

Instability and Failure Phenomena in Polymer Processing with Application to Elastomer Mill Behavior

JAMES L. WHITE* and NOBORU TOKITA, *Research
Center of Uniroyal, Inc., Wayne, New Jersey 07470*

Synopsis

The mill behavior of different elastomers is discussed in some detail and contrasted with melt fracture in extrusion. The mill characteristics of elastomers are discussed, with special emphasis on effect of roll speeds and nip and on molecular structure of elastomer. Theories of failure mechanics in polymer processing are contrasted, and a theory of a viscoelastic material that exhibits rupture above a critical recoverable energy is analyzed. Mixing with carbon black is briefly discussed.

INTRODUCTION

A large portion of the materials processed in the chemical industry is not studied within the classical rheological sciences of elasticity and hydrodynamics.^{1,2} Essentially polymeric systems, such as molten plastics, fiber spinning solutions, plastisols, and raw rubber compounds, are in the category of nonclassical materials. Concepts of purely viscous nonlinear fluids and viscoelastic fluids, which combine nonlinearity in viscosity with memory of their deformation history, have been developed³⁻⁵ and applied with varying degrees of success to polymer-processing operations.⁶⁻¹⁰

Real materials do not in practice always deform smoothly or flow steadily. Metals yield and rupture, and fluid motions become unstable and are dominated by uncontrolled eddies. The sciences of elasticity and hydrodynamics have been supplemented with the newer ones of plasticity, failure mechanics, hydrodynamic stability, and turbulence, which treat these phenomena.¹¹⁻¹⁴ Similarly, polymer systems show unstable deformation and flow phenomena in their performance and during processing. A few unstable deformations of polymer systems have been resolved by minor modifications of the new approaches. Dodge and Metzner¹⁵ were able to use a modified Reynolds number and cognizance of the nonlinearities of the shear viscosity to evaluate the pressure gradient in the turbulent flow of purely viscous polymer solutions. Rivlin, Thomas, Greensmith, and Mullins¹⁶⁻¹⁹

* Present address: Department of Chemical and Metallurgical Engineering, University of Tennessee, Knoxville, Tennessee.

found that they could apply a modified Griffith rupture criterion to analyze the tearing of sheets of vulcanized rubber.

In this paper we shall discuss the significance of polymer instability and rupture in industrial processing operations and give special attention to the mill behavior of gum elastomers. In the following section we shall discuss deformation instabilities observed in mill behavior. We shall then discuss theories of failure mechanics and instability in polymer fluid deformation and their application to milling and extrusion. In the concluding section we shall discuss the significance of the milling characteristics of materials when fillers are mixed into elastomers.

EXPERIMENTS ON GUM ELASTOMER MILL BEHAVIOR

Basic Experiment and Temperature Variation

Processing of bulk polymers on a two-roll mill (Fig. 1) as an industrial operation dates from the 1830's.²⁰ There have, however, been no careful experimental studies of the rheological phenomena involved until rather recently, although meaningful studies of mechanochemical degradation and reactions in this geometry have been carried out for about 35 years.²¹⁻²⁵ The first mention of unstable processing behavior of elastomers during milling in the literature seems to be in a 1959 paper by Hanmer and Railsback,²⁶ who described the variation in mill behavior of high-*cis*-polybutadiene polymer with temperature. A more detailed study of mill behavior of *cis*-polybutadienes was published by Bulgin,²⁷ and an experimental study of several different elastomers was published by Tokita and White,²⁸ who classified the observed mill behavior into four different regions (see Fig. 2): (1) elastomer remaining mainly in the bank of the mill, only a small quantity of material passing through the nip, (2) tight elastic band clinging to the mill roll, (3) material torn and granulated in the mill nip and hanging as a bag off the roll (the granulated nature of rubber in the bag does not allow transmission of high stresses, and (4) transparent fluid film band occurring at high temperature.

Elastomers generally do not exhibit all four regions of mill behavior and, indeed, the two well-known materials, natural rubber and emulsion SBR, do not show striking changes with temperature except insofar as natural

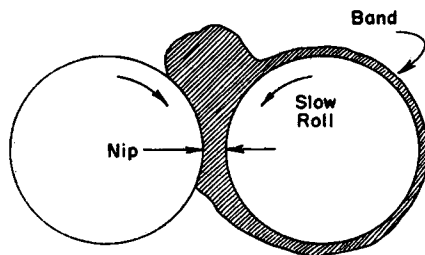


Fig. 1. Two-roll mill with banded elastomer.

rubber exhibits severe chemical degradation.²¹⁻²³ The aforementioned materials largely exhibit regions 1 and 2 over a wide temperature range, never showing a clear-cut region 3. *cis*-Polybutadiene, butyllithium polybutadiene and butadiene-styrene copolymer and ethylene-propylene

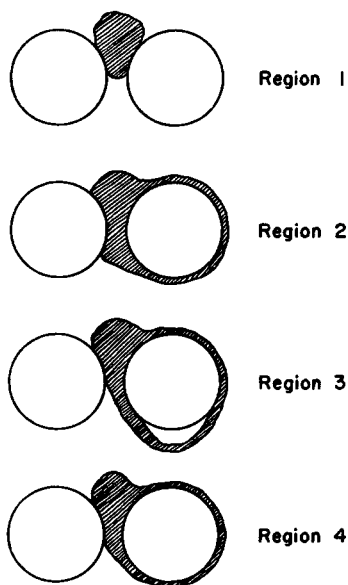


Fig. 2. Regions of mill behavior.

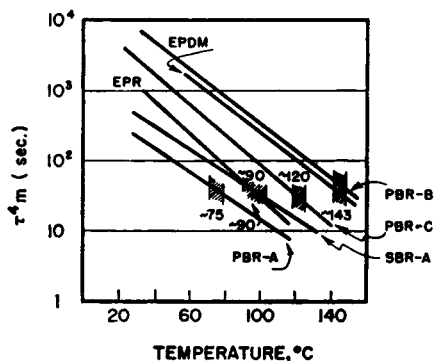


Fig. 3. Maximum relaxation time at region 4; τ_m^4 is about 30–40 sec. Sample description is given in Table I.

copolymer, on the other hand, clearly exhibit region 4 at high temperature, and if the temperature is lowered, they exhibit a striking transition to region 3.²⁸

The transition between regions 4 and 3 has been found by Tokita and White to occur at a critical temperature T_4 , which corresponds to the same

characteristic value²⁹ of the maximum relaxation time τ_m , which is defined by

$$\tau_m = \lim_{t \rightarrow \infty} [-1/(d \log G(t)/dt)] \quad (1)$$

for all stereo solution elastomers studied, if the mill nip and roll speeds are maintained constant. This is shown in Figure 3.

Variation of Roll Speed and Nip Distance

The work of Tokita and White²⁸ presented a detailed account of behavior in region 4 and in the transition between regions 4 and 3, which happen at one value of τ_m regardless of the elastomer, when the geometrical and kinematic conditions of the mill roll are given. These workers were, however, limited to a single speed mill and generally gave little attention to regions 2 and 3. They have attempted to remedy these deficiencies. A 3-in. diam. variable speed and nip laboratory mill was used. The friction ratio was maintained constant at 1.4.

We first note that regions 4 and 2 are superficially similar in appearance, though they actually differ in nature, a difference readily found by cutting the band with a mill knife. Region 4 is actually a fluid adhering to the roll and shows a negligibly small overall tension around the roll. Thus, if the roll were isolated, the elastomer would continue to cling to it except insofar as it was affected by gravitational forces. This is not the case of region 2, which consists of an elastic band clinging tightly to the roll. When the mill roll is held stationary, the elastic band starts to contract because of the overall tension. If inhomogeneities, such as severe thickness variations, holes, or other stress raisers exist, then the rubber begins to tear on the stationary roll.

The appearance of the mill roll band necessarily depends not only on the material properties and the kinematic conditions of the mill but also on the state of the material at the nip entrance. Unfortunately, in most materials these "boundary" conditions are exceedingly complex. Direct observations indicate a more or less random piling up and churning of the material at the nip entrance, so that the material geometry is grossly irregular, and the initial state of strain is highly heterogeneous. Concomitant variations may also be expected to occur in the initial temperature distribution.

With these facts in mind we may discuss the phenomena observed when the nip and roll speed are varied for materials in regions 2 and 4. Consider first the tight elastic-band behavior of region 2, which is represented by emulsion SBR and high-*cis*-polybutadiene at room temperature. In the case of SBR, as the roll speed is increased while a constant nip distance is kept, more surface irregularities develop. Minute local tears occur but never propagate during one revolution of the roll. However, when the mill roll is held stationary after banding, the larger number of surface irregularities associated with the higher roll speed induce a more extensive development of tearing. These observations indicate immediately that the

TABLE I
Molecular Structure of Polybutadiene and Styrene-Polybutadiene

Sample	Catalyst	Microstructure		ML-4 at 100°C.	$[\eta]$ at 30°C. in toluene	M_n	M_w/M_n
		<i>cis</i>	<i>trans</i> Vinyl				
Polybutadiene:							
A	Butyllithium	35	55	10	2.1	114,000	1.5
B	Butyllithium	35	55	10	2.6	177,000	1.5
C	Aluminum trialkyl titanium tetraiodide	93	4	3	2.6	157,000	3.5
D	Nickel transition-metal Ziegler-type catalyst	98	—	—	2.9	120,000	4.0
Styrene-butadiene copolymer: ^a							
A	Butyllithium			50	1.7	208,000	1.5
B	Butyllithium			50	1.7	94,000	5
C	Cold emulsion			45	1.8	88,400	10

^a Styrene/butadiene ratio for A, B, and C: 25 : 75.

appearance of a tight band is controlled mainly by tear initiation and a balance between the rate of tear propagation and the rotation speed of the roll. When the nip distance is reduced, the SBR tends to form a smooth tight band on the roll. We now turn to the effects of nip width and roll speed on region 4. Both the speeding up of the mill rolls and the decreasing of the nip width are seen to have similar effects. Each action causes disruption rather than stabilization of the material surface, tending to shift the mill behavior back to region 3.

It is worth while to discuss briefly the behavior of *cis*-polybutadiene; see Table I. Above 120°C. this material exhibits a typical region 4, and at room temperature it shows a striking region 2. Above 50°C. it shows a region 2-3 transition, at which tearing occurs, and then no banding on the roll, and the appearance changes from transparent to opaque. Increasing the roll speed tears the elastomer. A similar effect is obtained by opening the nip. However, the temperature effect is more striking. We cannot observe the tight band above 50°C., even though the nip distance is extremely reduced. Thus, the opinion of Bulgin²⁷ that high mill nip shear strain introduces crystallization in high-*cis*-polybutadiene appears to be correct. The narrow molecular weight distribution low-*cis*-polybutadiene, which is not crystallizable, does not show region 2 under any conditions. The effect of molecular structure on mill behavior will be discussed next.

Effect of Molecular Structure

First the molecular weight distribution effect on the mill behavior of noncrystallizable polymers was examined. The samples are butadiene-styrene copolymers (75:25), which are polymerized by butyllithium catalyst (A and B in Table I) and by emulsion polymerization (C). The Mooney viscosities of all of them are almost the same (45-50), and the intrinsic viscosities $[\eta]$ are 1.7-1.8. A noticeable decrease in crumbling and mill behavior characteristic of region 3 was observed as the width of the molecular weight distribution increased.

The effect of varying the absolute molecular weight of a particular homopolymer at constant narrow molecular weight distribution has been examined. The polymers are butyllithium polybutadiene (see Table I). They show a severe crumbling at low temperature and a clear region 4 at higher temperatures. The effect of increasing molecular weight is simply to increase the temperature T_4 at which the polymer shows the fluid-like behavior. These polymers are noncrystalline and do not show strain-induced crystallinity. Comparing the behavior of this low *cis*-polybutadiene to the striking appearance of region 2 for high-*cis*-polybutadiene at low temperature, it is evident that the *cis* content is one of the most important factors in mill behavior. Actually, a polybutadiene with high *cis* content and broad molecular weight distribution shows region 2 over a wide range of temperatures (sample D, Table I).

FAILURE CONSIDERATIONS

We now come to the question of the rational-continuum basis of failure and hydrodynamic instability in the mill behavior. What we wish to accomplish is to contrast the mechanisms of tearing the rupture of elastomers and hydrodynamic instability in milling. Tokita and White attempted to resolve this by suggesting that the transition between regions 4 and 3 (fluid-like) was due to a viscoelastic hydrodynamic instability and that the transition between regions 2 and 3 at low temperature was due to a tearing phenomenon.

Before discussing mill behavior we shall review briefly these two major concepts as applied to melt-fracture phenomena observed in extrusion.³⁰⁻⁴³ Pearson and Petrie^{44,45} and White⁴⁶ suggested that melt fracture in extrusion could be considered the result of the growth of a disturbance propagated through the melt by elasticity in a manner analogous to that of Reynold's turbulence. The hydrodynamic-stability theory will lead, as shown by dimensional analysis, to an onset criterion consisting of a product of a characteristic time τ and the ratio of a characteristic velocity V to a characteristic length L .^{10,46,47} This dimensionless group is known as a Weissenberg number:⁴⁸

$$N = \tau(V/L) \quad (2)$$

Another dimensionless group not containing kinematic quantities and relating to the viscoelastic behavior (known as the viscoelastic ratio number) may also affect the criterion and cause variations from material to material, but the Weissenberg number will be dominant.

The application of the failure mechanics of solids to melt fracture originating in the inlet of a die was done by Tordella,³⁵ who proposed that this phenomenon was due to the fact that the local absorption of strain energy was above a critical value characteristic of the material. This approach to failure and also to plasticity was taken by Huber and Hencky,^{11,49-51} who applied it to elastic solids. The generalization of failure phenomena to viscoelastic (Maxwellian and Voigt) materials, was carried out by Reiner, Freudenthal, and Weissenberg.⁵⁰⁻⁵² For the particular case of a Maxwell material failure occurs when the recoverable elastic-energy density U reaches a critical value U_c , here:

$$U = (\text{tr } P^2)/2G = \tau(\text{tr } P^2)/2\mu \quad (3)$$

P is the deviatoric stress tensor, τ is the Maxwellian relaxation time, and G is the shear modulus of elasticity. Both of these hypotheses were developed with specifically extrusion melt fracture in mind.

It must be remarked that any true theory of failure of viscoelastic materials will include both of these hypotheses and will reduce to one or the other depending upon whether the material is more nearly a viscous fluid or an elastic solid.

TABLE II
 Critical Strain-Energy Density U_c (100%/sec.), Shear Modulus $G(0.1)$, at 0.1 sec.,
 Maximum Relaxation Time τ_m , and Zero Shear Viscosity η_0

Sam- ple no.	$[\eta]$ at 30°C. in toluene	M_w/M_n	U_c at 30°C., dyne-cm./cm. ³	$G(0.1)$ at 30°C., dyne/cm. ²	τ_m at 30°C., sec.	η_0 at 30°C., poise	Mill behavior
1	40	2.25	3×10^6	5.1×10^5	400	0.28×10^8	Severe crumbling (region 3)
2	40	3.6	15×10^6	1.9×10^5	3000	1.7×10^8	Good band (region 2)

Huseby⁵³ has recently attacked the problem of melt fracture along yet another line. He suggested that a discontinuity in stress predicted by Pao's theory of nonlinear viscoelasticity⁵⁴ is the cause of this phenomenon.

Turning now to elastomer mill behavior, the observations of noncrystallizable polymers, such as butyllithium polybutadiene and emulsion SBR, indicate that a tearing phenomenon occurs at low temperature. The appearance of region 3 seems to be due to tear initiation and the balance of tear propagation rate and roll speed. First we shall consider the failure concept in explaining the observed experimental results. When the elastomer is passing through the nip, elastic energy is stored. If this energy reaches the critical elastic-energy density U_c , a tear will be initiated and then begin to propagate. The elastic energy built up during passage through the nip may be expressed roughly by $(1/2)G(\Delta t)\epsilon^2$, where $G(\Delta t)$ is a shear modulus at a time scale of the nip residence time, and ϵ is a shear strain. For viscoelastic materials in general $G(\Delta t)$ decreases with increasing nip residence time and increasing temperature.

On the basis of this criterion we may explain the observation of region 3-4 transition and the existence of region 2 in some elastomers. Consider the 3-4 transition and the various factors through which such a transition may occur. In a material exhibiting region 3 behavior increasing the temperature decreases $G(\Delta t)$ and reduces the stored energy below the critical value required for tear initiation. The material then bands smoothly on the mill roll, and its behavior is characterized by region 4. The effect of mill roll speed is to vary the nip residence time Δt . Thus, decreasing the mill roll speed increases Δt and decreases $G(\Delta t)$, the material behavior then tending towards region 4 type. Opening the mill nip causes a decrease in shear strain ϵ , which lowers the strain energy density, so that again the material behavior shifts toward region 4. This phenomenon was clearly observed on narrow molecular weight distribution polymers. The narrower the distribution, the more distinctive the appearance of the transition.

The capacity of some elastomers to exhibit region 2 in place of region 3 or to show a 3-2 transition is due either to a higher value of U_c or to very slow rates of tear propagation or both. Table II shows the values of U_c , $G(\Delta t)$, τ_m , and η_0 for two polybutadiene polymers (ML-4: 40); the one is narrow in molecular weight distribution ($M_w/M_n = 1.2$) and shows severe crumbling with no region 2, whereas the other is broad ($M_w/M_n = 4.0$) and gives a good band on the mill with no region 3 over a wide range of temperature. The broadening of the molecular weight distribution introduces a higher U_c , a lower $G(\Delta t)$ at high rates of extension and, of course, a longer relaxation time, which is related to the rate of tear propagation. In general, wide distribution elastomers have lower short-time elastic moduli than narrow distribution materials at the same Mooney viscosity. For example, hot-emulsion SBR has a lower value of $G(\Delta t)$ than narrower distribution cold SBR, which in turn has a lower modulus than the much narrower-distribution butyllithium SBR.

The hydrodynamic instability hypotheses can also qualitatively interpret [by eq. (1)] the effects of roll speed and nip distance on the 3-4 transition that was observed clearly for narrow molecular weight polybutadiene. However, for the disappearance of region 3 for broad molecular weight polymers and the appearance of elasticity and tear at low temperatures, another hypothesis is definitely necessary. We believe that the hypothesis of Reiner and Freudenthal⁵⁰⁻⁵² (i.e., that a viscoelastic material fails when it absorbs more than a critical recoverable elastic-energy density) and the tear propagation concept are more attractive, because they allow a more unified approach to elastomer mill behavior. More work is needed to develop a unified theory of failure of viscoelastic materials.

MILL BEHAVIOR AND CARBON BLACK DISPERSION

We shall now discuss a series of experiments on carbon black mixing by milling, in which 13 parts of HAF carbon black were dispersed in 100 parts of elastomer. The raw rubber was sheeted out, and the total amount of carbon black was spread out on the resulting sheet. Experiments were run at room temperature, 110, 160, 220, and 300°F. for 10 min. on various polybutadienes, ethylene-propylene rubber, and commercial butyllithium SBR, which show a clear 2, 3, and 4 transition in mill behavior. Photographs were taken of the carbon black dispersion. It was found that, in general, the best mixing is found in region 2, and the worst mixing of fillers in region 3. Region 4 at higher temperature gives a dispersion intermediate between that obtained in regions 2 and 3. We thus find that a plot of mill dispersion versus temperature will show a minimum corresponding to the region 3 temperature range and that materials exhibiting severe region 3 crumbling will show excessively bad dispersing properties in comparison with polymers which continue to band tightly on the mill. A broad molecular weight distribution can definitely improve carbon black mixing.

SUMMARY AND CONCLUSIONS

An experimental study of elastomer mill behavior has been presented, with emphasis, on rupture of the material in the mill nip and on the roll, and similarities and differences between this phenomenon and extrusion melt fracture.

The effects of mill roll speed and mill nip are described, and the relationship between molecular structure and mill behavior is analyzed. At high temperatures the narrow molecular weight distribution polymers give smooth, transparent, fluid films on the rolls (region 4). If the temperature is lowered, these films tear, crumble, and become a bag (region 3). Increasing the roll speed will accelerate this effect, as apparently also will decreasing the nip. Wide molecular weight distribution elastomers, when cooled, move from region 4 into region 2 (elastic band), and no region 3 behavior occurs under normal conditions.

The concepts of rupture theory by Reiner and his colleagues, combined with tear propagation mechanisms, were applied to explain the experimental observations. The need of further theoretical work on the rupture of viscoelastic materials is emphasized.

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