Milling Behavior of Gum Elastomers: Experiment and Theory*

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Synopsis

When an uncompounded elastomer is processed on a two-roll mill, four different regions of mechanical behavior are observed, depending upon the temperature and the severity of the nip deformation. This behavior is observed on materials with a wide variety in chemical composition, though the severity varies. The flow at high temperatures is typical of melt or polymer solution behavior. At lower temperatures unstable flow and elastic solidlike regions are observed. By presuming the elastomer to be an isotropic viscoelastic medium, the stress and velocity fields were computed in the polymer melt region. The unstable regime was found to correspond to a critical value of the ratio of viscoelastic to viscous forces. The mathematical analysis, done in terms of the Green-Rivlin-Noll theory of viscoelastic media, extends earlier studies of deformation in this geometry by Gaskell and Bergen.

INTRODUCTION

The elastomer milling operation illustrated in Figure 1 represents one of the more important unit operations in the manufacture of mechanical rubber goods. While it no longer maintains the prominence that it held before the First World War,† milling has remained an important processing operation for dispersion of carbon black in masterbatches leaving Banbury mixers and for warming stocks.[4] Mills are also a common laboratory method for mechanically mixing fillers.

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† The steam-heated, variable-speed two-roll mill was invented by Edwin M. Chaffee of the Roxbury Rubber Company (Roxbury, Massachusetts) and was constructed towards the end of 1835.[1,2] It was labeled in the patent as a preparing machine and was intended as a device to mix in fillers. At the time, mixing of ingredients into rubber was evidently carried out in masticators of the type devised by Hancock, which consisted of a spiked rotor moving inside of a tooth-studded cylindrical cavity.[2,3] The Chaffee mill soon replaced other masticators and its extensions generally held sway in mixing until the introduction of fine particle size carbon black as a major compounding ingredient.[4] Carbon black, by its fineness and lightness, would blow off an open mill and about a plant at the slightest provocation, which together with the adverse effects of new chemicals upon millroom workers and increased demand for rubber goods, led to the introduction of the automated enclosed, internal Banbury mixers.[4] An interesting description of rubber goods factories in the era of mill mixing is given by Geer.[5]
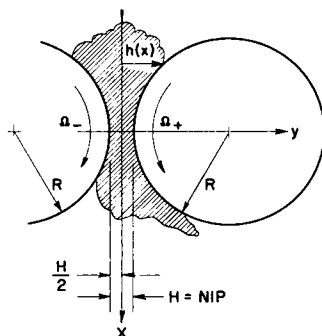
Fig. 1. Milling of an elastomer.

Although mills have been used for dispersing fillers in and breaking down rubber for 130 years, there appears to have been little organized study of the mechanical processes involved. New synthetic rubbers are frequently described as having an anomalous milling behavior, and lots of rubber received at different times in factories are described as having "good" or "bad" processing behavior. The term "bad" is often used to encompass phenomena as diverse as bagging, crumbling, and nerve.

Several authors have studied the problem of flow between two rolls, and some have been concerned with the calendering of polymers. However, no analysis has carefully considered the viscoelastic behavior of such materials. The earliest quantitative study of flow between rolls is that of Ardichvili[6] who considered the problem in terms of Reynolds lubrication theory of Newtonian hydrodynamics.[7,8] Later Eley[9] and Gaskell[10] also gave independent analyses of the hydrodynamic problem. Eley's analysis is basically naive in that he presumes the mechanics of deformation to be compression rather than shearing, while Gaskell's approach is similar to that of Ardichvili. Gaskell, however, indicates in his paper how this problem might be solved for a purely viscous non-Newtonian fluid, and he gives a detailed solution for the Bingham plastic model. More recently, McKelvey[11] used the Gaskell method to obtain a solution for a purely viscous power law fluid. Only Pasley[12] has studied the flow of a nonlinear viscoelastic fluid through mill rolls. His work unfortunately suffers from two defects. First, he makes use of a rather special and empirical constitutive equation and second in his analysis of the equation of motion he essentially neglects the contribution of viscoelasticity (though maintaining non-Newtonian viscosity) without indicating such. In all of the papers mentioned thus far, both rolls have been considered to have the same linear velocity. This restriction has been removed for the case of Newtonian fluids by Bergen.[13]* Banks and Mill[14] and Myers and his co-workers[15] have published detailed experimental studies of the flow of Newtonian oils through the nips of roll coaters. They find the flow in the mill nip to be

* Bergen[13] also gives the most complete study of mixing and the dispersion of fillers in milling.

divided into four regions. A bank region containing secondary flows; a shearing region obeying the Ardichvili-Gaskell theory; a cavitation region caused by the pressure drop after the nip; and a filamentation region where the rolls are separating. Pearson[16] has treated the hydrodynamic stability of Newtonian fluid moving between two rollers and has been able to explain the ribbing phenomenon observed in the coating of printing inks. One noteworthy experimental study on the mill behavior of raw rubber has appeared. In this paper, Bulgin[17] compares the mill behavior and physical properties of natural rubber and high *cis*-polybutadiene.

Some mention must be made of the extensive studies of the mechano-chemical phenomena occurring during the milling of elastomers. The work of Busse[18] and Watson[19-21] has shown that the shearing stressing in the nip of the mill causes the degradation of high molecular weight polymer chains into smaller chains containing free-radical ends which are highly reactive to oxygen but may react with other polymer chains, fillers, or other radical acceptors. This phenomenon is most severe with high molecular weight polyisoprene and is of lesser consequence with, say, polybutadienes and styrene–butadiene copolymers (SBR).

It is our purpose in this paper to present in an organized manner an experimental and theoretical study of the dynamic processes involved in milling. We shall limit our study to uncompounded gum elastomers.

QUALITATIVE EXPERIMENTS

We have studied the variation in mill behavior of a series of elastomers with temperature and with nip. A mill with 3-in. diameter rolls was used in these experiments. The slow roll speed was 16.2 rpm and the fast roll speed was 22.7 rpm. In attempting to make this study as general as possible, we have made use of a wide variety of elastomers. Among the materials studies are three polybutadienes, having different microstructures

TABLE I

Polymers	Remarks
Polybutadiene A	High-*cis* ($\sim$94%) material polymerized by AlR$_3$-TiI$_4$ (Ziegler) catalyst (R = alkyl)
Polybutadiene B	35% *cis*, 8% vinyl material polymerized by a butyllithium catalyst
Polybutadiene C	37.5 part oil-extended cold (5°C.) emulsion-polymerized elastomer
SBR-A	A 25 wt.-% random copolymer whose butadiene content is 35% *cis*. This material is polymerized by a butyllithium–ether catalyst
SBR-B	A 25 wt.-% random copolymer polymerized by the cold (5°C.) emulsion method
Ethylene–propylene copolymer	—

(*cis, trans,* and vinyl contents[22]), molecular weight distributions, and degrees of branching. Two styrene–butadiene copolymers which were polymerized by different methods have also been studied, as has been an eth-
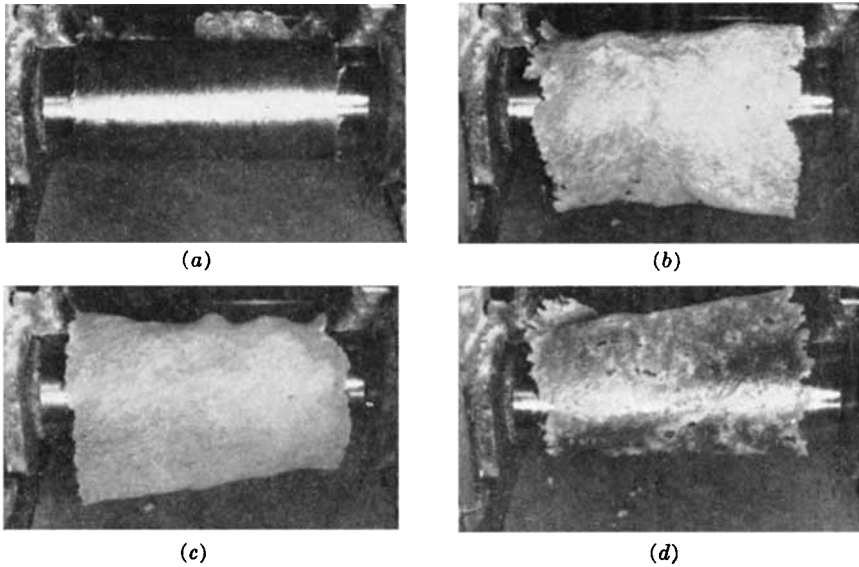

(*a*)

(*b*)

(*c*)

(*d*)

Fig. 2. Mill behavior of polybutadiene A: (*a*) room temperature; (*b*) 160°F.; (*c*) 212°F.; (*d*) 250°F.
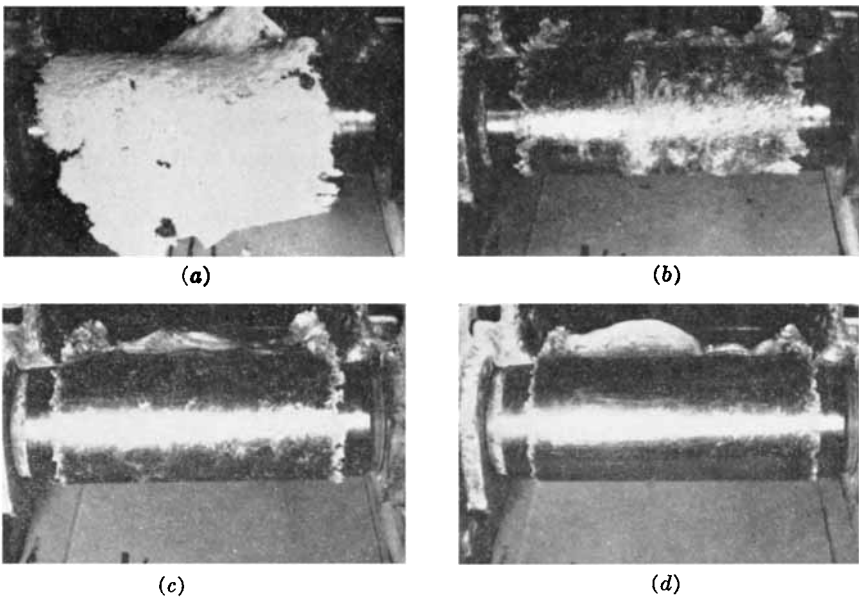

(*a*)

(*b*)

(*c*)

(*d*)

Fig. 3. Mill behavior of polybutadiene B: (*a*) room temperature; (*b*) 160°F.; (*c*) 212°F.; (*d*) 250°F.
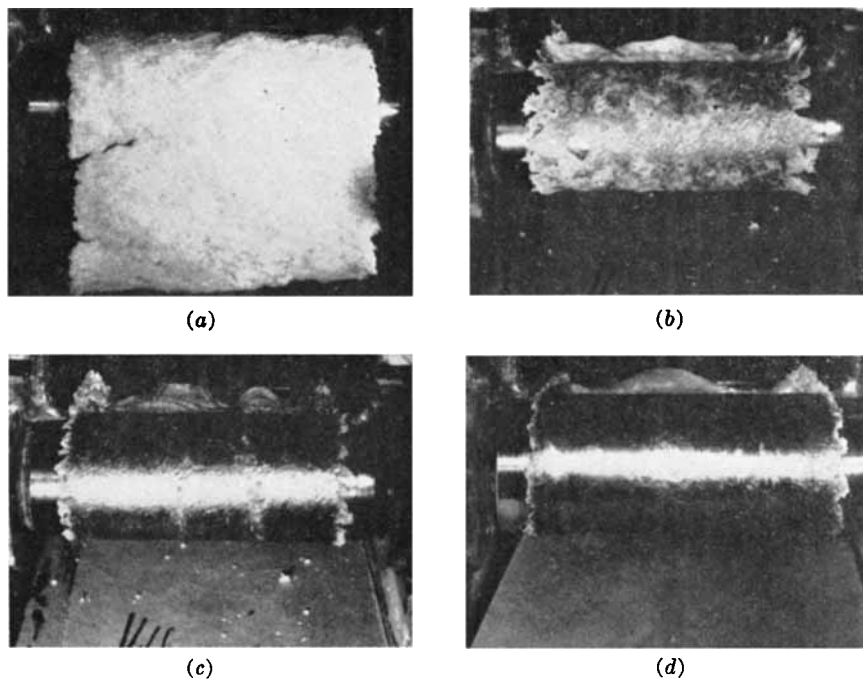
Fig. 4. Mill behavior of styrene–butadiene copolymer A: (a) room temperature; (b) 150°F.; (c) 212°F.; (d) 250°F.

ylene–propylene copolymer. The properties of these materials are summarized in Table I. All polymers had Mooney viscosities (ML-4) between 35 and 50.

Gum elastomers show striking changes in their mechanical behavior on a mill when the temperature of the rolls is varied. The general behavior is shown in Figures 2–5. A nip of 0.055 in. was used in these experiments. It would appear to be true for all elastomers that if the roll temperature is raised to a high enough value, the material will become a transparent viscoelastic fluid which usually adheres to the slower roll.* If the temperature is lowered, waves seem to appear on the fluid leaving the nip, the material tears, and opacity is introduced. If we continue to lower the roll temperature, the elastomer changes from a transparent fluid to an opaque, often crumbling, bag on the same roll. Increasing the temperature will return the opaque bag to a transparent fluid. The region in which an elastomer on a mill is a transparent fluid, we shall call region 4 and the range in which the elastomer is an opaque bag, we name region 3. The critical temperature at which a material in region 4 changes to region 3, we shall call T_4, recognizing of course that this value may be dependent upon the severity of deformation in the nip (e.g., roll speeds, nip distance). The severity of the deformation in region 3 varies from material to material, being generally

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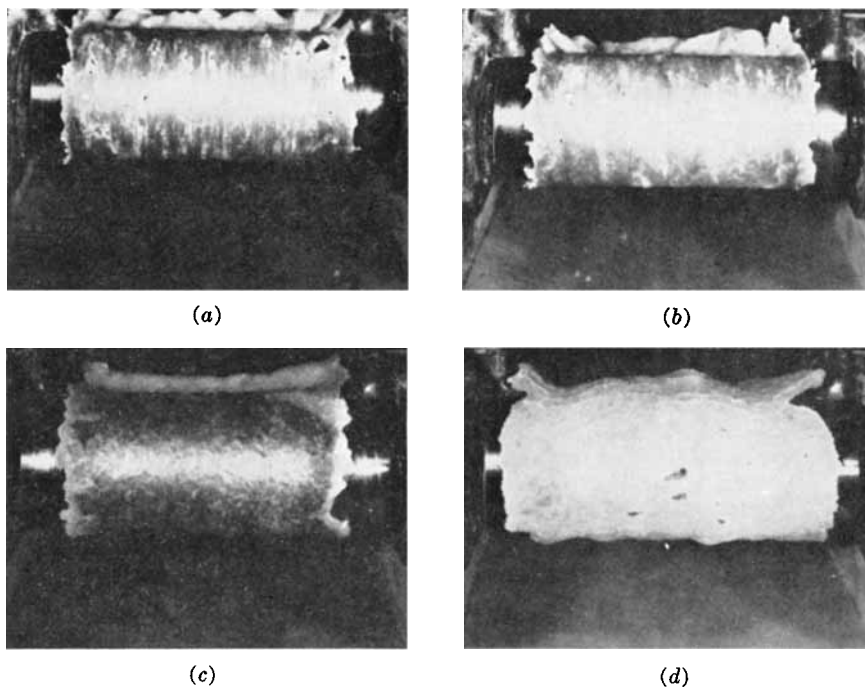* In some instances, the transparent fluid has changed rolls.

Fig. 5. Mill behavior of styrene–butadiene copolymer B: (a) room temperature; (b) 150°F.; (c) 212°F.; (d) 250°F.

the worst in narrow molecular weight distribution elastomers synthesized by butyllithium and Ziegler-type catalysts.   Emulsion-polymerized rubbers become slightly rougher and bag to a limited extent, but show little tendency to crumble.   Thus, polybutadienes A and B bag severely and crumble, while polybutadiene C exhibits mild bagging. Similarly butadiene–styrene copolymer (SBR) A bags and crumbles in region 3 and SBR B shows little bagging.   If we continue to lower the temperature, either of two phenomena may be observed.   In some cases the crumbling of the opaque bag becomes increasingly severe and the polymer is eventually reduced to a powder.   In the more common case the opaque bag gradually becomes tighter and often again transparent with decreasing temperature. The opaque bag changes to a tight elastic band on the same slow roll.   This lower tight band regime we shall call region 2.   We have also observed cases in which the elastic band will form on the faster roll.   Lowering the temperature still further changes the tight band to a nervy wedge of rubber in the bank with only strands still moving through the nip.   These elastomer strands exist on both the slow and fast rolls though usually predominantly on the first roll.   This final region of milling behavior we name 1.

Variation of the mill nip, at constant roll speed and temperature (neglecting viscous heating) causes significant changes.   Decreasing the mill nip tends to cause crumbling elastomers to cling tightly to the rolls.

One must be wary of mechanical degradation of the elastomers during the experiment.[21] Polyisoprenes are thus the most difficult materials to work with and are not discussed here.

It might at first be thought that these changes in mechanical behavior with temperature were material structure transitions, such as the second-order transition which divides the glassy and rubbery states. However, investigations of the polymers in question using differential thermal analysis yielded no such quasithermodynamic transitions. Bianchi and his co-workers[23] claim to find a higher-order transition in high-cis-polybutadiene which occurs at the temperature at which region 2 changes to region 3. Their argument that this is a significant change in properties is not convincing. Bulgin[17] argues that the phenomena is related to strain-induced crystallinity, but he is unable to generally substantiate this. It would thus seem that mechanical milling behavior may be interpreted in terms of the equations of force equilibrium and material rheological properties.

THEORY OF THE DEFORMATION OF ELASTOMERS BETWEEN MILL ROLLS

Mechanics of Isotropic Viscoelastic Materials

Raw gum elastomers fall into neither of the classical rheological groupings of elastic solids or viscous fluids, although they approach the properties of the former at low temperatures and the latter at high temperatures. Basically, elastomers are isotropic materials, in that they exhibit no directional properties in their virgin state and show hereditary behavior in the sense that stresses are determined by the deformation history in such a manner that strains in the distant past have less effect than those in the recent past.* The quantitative study of the relationship between stress and deformation in isotropic hereditary materials was initiated in 1876 by Boltzmann, who derived an expression for the linear case of infinitesimal deformations. A complete theory including the nonlinear effects† of finite strains and rotations was first given by Green and Rivlin[24] in 1957 and has been analyzed by other authors.[25–27] The historical development of the nonlinear theory has been discussed by Rivlin[28] and a general review of the area is given in a recent book by Fredrickson.[29] Bernstein, Kearsley, and Zapas[30] and White and Tokita[31,32] have applied the continuum theory of viscoelastic materials to large deformations of raw elastomers. The constitutive expression introduced by Bernstein and his co-workers is somewhat simpler than the Green-Rivlin expansion of integrals in strain or deformation rate which is expected from the mathematical theory.[24–27] The Bernstein-Kearsley-Zapas theory expresses the stress in terms of a single

* We are, of course, ruling out strain-induced crystallinity as observed in cis-polyisoprenes.

† Raw gum elastomers show many well-known nonlinear phenomena, including non-Newtonian viscosity,[32] Weissenberg normal stress effects,[32] and nonlinear stress–strain curves.[31]

integral in the strain, which is justified on the basis of a series of multistep stress relaxation experiments performed by Zapas and Craft.[33]

In this paper, we shall follow our earlier work[26,31] and express the stress, $\mathfrak{d}$, as:

$$\mathfrak{d} = -p\mathbf{I} + \int_{-\infty}^{t} \Phi(t - \phi)\mathbf{e}(\phi)d\phi +$$

$$\int_{-\infty}^{t} \int_{-\infty}^{t} \psi(t - \phi_1, t - \phi_2)\mathbf{e}(\phi_1)\mathbf{e}(\phi_2)d\phi_1 d\phi_2 + \dots \quad (1)$$

where $\mathbf{e}$ is the Finger strain measure and $\Phi(s)$ is related to the relaxation modulus $G(s)$ of linear viscoelasticity by:

$$\Phi(s) = -2dG(s)/ds \quad (2)$$

where

$$G(t) = \int_0^{\infty} e^{-t/\tau} H(\tau)d \ln \tau \quad (3)$$

It has been noted by Alfrey[34] that the response of a viscoelastic material to a steady deformation depends upon the time scale of the experiment relative to the time scale of the material. This notion has been discussed in an interesting manner by Reiner,[35] who introduced the concept of a Deborah Number, and has been formulated by White and Tokita[32] for nonlinear viscoelasticity. These authors note that for short time periods, the material behaves as an elastic solid; but when the period of deformation approaches the order of the time required for the relaxation moduli to decay, a viscoelastic medium behaves as a Rivlin-Ericksen fluid.[25,26,28,36,37] If we were to derive the equivalent result in terms of the linear theory of viscoelasticity, it would be found that the material after large deformation times behaves as a Newtonian fluid. The Rivlin-Ericksen fluid is the nonlinear generalization of this asymptote. We may express the Rivlin-Ericksen expansion in the manner:[25,26,31,36,37]

$$\mathfrak{d} = -p\mathbf{I} + \sum_n \mathbf{M}_n \quad (4a)$$

with

$$\mathbf{M}_1 = \omega_1 \mathbf{B}_1 \quad (4b)$$

$$\mathbf{M}_2 = \omega_2 \mathbf{B}_1{}^2 + \omega_3 \mathbf{B}_2 \quad (4c)$$

$$\mathbf{M}_3 = \omega_4 [\text{tr } \mathbf{B}_1{}^2]\mathbf{B}_1 + \omega_5 \mathbf{B}_3 + \omega_6 [\mathbf{B}_1 \mathbf{B}_2 + \mathbf{B}_2 \mathbf{B}_1] \quad (4d)$$

The ω_j coefficients may be written as integrals of the relaxation kernels and in particular the coefficients of the $\mathbf{B}_n$ matrices may be expressed:[31,36]

$$\omega_3 = -J_e \omega_1{}^2 \quad (5a)$$

$$\omega_{j(n)} = \frac{(-1)^{n+1}}{(n - 1)!} \int_0^a s^{n-1}G(s)ds = (-1)^{n+1}n \int_0^{\tau_m} m^{n+1}H(\tau)d\tau \quad (5b)$$

where ω_1 = zero shear viscosity and J_e = steady-state shear compliance. White and Tokita[31] have analyzed the properties of the equations of motion for a viscoelastic material in the Rivlin-Ericksen asymptote and have found that at low Reynolds Numbers[7,8] the behavior of the material is largely specified by the dimensionless group:

$$N_{We} = \tau_m U/L \tag{6}$$

where U = characteristic velocity, L = characteristic length, and the maximum relaxation time τ_m is given by:[38]

$$\lim_{\substack{\tau_m \\ t \to \infty}} = \frac{1}{[-d \log G(t)/dt]} \tag{7}$$

This dimensionless group, which represents a ratio of viscoelastic to viscous forces, is a form of an/or a generalization of the Weissenberg Number described in earlier publications.[36,39] Together with the viscoelastic ratio numbers[31,36,39] it defines the dynamic state and stability of the fluid system.

Laminar Flow between Rolls

For steady two-dimensional flows of a continuous fluid the equations of motion take the form:[8,29]

$$\rho \left[u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right] = - \frac{\partial p}{\partial x} + \frac{\partial t_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} + \rho g \tag{8a}$$

$$\rho \left[u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right] = - \frac{\partial p}{\partial y} + \frac{\partial t_{yy}}{\partial y} + \frac{\partial \sigma_{xy}}{\partial x} \tag{8b}$$

where

$$\sigma_{ij} = -p\delta_{ij} + t_{ij} \tag{9}$$

If we consider the geometry of Figure 1 we may introduce the following simplifying assumptions common to lubrication theory:[7,8]

$$u \sim U \qquad (\partial u/\partial y) \sim (U/H) \qquad (\partial u/\partial x) \sim U/L \tag{10}$$
$$L \gg H$$

$$v \sim U(H/L) \qquad (\partial v/\partial x) \sim U(H/L^2) \qquad (\partial v/\partial y) \sim U/L \tag{11}$$

If we substitute these orders of magnitude approximations into eq. (9) we have:

$$\rho U^2/L = \sim \partial p/\partial x \sim (t_{xx})_{\text{nip}}/L \sim (\sigma_{xy})_{\text{nip}}/H \gg \rho g \tag{12a}$$

$$(\rho U^2/L)(H/L)^2 = \sim \partial p/\partial y \sim (t_{yy})_{\text{nip}}/H \sim (\sigma_{xy})_{\text{nip}}/L \tag{12b}$$

Dropping out terms of obviously lower order of magnitude and presuming:

$$(\sigma_{xy})_{\text{nip}} \gg \rho U^2(H/L) \tag{13}$$

which certainly is true for milling of elastomers, we obtain:

$$0 = -(\partial p/\partial x) + (\partial t_{xx}/\partial x) + (\partial \sigma_{xy}/\partial y) \tag{14a}$$

$$0 = -(\partial p/\partial y) + (\partial t_{yy}/\partial y) \tag{14b}$$

or

$$0 = \frac{\partial^2 \sigma_{xy}}{\partial y^2} + \frac{\partial^2}{\partial x \partial y}(t_{xx} - t_{yy}) \tag{15}$$

If we presume both terms in eq. (15) to be of the same order of magnitude, then (compare White and Metzner[39]):

$$\sigma_{xy}/H^2 \sim (t_{xx} - t_{yy})/LH \tag{16a}$$

or

$$t_{xx} - t_{yy} \sim (L/H)\sigma_{xy} \tag{16b}$$

As L/H might be of order 50–100, this means that normal stresses are not significant until they are almost two orders of magnitude greater than the shearing stress.

One important, apparently general conclusion that may be reached at this point is that if a mill is to be scaled at constant Weissenberg and Deborah Numbers, it follows that the nip must vary proportionally to the roll radius and the roll revolution rate must remain unchanged. In arriving at this conclusion, we have used the Deborah Number in the form of a ratio of a residence time to a relaxation time and for the Weissenberg Number, presumed the linear roll speed to be the characteristic velocity and the nip to be the characteristic length. It should be noted that the resulting scaling criteria differ from those derived by Bergen.[13]

First let us consider the general case of a virgin material entering the nip at time zero. We shall compute the stress components from eq. (1) and substitute them into eqs. (14a) and (14b) or eq. (15). For the case of a slowly decaying modulus, eq. (1) becomes (compare White and Tokita)[31]:

$$\mathbf{\sigma} \cong -p\mathbf{I} + G(t)\mathbf{e} + A(t)\mathbf{e}^2 + \ldots \tag{17}$$

where $\mathbf{e}$ = total strain since time zero. For the case where the velocity field may be approximated by:

$$u = \Gamma y \qquad\qquad v = w = 0 \tag{18}$$

and

$$G(s) = G(0) - \epsilon s \tag{19}$$

we have after deformation time Δt:

$$\sigma_{xy} = [G(0) - (\epsilon \Delta t/2) + \ldots]K + \ldots$$

$$t_{xx} - t_{yy} = [G(0) - {}^2/_3 \epsilon \Delta t + \ldots]K^2 + \ldots \tag{20a,b}$$

with $K = \Gamma\Delta t =$ shearing strain. These equations are similar to those of nonlinear elasticity with relaxing moduli (compare Green and Zerna[40]).

This approach is probably a valid one for milling regions 1 and 2. It does, however, lead to difficulties when formulated into a dynamic initial and boundary value problem, which must be solved simultaneously with the compatibility equations for large strains.[40]

In region 4, where we have more fluid behavior, we probably may use the Rivlin-Ericksen expansion. Simplifying eqs. (4) by means of eqs. (10) and (11) we obtain

$$\sigma_{xy} = \omega_1\left(\frac{\partial u}{\partial y}\right) + \omega_3\left(u\frac{\partial^2 u}{\partial x\partial y} + v\frac{\partial^2 y}{\partial y^2} + 2\frac{\partial u}{\partial x}\frac{\partial u}{\partial y}\right) + \ldots \quad (21a)$$

$$t_{xx} = (\omega_2 - 2\omega_3)(\partial u/\partial y) + \ldots \ldots \quad (21b)$$

$$t_{yy} = \omega_2(\partial u/\partial y)^2 + \ldots \ldots \quad (21c)$$

Substitution into eq. (15) yields

$$0 = \omega_1\frac{\partial^3 u}{\partial y^3} + \omega_3\frac{\partial}{\partial y}\left[\frac{\partial}{\partial x}\left(u\frac{\partial^2 u}{\partial y^2}\right) + v\frac{\partial^3 u}{\partial y^3} + \frac{\partial u}{\partial y}\frac{\partial^2 v}{\partial y^2}\right]\ldots \quad (22)$$

for the case of large normal stresses. When these stresses are below the critical value of eq. (16) we have, within the approximation of the second-order fluid:[25,36,37]

$$0 = \omega_1(\partial^3 u/\partial y^3) \quad (23)$$

or

$$0 = -(\partial p/\partial x) + \omega_1(\partial^2 u/\partial y^2) \quad (24)$$

It would seem from observation that slippage here is negligible. The boundary conditions on the velocity field are then:

$$u[h(x), x] = 2\pi R\Omega_+ \quad (25a)$$

$$u[-h(x), x] = 2\pi R\Omega_- \quad (25b)$$

$$\Omega_+ = f\Omega_- \quad (25c)$$

where $f =$ friction ratio. The hydrodynamic equation and boundary conditions are the same as those in the analysis of Bergen.[13] The resulting velocity field is:

$$u = (f+1)\pi R\Omega_- + (f-1)\pi R\Omega\left(\frac{y}{h}\right) + \frac{1}{2\omega_1}\frac{\partial p}{\partial x}(y^2 - h^2) \quad (26a)$$

$$v = \frac{(f-1)\pi R\Omega}{2h}[y^2 - h^2]\frac{dh}{dx} - \frac{1}{6\omega_1}\frac{\partial^2 p}{\partial x^2}[2h^3 + y^3 - 3h^2 y]$$

$$+ \frac{h}{\omega_1}\frac{\partial p}{\partial x}\frac{dh}{dx}(y - h) \quad (26b)$$

From Figure 1 and earlier studies, we have that

$$h = H + (x^2/2R) \tag{27a}$$

and

$$dh/dx = \frac{x}{R} \tag{27b}$$

The flow rate and pressure gradient are, respectively:

$$Q = \left(\frac{3f + 1}{2}\right) \pi R\Omega - h - \frac{4}{3} \frac{h^2}{\omega_1} \frac{\partial p}{\partial x} \tag{28}$$

$$\frac{\partial p}{\partial x} = \frac{3\omega_1}{4h^2} \left[\frac{(3f + 1)}{2} \pi R\Omega_- - h - Q\right]$$

The normal stress σ_{xx} in the direction of flow between the rolls is:

$$\sigma_{xx} = -p + t_{xx}$$

$$\tag{29}$$

$$= -p(0) + t_{xx} - t_{yy}$$

The centerline pressure may be obtained approximately from the Gaskell-Bergen solution and

$$t_{xx} - t_{yy} = 2J_e\omega_1^2 \left\{(f - 1) \frac{\pi R}{h} \Omega_- + \frac{3}{4}\left[\frac{(3f + 1)}{2} \frac{\pi R\Omega}{h} - \frac{Q}{h^2}\right]y\right\}^2 \tag{30}$$

The normal stress difference is seen to be an increasing function of the friction ratio and roll speed if the dimensions and milling rate are maintained constant. From eq. (30) we may see that use of eq. (23) apparently implies that $J_e\omega$, Ω_- is less than order unity.

Returning to eq. (22) we note that an exact analytical solution of this expression is not possible, and it would seem that the only feasible procedure to solve such an equation would be the method of perturbations. Langlois and Rivlin[37,41] introduced this method into viscoelastic fluid dynamics and Langlois[42] has discussed its application to lubrication problems. This author unfortunately finds that the perturbation procedure breaks down for such problems.

Region 3 Behavior

The region of crumbling and bagging behavior is the most interesting and often the most critical to commercial applications. Fillers are found to be far more poorly dispersed in this region, and a material which crumbles in a factory process would prove impossible to handle. If we proceed upwards in temperature from region 2 and observe the 2–3 transition, it appears as a tearing process such as the rupture of a brittle solid into small particles. On the other hand if one begins in region 4 and decreases the

temperature so as to observe the 4–3 transition, the phenomenon appears to us as a hydrodynamic instability. Both Pearson and Petrie[43] and White[36] have conjectured that the melt fracture phenomena[44-47] observed in polymer extrusion is a hydrodynamic instability involving elastic and viscous forces. Petrie[43] has analyzed the inertialess stability equations for this problem and evaluated the conditions for the propagation of disturbances through the melt. White[36] has emphasized that melt fracture, if an instability, would occur at a critical Weissenberg Number. The disturbance is then only propagated when the viscoelastic forces in the melt achieve a certain magnitude relative to the viscous forces. Viscoelasticity was suggested by this author to play a role analogous to inertia in initiating instabilities in Newtonian fluids.[8] If the 4–3 transition may be interpreted as a hydrodynamic instability of this type, then the Weissenberg Number will again be the criterion. While it is not readily apparent what the characteristic velocities and lengths are, the stability criterion may be tested by finding the values of τ_m for several polymers at the 4–3 transition temperature. The maximum relaxation time may be obtained by standard extension stress relaxation measurements,[38] and the rotor speeds and nip would be maintained constant throughout all of the experiments. We have carried this out for several elastomers, and the results are given in Table II. It may be seen that there is a good correlation with τ_m being in the neighborhood of 25–40 sec. It is interesting to note that the Deborah Number, rather than the Weissenberg Number, could be the criterion and still perhaps be compatible with a critical τ_m.

TABLE II

Polymer	T_4 (4–3 transition temperature), °F.	τ_m, sec.
Polybutadiene A	260	27
Polybutadiene B	170	35
SBR-A	195	35
Ethylene–propylene copolymer	195	35–40

When one is approaching the temperature of the 2–3 transition, it appears that we definitely do not have a hydrodynamic stability problem but one of tearing. In such a severe shear deformation as a roll mill at low temperature, the material behaves like an elastic solid rather than viscous fluid. We have to consider fracture phenomena in addition to elastic deformation in such a condition. Energetically, the phenomenon of crumbling and smooth tight rolling are due to the balance of tearing and elastic energies under a shear deformation. One might interpret this effect dynamically in terms of stress waves imparted to the material as it enters the nip. Bulgin[17] conjectures that the 2–3 transition in cis-polybutadiene is related to strain-induced crystallinity. While Bulgin could be correct in this one material,

his ideas are probably generally in error, for this phenomenon has been observed for several noncrystallizing elastomers.

SUMMARY

The variation of gum elastomer mill behavior with temperature may be divided into four distinguishable regimes. At very high temperatures, elastomers behave as melts analogous to polymer solutions (region 4). When the temperature is lowered the material becomes a rough, often crumbling bag (region 3). Lowering the temperature still further results in the polymer crumbling into a powder or in the more usual case becoming a tough elastic bag (region 2), and further decrease in temperature causes the elastomer to sit in the mill nip with strands passing onto both rolls (region 1). Region 3 is most severe for narrow distribution low molecular weight elastomers.

An approximate analysis of the velocity and stress fields is given for region 4 behavior and an approach to the region 2 problem is conjectured.

The cause of the 2–3 transition in milling is conjectured to be tearing and the 4–3 transition to be an instability caused by viscoelastic forces propagating disturbances. Experimental results are cited which support the latter conjecture.

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Résumé

Lorsqu'on travaille un élastomère vierge sur un moulin à deux rouleaux on observe 4 régions de comportement mécanique, ce-ci dépend de la température et de la sévérité de la déformation. On observe ce comportement avec des matériaux qui varient fortement en composition chimique mais l'intensité de l'effet varie largement. L'écoulement observée aux températures élevées se retrouve également dans le cas de polymères fondus ou de solutions. À des températures plus basses on observe une région d'écoulement enstable et de comportement élastique. En postulant pour l'élastomère une structure viscoélastique isotrope on calculé les champs de tension et de vitesse pour le polymère dans la région d'écoulement. On a constaté que la région instable correspondait à un rapport critique de force viscoélastique et des forces visqueuses. L'analyse mathématique qui a été faite en utilisant la théorie de Green-Rivlin-Noll pour des milieux viscoélastiques, constitue une extension des études antérieures de Gaskell, Pasley et Pearson.

Zusammenfassung

Bei Behandlung eines ungefüllten Elastomeren auf einem Zwei-Walzen-Kalander werden in Abhängigkeit von der Temperatur und der Schärfe der Faltungsdeformation vier verschiedene Bereiche des mechanischen Verhaltens beobachtet. Ein solches Verhalten wird bei einer weiten Variation der chemischen Zusammensetzung beobachtet, wobei immer die Schärfe variiert. Das Fliessen bei hoher Temperatur ist typisch für das Verhalten einer Schmelze oder Polymerlösung. Bei niedrigerer Temperatur werden instabiles Fliessen sowie elastische, festkörperartige Bereiche beobachtet. Unter der Annahme, dass das Elastomere ein isotropes, viskoelastisches Medium bildet, werden Spannungs- und Geschwindigkeitsfelder im Schmelzbereich des Polymeren berechnt. Der instabile Bereich entsprach einem kritischen Wert des Verhältnisses von viskoelastischen zu viskosen Kräften. Die im Rahmen der Green-Rivlin-Noll-Theorie viskoelastischer Medien durchgeführte mathematische Analyse führt zu einer Erweiterung früherer Untersuchungen der Deformationsgeometrie von Gaskell, Pasley und Pearson.