}{}^{i} g^{mj} + V_{,m}{}^{j} g^{im} - 2V_{,m}{}^{m} g^{ij} \tag{1a}$$

$$\overset{(n+1)}{B}{}^{ij} = \frac{D}{Dt}\overset{(n)}{B}{}^{ij} + 2V_{,m}{}^{m}\overset{(n)}{B}{}^{ij} - V_{,m}{}^{i}\overset{(1)}{B}{}^{mj} - V_{,m}{}^{j}\overset{(1)}{B}{}^{im} \tag{1b}$$

These equations are in standard tensor notation. (A rather good development of this subject is given in the text by Aris.[31]) The g^{ij} represents the conjugate metric tensor; the commas denote covariant differentiation, and summation notation is used. The quantity $\overset{(1)}{B}{}^{ij}$ for incompressible media should be noted to be equivalent to the classical deformation rate tensor for Newtonian fluids. For the case of isochoric motions, eq. (1) becomes identical to the matrices used by Giesekus,[32] White and Metzner,[33] and Fredrickson.[29]

We shall use a fixed space cylindrical coordinate system with the origin at the center of the upper face of the disk.

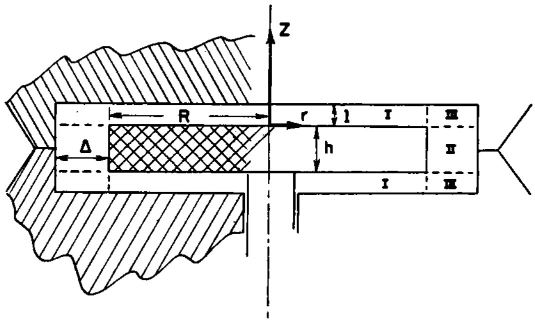

Fig. 1. Disk and stator in shearing disk viscometer.

The velocity field in region I may be specified to be

$$\mathbf{V} = V_\theta \mathbf{e}_\theta = rf(z)\mathbf{e}_\theta \tag{2}$$

and in the region II to be

$$\mathbf{V} = V_\theta \mathbf{e}_\theta = rw(r)\mathbf{e}_\theta \tag{3}$$

The velocity is presumed to vary linearly with radius in region I and to be independent of z in region II. That such a flow pattern is realistic will follow from our ability to satisfy the equations of force equilibrium when we make use of this presumption, together with our knowledge of the stability of flow and faith in the uniqueness of the solution of the equations of motion.

The cylindrical coordinate physical components of the kinematic tensors defined by eq. (1) are then:

$$\mathbf{B}_1 = \left\|\overset{(1)}{B}{}^{\langle ij\rangle}\right\| = \begin{vmatrix} 0 & \Gamma & 0 \\ \Gamma & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{4a}$$

$$\mathbf{B}_2 = \left\|\overset{(2)}{B}{}^{\langle ij\rangle}\right\| = \begin{vmatrix} -2\Gamma^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{4b}$$

$$\mathbf{B}_n(n > 3) = \left\|\overset{(n)}{B}{}^{\langle ij\rangle}\right\| = \mathbf{0} \tag{4c}$$

For region I

$$\Gamma_{\mathrm{I}} = \frac{\partial V_\theta}{\partial Z} \tag{5a}$$

and in region II

$$\Gamma_{\mathrm{II}} = \frac{1}{r}\frac{d}{dr}\left(r\frac{dw}{dr}\right) \tag{5b}$$

We now turn to computing the stress components in the instrument. If we neglect thixotropy and presume an elastomer to be an isotropic viscoelastic material, the stress tensor for motions in which the kinematic tensors may be expressed by eq. (4) is given by Ref. 30;

$$\boldsymbol{\tau} = p\mathbf{I} + \mathbf{t} \tag{6a}$$

$$= -p\mathbf{I} + \mu\mathbf{B}_1 - (1/2)\beta_1\mathbf{B}_2 + \beta_2[\mathbf{B}_1{}^2 + (1/2)]\mathbf{B}_2 \tag{6b}$$

This may be expressed in matrix form as:[30,29,32]

$$\begin{vmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{12} & \tau_{22} & \tau_{23} \\ \tau_{13} & \tau_{33} & \tau_{33} \end{vmatrix} = -\begin{vmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{vmatrix} + \begin{vmatrix} \beta_1\Gamma^2 & \mu\Gamma & 0 \\ \mu\Gamma & \beta_2\Gamma^2 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{7}$$

The parameters of μ, β_1, and β_2 are rheological material properties and are functions of Γ^2. Component 1 represents direction of flow and component 2, the direction of shearing.

The non-Newtonian viscosity, μ, may often be represented over a substantial shear rate range by a power law. This has been found to be the case for several bulk polymers, including butadiene–styrene copolymer and its carbon black compounds,[14,34] poly(vinyl chloride),[35] polyethylene,[36,37] and polypropylene.[37] The power law may be expressed:

$$\mu = K\Gamma^{n-1} \tag{8a}$$

The functions β_1 and β_2 have received only limited study, and no satisfactory direct measurements for bulk polymers have appeared in the literature. White and Metzner,[33] summarizing existing data for polymer solutions, find that for solutions of nonpolar polymers in hydrocarbon solvents

$$\beta_1 \sim C\mu^2 \tag{8b}$$

$$\beta_2 \sim 0 \tag{8c}$$

These results are reinforced by the more recent work of Ginn and Metzner.[38]

The stress components must satisfy the equations of force equilibrium which for regions I and II, respectively, given by eqs. (9) and (10):

$$0 = \frac{\partial \tau_{12}}{\partial z} \tag{9a}$$

$$-\frac{\rho V_\theta{}^2}{r} = \frac{\partial \tau_{33}}{\partial r} + \frac{\tau_{33} - \tau_{11}}{r} \tag{9b}$$

$$0 = \frac{\partial \tau_{22}}{\partial z} \tag{9c}$$

$$0 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\tau_{12}) \tag{10a}$$

$$-\rho\frac{V_\theta{}^2}{r} = \frac{\partial \tau_{22}}{\partial r} + \frac{\tau_{22} - \tau_{11}}{r} \tag{10b}$$

$$0 = \frac{\partial \tau_{33}}{\partial z} \tag{10c}$$

$$p_{\mathrm{I}}(r,z) = p_{\mathrm{I}}(R,0) + \int_r^R \beta_1 \Gamma_{\mathrm{I}}^2 d \ln r \tag{11a}$$

$$p_{\mathrm{II}}(rz,) = p_{\mathrm{II}}(R,0) + \beta_2 \Gamma_{\mathrm{II}}^2 \Big]_R^r + \int_R^r \frac{(\beta_2 - \beta_1)}{r} \Gamma_{\mathrm{II}}^2 dr \tag{11b}$$

The pressures are both measured from the values at the outer rim of the disk.

If we introduce the reasonable boundary condition that the radial normal stresses in regions I and II are equal at the points $(R,0)$, $(R,-h)$

$$[\tau_{rr}(R,0)]_{\mathrm{II}} = [\tau_{rr}(R,0)]_{\mathrm{I}} \tag{12a}$$

i.e.,

$$[\tau_{22}(R,0)]_{\mathrm{II}} = [\tau_{33}(R,0)]_{\mathrm{I}} \tag{12b}$$

We have then

$$\begin{aligned} p_{\mathrm{I}}(R,0) &= -[\tau_{rr}(R,0)]_{\mathrm{II}} \\ &= p_{\mathrm{II}}(R,0) - \beta_2 \Gamma_{\mathrm{II}}^2(R) \end{aligned} \tag{13}$$

or equivalently it may be shown

$$p_{\mathrm{I}}(R,0) = -[\tau_{22}(R + \Delta,0)] + \int_R^{R+\Delta} \frac{\beta_1 - \beta_2}{r} \Gamma_{\mathrm{II}}^2 dr \tag{14}$$

To evaluate Γ_{I} and Γ_{II}, eqs. (9a) and (10a) must be solved, respectively. Making use of no slippage boundary conditions, we may show that

$$\begin{aligned} V_\theta &= r\Omega[1 - (z/l)] \\ \Gamma_{\mathrm{I}} &= r\Omega/l \end{aligned} \tag{15}$$

To evaluate Γ_{II}, the function μ must be known.

Shear Stress–Shear Rate Relationship

We will make use of the results of the previous section to derive an expression for the shearing stress $(\tau_{0z})_R$ at the outer edge of the face of the disk. Since the shear rate Γ_{I} at his point is equal to $R\Omega/l$, the result obtained may readily be used for shear stress–shear rate data, i.e., to obtain the laminar shear viscosity μ.

The torque on the Mooney viscometer rotor may be expressed in terms of the shear stresses in regions I and II.

$$T = 2\left[\int_0^R 2\pi r(r\tau_{\theta z})dr\right] + 2\pi R[R(\tau_{r\theta})_R]h \tag{16}$$

Elimination of the radius r in this expression by means of eq. (15) yields

$$T = 2\pi\left[(l/\Omega)^3 \int_0^{\Gamma_{\mathrm{I}R}} \Gamma_{\mathrm{I}}^2 \tau_{\theta z} d\Gamma_{\mathrm{I}} + R^2 h(\tau_{\theta r})_R\right] \tag{17}$$

Differentiating eq. (17) with respect to Γ_{IR} and applying the Leibnitz rule for the differentiation of integrals gives, after rearranging,

$$(\tau_{0z})_R = \frac{T}{\pi R^3}\left[\frac{3+N}{4}\right] - \frac{h}{2R}(\tau_{\theta r})_R\left[3 + \frac{d \log (\tau_{r0})_R}{d \log \Gamma_{IR}}\right] \quad (18)$$

where

$$N = \frac{d \log T}{d \log \Gamma_{IR}} = \frac{d \log [\mathrm{DR}]}{d \log [\mathrm{rpm}]} \quad (19)$$

where DR refers to the dial reading (portional to torque). For a power law fluid, $N = n$.

Differentiation procedures for evaluating shear stress–shear rate data are due to Weissenberg and Rabinowitsch,[39] these authors applying it to capillary flow data. Mooney[3] later extended its applicability in capillary flow and used it for flow between coaxial cylinders. A recent series of papers by Savins, Wallick, and Foster discuss in detail its utility for capillary[40] and coaxial cylinder[41] instruments as well as for slits and narrow annuli.[40] It would appear that the earliest derivation of this type of expression for pure torsional flow is due to Ether and Mooney,[42] though it was independently derived by the authors. Ether and Mooney's result would be equivalent to one-half of the first term on the right-hand side of eq. (18).

A more convenient way of writing eq. (18) is in the form

$$(\tau_{\theta z})_R = (T/\pi R^3)F \quad (20)$$

where F represents $(N + 3)/4$ times the fraction of the torque due to region I in the viscometer. If we make use of Mooney's artifice[5,27] discussed in the previous section, then for a Newtonian fluid

$$F = 1\Big/\left[1 + \frac{16hl}{R^2[1 - (R/R + \Delta)^2]}\right] \quad (21a)$$

while for a fluid obeying the power law

$$F = \left(\frac{n+3}{4}\right)\Big/\left[1 + \frac{2(2/n)^n(n+3)hl^n}{R^{n+1}[1 - (R/R + \Delta)^{2/n}]}\right] \quad (21b)$$

If we now specialize these results for those of the standard large disk viscometer manufactured by Scott Testers and used throughout the rubber industry, we have

$$(\tau_{\theta z})_R = 4.16 \times 10^4 F \cdot [\mathrm{DR}]\mathrm{dynes/cm.}^2 \quad (22)$$

where DR refers to the instrument dial reading which is proportional to the torque. If eq. (22) is to be used to determine shear stress–shear rate data, then some method must be given to determine F. The easiest and most practical procedure is undoubtedly to use the power law expression of eq. (21) to calculate F, by using the slope of a logarithmic plot of DR versus rate of revolution (rpm) to obtain n. The error introduced by this procedure to determine $(\tau_{0z})_R$ should not be too serious, as the power law is

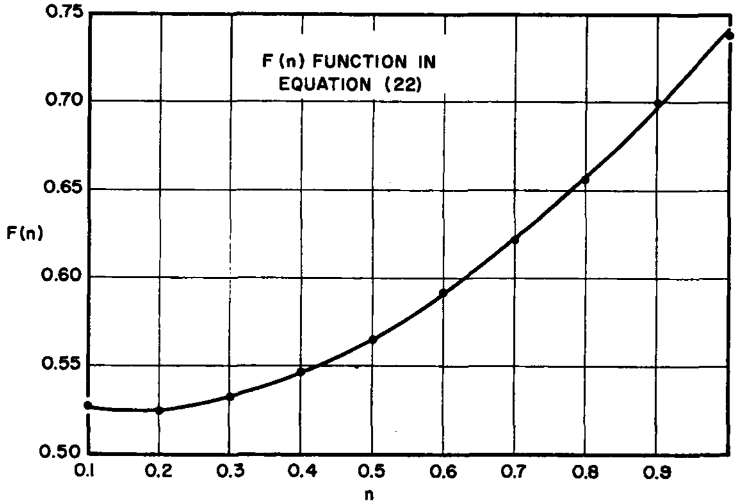

Fig. 2. $F(n)$ function in eq. (22).

actually only being used for a 30% correction. In fact, considering the kinematic oversimplifications of the Mooney method of dividing the instrument into three regions, it should be insignificant. The function $F(n)$ for the dimensions of the large disk Mooney machine is given in Figure 2.

Two points should be mentioned here. Both Mooney[5] and Treloar[34,43] have expressed the opinion that viscosity data obtained from this instrument are a bit larger in magnitude than the correct value. They credit this to the neglect of region III and edge effects in Mooney's original analysis. This problem has been studied by Oka[44] for Newtonian fluids, but this method does not appear to be readily generalized to nonlinear viscoelastic flow.

It should also be noted that we have not considered nonisothermal effects caused by viscous heat generation. The significance of this aberration may be calculated by solving the energy equation in this geometry. The procedure is similar to, but more complex than that carried out by Bird and Turian[45] for the cone-plate viscometer. This problem is currently under study.

Normal Stress Effect

The significance of normal stresses in steady shearing flows of viscoelastic fluids was first noted and explained by Weissenberg.[46]* Weissenberg gave illustrations showing that an axial normal stress exists during torsional flow between parallel disks which forces the disks apart. This behavior is

* Normal stress effects were observed earlier but investigators did not grasp their full significance. The following quote comes from a 1936 paper by Mooney[7]: "There are two serious deficiencies of the conventional cylindrical viscometer as applied to raw rubber, in that firstly the rubber being semi-solid would be likely to slip on the moving surface and secondly, if the rubber did not slip but sheared as it should, it would soon roll and climb out of the viscometer against the force of gravity."

well known in torsional deformation of vulcanized rubber rods, where it is called the Poynting effect. The Poynting effect has been analyzed both theoretically[47] and experimentally[48] by Rivlin. A dramatic example of such a normal stress effect in torsional flow of molten plastics is the Maxwell-Scalora screwless extruder.[49]

Torsional flow of viscoelastic fluids was first analyzed by Mooney[50] in 1951, and later more generally by Rivlin.[51] The Mooney-Rivlin analysis makes use of equations equivalent to eqs. (7) and (9), except that Mooney essentially chooses specific functional forms for μ, β_1, and β_2. Neither author considers the special application of the Mooney shearing disk viscometer.

The aspect of the normal stress effect that we shall be concerned with here is the vertical stresses between the disk and the upper platen. From eqs. (7), (11a), (13), and (15),

$$[\tau_{22}(r,z)]_{\mathrm{I}} = -p_{\mathrm{I}}(r,z) + \beta_2(r\Omega/l)^2 \tag{23a}$$

$$[\tau_{22}(r,z)]_{\mathrm{I}} = -p_{\mathrm{I}}(R,0) + (\Omega/l)^2\left[\beta_2 r^2 - \int_r^R \beta_1 r dr\right] \tag{23b}$$

$$[\tau_{22}(r,z)]_{\mathrm{I}} = [\tau_{rr}(R,z)]_{\mathrm{II}} + (\Omega/l)^2\beta_2 r^2 - \left[\int_r^R \beta_1 r dr\right] \tag{23c}$$

$$[\tau_{22}(r,z)]_{\mathrm{I}} = [\tau_{rr}(R+\Delta,z)]_{\mathrm{II}} + (\Omega/l)^2\left[\beta_2 r^2 - \int_r^R \beta_1 r dr\right] - \int_R^{R+\Delta} [(\beta_1 - \beta_2)/r]\Gamma_{\mathrm{II}}^2 dr \tag{23d}$$

where $[\tau_{rr}(R + \Delta,z)]_{\mathrm{II}}$ is the enclosure pressure π at the outer edge of the cavity. If the dependence of the rheological functions μ, β_1, and β_2 upon shear rate are known, then the variation of the axial normal stress (in region I) with radius may be evaluated. If we presume that the three material functions have the values specified by eq. (8),

$$[\tau_{22}(r)]_{\mathrm{I}} = CK^2\left\{\frac{1}{2n}\left(\frac{R\Omega}{l}\right)^{2n}\left[\left(\frac{r}{R}\right)^{2n} - 1\right] + \int_{R+\Delta}^{R} \frac{1}{r}\left(r\frac{dw}{dr}\right)^{2n} dr\right\} + \pi \tag{24}$$

and as it may be shown that[52]

$$w = \frac{\Omega}{\left(\frac{1}{R}\right)^{2/n} - \left(\frac{1}{R+\Delta}\right)^{2/n}}\left[\frac{1}{r^{2/n}} - \left(\frac{1}{R+\Delta}\right)^{2n}\right] \tag{25}$$

$$[\tau_{22}(r)]_{\mathrm{I}} = CK^2\left(\frac{R\Omega}{l}\right)^{2n}\left\{\left(\frac{1}{2n}\right)\left[\left(\frac{r}{R}\right)^{2n} - 1\right] - \left(\frac{l}{R}\right)^{2n}\frac{(2/n)^2}{4}\frac{\left[\left(\frac{1}{R}\right)^4 - \left(\frac{1}{R+\Delta}\right)^4\right]}{\left[\left(\frac{1}{R}\right)^{2/n} - \left(\frac{1}{R+\Delta}\right)^{2/n}\right]^{2n}}\right\} + \pi \tag{26}$$

The total upward force on the platen above the disk is

$$\mathfrak{F} = - \int_0^R 2\pi r [\tau_{22}(r)]_{\mathrm{I}} dr \tag{27}$$

Kotaka, Kurata, and Tamura[53] have pointed out that the Weissenberg-Rabinowitsch differentiation procedure may be applied to the above expression. They derive a result equivalent to

$$[\tau_{22}(R)]_{\mathrm{I}} = - \frac{2\mathfrak{F}}{\pi R^2}\left[1 + \frac{1}{2}\frac{d \log \mathfrak{F}}{d \log \mathrm{rpm}}\right] \tag{28}$$

It should be noted that from eq. (23)

$$[\tau_{22}(R)]_{\mathrm{I}} = \left(\frac{\Omega}{l}\right)^2 \left[\beta_2 R^2 - \int_R^{R+\Delta} \left(\frac{\beta_1 - \beta_2}{r/l}\right) \left\{ \frac{1}{r}\frac{d}{dr}\left(r \frac{d\frac{w}{\Omega}}{dr/l}\right)\right]^2 \right\} dr + \pi \tag{29}$$

Use of the experiment of Kotaka et al.[53] on the Mooney viscometer would not yield the simple results obtained in pure torsional flow.

Semiquantitatively, upward force measurements may have some value. If we presume again the material functions μ, β_1, and β_2 to be given by eq. (8).

$$\frac{\mathfrak{F}}{\pi R^2} = CK^2 \left(\frac{R\Omega}{l}\right)^{2n} \times \left\{ \frac{1}{4n+4} + \left(\frac{l}{R}\right)^{2n} \frac{(2/n)^2}{4} \frac{\left[\left(\frac{1}{R}\right)^4 - \left(\frac{1}{R+\Delta}\right)^4\right]}{\left[\left(\frac{1}{R}\right)^{2/n} - \left(\frac{1}{R+\Delta}\right)^{2/n}\right]^{2n}} \right\} \tag{30}$$

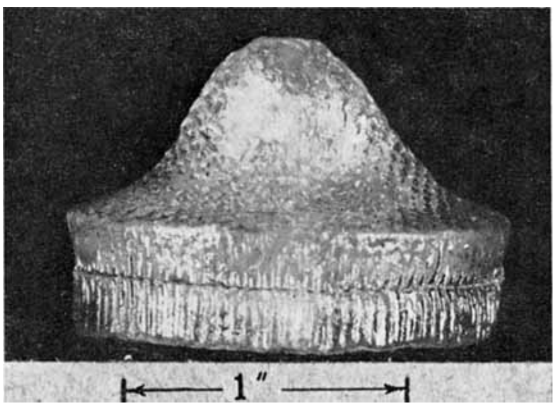

Fig. 3. Distorted plug of polymer removed from the cavity of Mooney viscometer. The dome shape is due to "strangulation" normal stresses and is a typical Weissenberg effect. The elastomer shown is Vistanex L100. The marks below the photograph indicate 1 in.

The normal forces operative between the disk and the upper platen give rise to an interesting phenomenon when the plug of elastomer is removed from the cavity after operation of the machine. If the material is highly elastic and cools rapidly, the unrelieved normal stresses will remain. The elastomer plug is then found to distort in the manner shown in Figure 3. This example of the normal stress effect in elastomers has been used by Mooney in lectures given in recent years.

Elastic Recoil

Elastic recovery measurements obtained on rotational viscometers have been shown by Philippoff and his co-workers[54] to be at least a semiquantitative measure of normal stresses in viscoelastic materials. Basing their analysis on a concept first put into quantitative form by Mooney,[50] they argued that the elastic recovery S from a shearing flow is related to the normal stresses by

$$S = (\tau_{11} - \tau_{22})/\tau_{12} \tag{31}$$

Markovitz and Brown[55] and more explicitly White[56] have shown that a rigorous expression for low shear rates is

$$S = (\tau_{11} - \tau_{22})/2\tau_{12} \tag{32}$$

or

$$\tau_{11} - \tau_{22} = 2\tau_{12}S \tag{33}$$

which we will accept for high shear rates in lieu of eq. (31). This view is supported by a study by White and Metzner.[33]

If an elastic recovery unit is placed on a Mooney viscometer, the recoil angle ϕ_e may be approximately related to S. Such an analysis was originally carried out by Wolstenholme,[57] who showed that

$$S(R,z) = S(\Gamma_R) \cong (2\pi R/360)\phi_e \tag{34}$$

which in terms of the dimensions of the Mooney viscometer is

$$S(\Gamma_R) = 0.13\phi_e \tag{35}$$

Substitution of this result and eq. (22) into eq. (32) gives

$$[\tau_{\theta\theta} - \tau_{zz}](\Gamma_R) \cong (\beta_1 - \beta_2)\Gamma_R^2 = 1.08 \times 10^4\ [\mathrm{DR}]\phi_e F \text{ dynes/cm.}^2 \tag{36}$$

Not only is the elastic recovery of importance in determining normal stresses, but as a dimensionless group it is valuable in its own right. Bagley[13] has shown that a critical value of this parameter determines melt fracture in plastics, and more recently it has been pointed out[56] that it represents the ratio of viscoelastic to viscous forces in the Coleman-Noll second-order fluid.

EXPERIMENTAL

In this section, we shall discuss the results of some experiments performed with the Mooney shearing disk viscometer. Our purpose here is mainly to

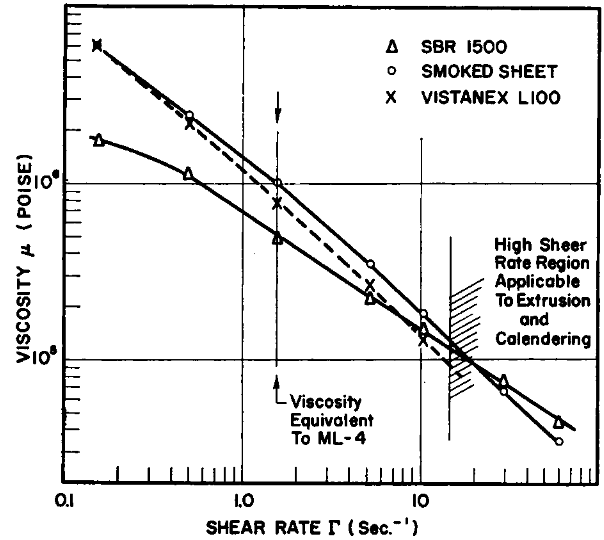

Fig. 4. Comparison of non-Newtonian viscosity of elastomers at 100°C.

illustrate the results of earlier sections. The experimental details of operation of the instrument will not be discussed here, as they have essentially been described elsewhere.[5,23–25,58] It should be remembered though that multispeed operation is different from the standard single-speed procedure. The material is first sheared at a moderate speed (usually 2 rpm), followed by operation at higher shear rates and then returning the rotation rate to its initial value. Low rotation rates are then investigated, and the rotor velocity is finally raised to the initial speed. One must take care to note the possible occurrence of three different phenomena which may alter the meaning of experimental data. First, elastomers having high carbon black contents may be highly thixotropic, a phenomenon known as the Mullins effect.[59,60] Multispeed data become less meaningful if such behavior is significant as the viscosity is a function of time in addition to shear rate. Second, elastomers containing free radical acceptors such as benzoquinone and nitro- or thiophenol will show significant mechanical degradation in the cavity of a Mooney viscometer at low temperatures.[61,62] Third, at higher temperatures some elastomers, even in the absence of vulcanizing agents, will crosslink (gel), while others will degrade. All three of these phenomena should be readily observable by comparison of the repetitive values of torque taken at a standard rotor speed.

The elastomers which we have investigated are polyisobutylene (Enjay Vistanex L100), butadiene–styrene copolymer (SBR 1500), and smoked sheet. In Figure 4, non-Newtonian viscosity-shear rate data are presented for the three polymers at 100°C. These results were computed from viscometer dial reading–rotor rpm data by means of eq (22) and Figure 2. We may designate the region of shear rates above 15 sec.$^{-1}$ as the region of processing interest. It is of interest to note that the 2-rpm reading which is the so-called ML-4 representing the viscosity at 1.6 sec.$^{-1}$ gives an erroneous impression of the order of viscosity in the high shear rate region of interest to shear mixing, calendering, and extrusion, which is above 1 sec.$^{-1}$. Results of the type shown in Table I, which are all too common, seem to indicate the need for multispeed viscometry in process control for elastomer processing operations. We also see that of the three materials only the butadiene–styrene copolymer may be represented by a power law over more than a small range of shear rates.

TABLE I

Order of one-point Mooney viscosities (ML-4)	Order of processing condition viscosities
Natural rubber	Butadiene–styrene copolymer
Polyisobutylene	Natural rubber
Butadiene–styrene copolymer (SBR)	Polyisobutylene

The variation of non-Newtonian viscosity of these polymers with temperature has also been studied. Figures 5, 6, and 7 show this variation, respectively, for the polyisobutylene, butadiene–styrene copolymer, and the smoked sheet. Only the SBR shows a regular variation of viscosity with temperature throughout the entire shear rate range. In the other two elastomers the viscosity change, while apparent if ML-4 values are evaluated, disappears in the range of processing interest. If we compute the activation energy at constant shear rate E[63,12] for these materials (at 10 sec.$^{-1}$) we would obtain the results shown in Table II.*

TABLE II

Elastomer	$(E_\Gamma)_{10\ \text{sec.}^{-1}}$, kcal./mole
Polyisobutylene	0.25
Butadiene–styrene copolymer	3.1
Smoked sheet	0.25

We wish to illustrate one final point. Elastomers are usually compounded with carbon black, oil, and vulcanizing and accelerating agents. Little work has been done to show the effect of these compounding agents upon the non-Newtonian viscous behavior of rubber. The two most extensive

* One should note that various activation energies for flow of non-Newtonian fluids may be used. Bestul and Belcher[63] describe constant shear stress and constant shear rate activation energies, while Wolstenholme[58] has used an "isoviscous" activation energy. We prefer E_Γ because it measures viscosity variation under constant kinematic conditions and is thus most readily interpretable in terms of processing operations and further because it is most readily adaptable into constitutive equations. An objection to E_Γ pointed out by Bestul and Belcher and Wolstenholme is that it is often quite dependent upon shear rate.

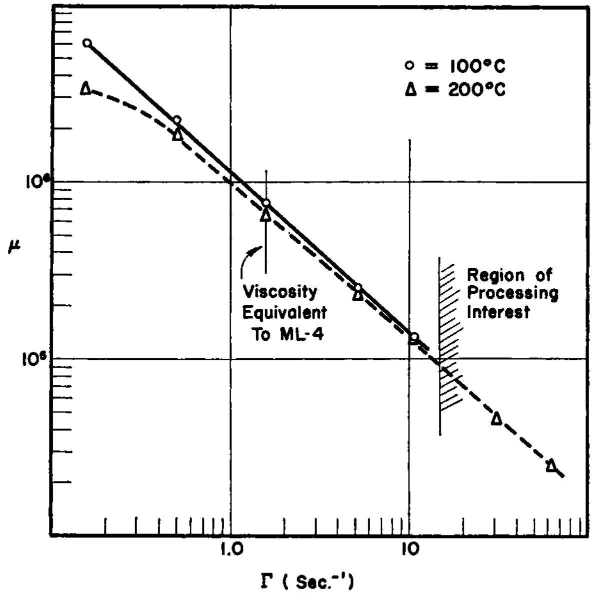

Fig. 5. Effect of temperature upon non-Newtonian viscosity of Vistanex.

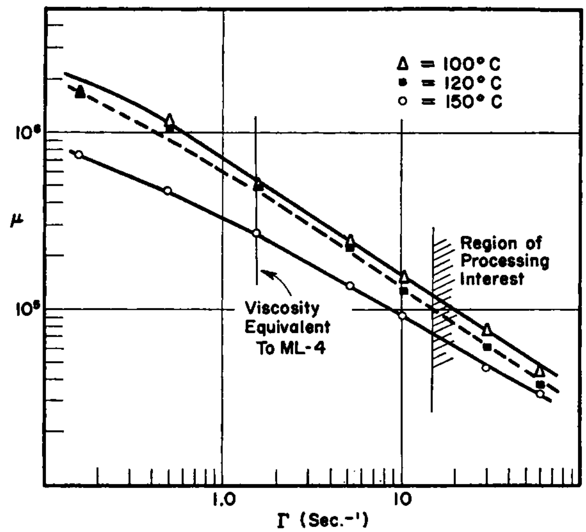

Fig. 6. Effect of temperature upon non-Newtonian viscosity of SBR 1500.

studies of the effect of carbon black, which is the major additive, upon the viscosity of rubbers are those of Studebaker[64] and Zakharenko et al.[65] The former author measured the 100°C. value of the ML-4 for different carbon black loadings of natural and butadiene–styrene rubber. His results may be interpreted as:

$$\left[\frac{\partial \ln (\mu - \mu_0)}{\partial W_B}\right]_{\substack{T = 100^\circ\text{C.} \\ \Gamma = 1.6 \text{ sec.}^{-1}}} = \begin{cases} 0.023 \text{ (SBR)} \\ 0.041 \text{ (natural rubber)} \end{cases} \tag{37}$$

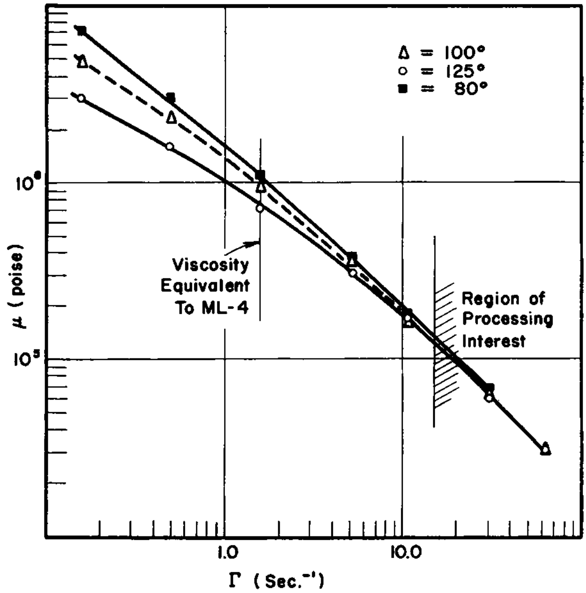

Fig. 7. Effect of temperature upon non-Newtonian viscosity of smoked sheet.

where μ_0 = viscosity of uncompounded rubber. W_B = weight fraction of carbon black. The absolute viscosity increase is seen to be greater for the natural rubber than for the butadiene–styrene rubber. He also found that the absolute viscosity increase is at constant black loading in general greater the smaller the black particle diameter. Zakharenko and his coworkers were more concerned with the effect of black loading upon the non-Newtonian characteristics. These authors studied lampblack compounds of polyisobutylene and sodium butadiene rubber at rather low shear rates (10^{-4}–10^{-1} sec^{-1}. They found the power law relationship to hold quite well for the compounds. The elastomers became increasingly non-Newtonian with increasing black content. The constant shear rate activation energy E_Γ decreased with increasing black.

Some of the data taken in our laboratories on compounded elastomers are shown in Figure 8. Non-Newtonian viscosity–shear rate data is given for an SBR 1500 at 150°C. with different levels of compounding. If we fit a power law to all of the SBR data over the higher shear rate range, we find the results given in Table III. Both this and more extensive data not

TABLE III

Compound	n
Uncompounded	0.44
25 phr HAF Black	0.32
75 phr SAF Black, 25 phr oil	0.23
75 phr SAF Black, 50 phr oil	0.23

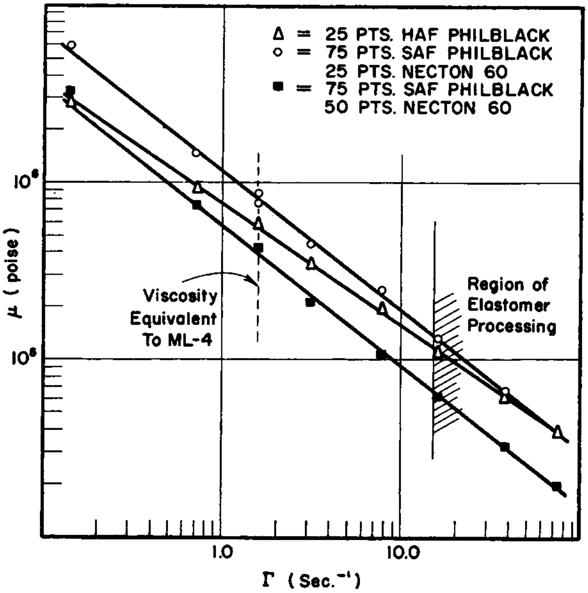

Fig. 8. Non-Newtonian viscous behavior of compound SBR 1500 at 150°C.

given lend support to the general conclusions of Zakharenko et al. Qualitative support has also been given to the conclusions of Studebaker.

CONCLUSIONS

In this paper, we have given a detailed analysis of the kinematics of flow and stress variation throughout the Mooney shearing disk viscometer. A new method has been developed to compute the non-Newtonian viscosity as a function of shear rate. We have in addition discussed nonlinear viscoelastic effects occurring in this instrument. Non-Newtonian viscosity measurements have been reported for polyisobutylene, smoked sheet, and butadiene–styrene copolymer.

We are quite indebted to W. E. Wolstenholme for many helpful discussions about the Mooney shearing disk viscometer. D. C. Branscombe obtained the experimental data. S. B. Turetzky pointed out ref. 65 to us.

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Résumé

Le viscosimètre à disque de Mooney peut être considéré comme un instrument d'étude d'élastomères, des plus importants, aussi bien en recherche analytique que lors du contrôle de la production. Dans cet article, on développe une nouvelle méthode qui permet de calculer la tension de cisaillement et la vitesse de cisaillement des matériaux à partir de l'expérience. De plus, on analyse le comportement visco-élastique non-linéaire des élastomères dans le viscosimètre en attachant une importance toute spéciale aux effets des tensions normales. On discute les résultats expérimentaux qui ont été obtenus pour le caoutchouc naturel, SBR et le polyisobutylène.

Zusammenfassung

Das Rotationsplastometer von Mooney ist eines der wichtigsten Instrumente für analytische Untersuchungen und Verarbeitungskontrollen bei Elastomeren. In der vorliegenden Mitteilung wird eine neue Methode zur Bestimmung der Schubspannung und der Schubgeschwindigkeit gewisser Stoffe aus mit diesem Instrument erhaltenen Daten entwickelt. Ausserdem wird das nichtlineare viskoelastische Verhalten von Elastomeren im Plastometer mit besonderer Berücksichtigung der Normalspannungseffekte analysiert. Versuchsergebnisse für Naturkautschuk, SBR und Polyisobutylen werden diskutiert.

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