

Elastomer Processing and Application of Rheological Fundamentals

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Synopsis

Elastomer processing operations are discussed and classified as unit operations. The theory of nonlinear viscoelasticity is applied to processing unvulcanized amorphous rubber and the significance of the maximum relaxation time τ_m is emphasized.

Introduction

The rubber industry is the oldest and remains one of the most important of the polymer processing industries. In recent years new discoveries in polymerization methods and mechanisms have led to the proliferation of new specialty and perhaps general purpose elastomers.¹⁻³ However, with these successes in development of new materials, there has been a lag in the rational study of methods of processing elastomers and a tendency to polymerize and compound rubbers to fit speeds and dimensions of existing equipment, rather than to study the mechanics of these operations so as to learn how such equipment might be modified.⁴ At the same time, little attention has been given to meaningful methods of specifying the deformation behavior of rubber and to the related problem of rational methods of quality control. Indeed, many of the currently used quality control methods are based on naive theoretical developments or improper scaling of processing equipment.⁵ The only meaningful surveys of raw elastomer rheology and processing are by Mooney⁶ and by Scott⁷ and each suffers from lack of a consistent rheological theory.

It is the purpose of this paper to present elastomer processing as an engineering science. In so doing we bear in mind the development of such sciences in other chemical and mechanical industries and the methods used by Reynolds,⁸ Nusselt,⁹ Colburn,¹⁰ and others to devise design and scaling procedures for low molecular weight fluids. We also consider the point that raw elastomers are viscoelastic materials and when processed must be analyzed by the theory of nonlinear viscoelasticity.¹¹ It is also recognized that elastomers constantly undergo mechanochemical reactions during the processing operations. We shall proceed by first outlining the basic processes involved in the manufacture of rubber goods and then divide these into unit operations. We are, of course, influenced here by the comments

and classifications of Bernhardt and McKelvey¹²⁻¹⁴ which were meant to mainly apply to plastics, and of Scott.⁷ To analyze these operations we shall introduce modern rheological theories of elastomer deformation. Finally, we will relate the processing characteristics of rubber to molecular structure.

Unit Operations

The basic problems of elastomer processing are first the mixing of compounding ingredients including curatives into the gum elastomer, second the shaping of the compound into a semifinal shape, and third the final forming and curing. The historical development of the rubber fabrication industry and its equipment have been described in a series of books and articles¹⁵⁻²⁰ which are recommended as aids in understanding the current status and problems in the area of elastomer processing. A typical elastomer fabrication plant is outlined in Figure 1. The rubber and fillers are added to the top of an internal (e.g., Banbury) mixer in which a rotating element disperses the additives in the rubber. After a specified time or temperature rise in the continuously sheared material, the compounded rubber is discharged and may be sheeted out by a mill or tuber (extruder). Curing agents may be added in a second Banbury cycle at lower temperatures or on mills. The compound is then calendered or extruded into a semifinal shape. There may then be a building step (as in tires) which is followed by final shaping and curing in the vulcanization press.

With these comments in mind, we now will try to identify the individual unit operations and the rheological and mechanochemical problems involved.

(1) *Mixing.* By this we mean the mechanics and chemistry of mixing compounding ingredients into elastomers both in internal Banbury type

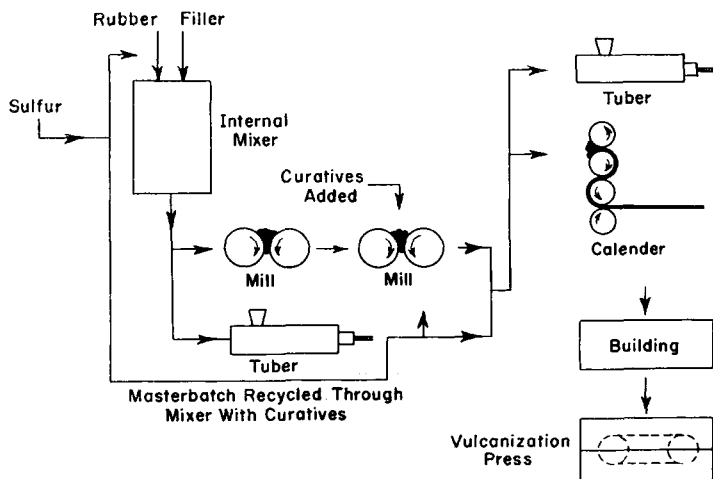


Fig. 1. Scheme of rubber goods factory.

mixers or externally on two roll mills. Of course, to analyze or understand the mixing process we must be concerned with the rheological properties of elastomers in these geometries.

(2) *Tubing.* The problem of shaping of compounded elastomers by conveying the material along a screw and then pushing it through a die is a second important unit operation having rheological and chemical aspects. Rheological problems include entrance region pressure losses and extrudate bulging and distortion while chemical problems include mechanical degradation and early vulcanization (scorching) caused by viscous heating.

(3) *Calendering.* This operation consists of a series of steel rolls which form sheets of polymers or coat fabrics with rubber. Rheological problems include the surface properties of the calendered sheet and chemical problems include scorching.

(4) *Building.* Here the previously fabricated elastomer parts are mechanically or manually put together in a semifinal shape. An important variable here is the adhesiveness or tack of those different parts.

(5) *Molding and Vulcanization.* In this final operation the extruded, calendered and/or built object is molded into final shape and vulcanized under temperature and pressure. The chemistry of the crosslinking reaction is of importance here especially as is the related rheological problem of the variation of material properties with extent of cure and the existence of residual stresses.

In order quantitatively to treat the mechanics of the individual unit operations and develop rational methods of quality control we must describe the rheological behavior of elastomers under typical processing conditions and we now turn to a discussion of this problem.

Theory of Viscoelastic Deformation

Raw gum elastomers and compounds are generally rheologically complex materials. These materials degrade chemically during mastication and will readily react with fillers.^{21,22} Some elastomers such as natural rubber²³ and high-*cis* polybutadiene²² crystallize during rapid deformations. At the same time these materials exhibit typical nonlinear viscoelastic characteristics as normal stress effects,⁵ non-Newtonian viscosity,^{5,6} and elastic recovery.⁶ If degradation and crystallizing phenomena may be neglected, we may devise an isotropic viscoelastic continuum theory of elastomer deformation. While significant thixotropic effects have been observed,²⁴ we believe these to be higher order effects unnecessary at this stage of development.

The stresses in a raw gum elastomer and many compounded materials may then be represented by the presumption that the stress is dependent upon the strain history in such manner that the elastomer is isotropic in its virgin state and that strains in the distant past have less effect upon the stress than strains in the recent past. If the strains are all infinitesimal and thus additive, this notion is equivalent to the Boltzmann superposition principle which was first applied to polymers by Leaderman.²⁵ The

many later contributions to our knowledge of the linear viscoelastic properties of polymers have been given in several recent books and review articles.²⁶⁻²⁸ However, in treating the processing of elastomers, we of necessity must be concerned with large deformations and nonlinear effects. The Boltzmann theory of linear viscoelasticity was generalized to finite strains by Green and Rivlin in 1957²⁹ and has been reformulated by various authors.^{11,30,31} In the nonlinear finite deformation theory, the stress tensor δ is related to the strain by the Frechet type expansion:

$$\begin{aligned} \delta = & -p\mathbf{I} + \int_{-\infty}^t \Phi(t - \phi)\mathbf{e}(\phi)d\phi \\ & + \int_{-\infty}^t \int_{-\infty}^t \psi(t - \phi_1, t - \phi_2)\mathbf{e}(\phi_1)\mathbf{e}(\phi_2)d\phi_1d\phi_2 \\ & + \int_{-\infty}^t \int_{-\infty}^t \Sigma(t - \phi_1, t - \phi_2)[\text{tre}(\phi_1)]\mathbf{e}(\phi_2)d\phi_1d\phi_2 + \dots \end{aligned} \quad (1)$$

The quantities Φ , ψ , Σ represent hereditary integral kernels, and \mathbf{e} is the Finger strain tensor defined in an earlier paper.¹¹ The kernel Φ is related to the relaxation modulus G of linear viscoelasticity by:^{32,33}

$$\Phi(t) = -2dG(t)/dt \quad (2)$$

and to the relaxation spectrum²⁶⁻²⁸

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

by:

$$\Phi(t) = +2 \int_0^{\infty} [H(\tau)/\tau^2]e^{-t/\tau}d\tau \quad (4)$$

Tobolsky^{34,35} first suggested on the basis of early data on polyisobutylene that $H(\tau)$ may be expressed as a "wedge-box" function:

$$\begin{aligned} H(\tau) &= A/\sqrt{\tau} & \tau_1 < \tau < \tau_2 & \quad (\text{wedge}) \\ H(\tau) &= H_0 & \tau_3 < \tau < \tau_m & \quad (\text{box}) \end{aligned} \quad (5)$$

which Fujita and Ninomiya^{36,37} and Tobolsky and Murakami^{38,39} have more recently shown to be characteristic of narrow molecular weight distributions. As τ_m is usually much greater than τ_3 , we may neglect the contribution of the wedge to some integrals of $H(\tau)$. In wide molecular weight distribution polymers, there are significant deviations from the box shape at higher τ (note the studies by Ninomiya and Fujita).^{36-38,40} Generally, widening molecular weight distribution increases elastic memory and τ_m .

There has been little study of the effects of fillers upon the relaxation modulus and spectrum in raw polymers, the limited results have been reviewed by Payne.⁴¹ Some earlier experimental data are described by Ferry.²⁶ This work almost completely consists of dynamic and loss modulus-frequency studies on vulcanizates and is of little use here.

In order to use eq. (1) for large deformations, we must, of course, greatly simplify the integral expansion. To accomplish this we shall presume that the elastomer remains in its virgin ground state, or at least has forgotten all previous history by time ϕ equal to zero, and from that instant to the present the deformation has been steady and smooth so that the strain tensor \mathbf{e} may be expressed as a Taylor series on time of form:^{11,29,33}

$$\phi > 0, \quad \mathbf{e}(\phi) = \sum \left[\frac{(-1)^{n+1}(t-\phi)^n}{2n!} \right] \mathbf{B}_n \quad (6a)$$

$$\phi < 0, \quad \mathbf{e}(\phi) = \mathbf{E} \quad (6b)$$

The \mathbf{B}_n are known as acceleration tensors and are based upon work of Rivlin and Ericksen.⁴² These particular tensors which are defined by the iterative equations

$$B_{ij}^{(1)} = \frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i} \quad (7)$$

$$B_{ij}^{(n+1)} = \frac{D}{Dt} B_{ij}^{(n)} - \sum_m \frac{\partial V_i}{\partial x_m} B_{mj}^{(n)} - \sum_m \frac{\partial V_j}{\partial x_m} B_{im}^{(n)}$$

have been derived and interpreted elsewhere.¹¹

Substitution of eq. (7) into eq. (1) allows us to write the integrals in this Frechet expansion as:

$$\int_{-\infty}^t \Phi(t-\phi) \mathbf{e}(\phi) d\phi = \left[\int_t^{-\infty} \Phi(s) ds \right] \mathbf{E} + \sum_n \left[\frac{(-1)^{n+1}}{2n!} \int_0^t s^n \Phi(s) ds \right] \mathbf{B}_n \quad (8a)$$

and from eq. (2):

$$\int_{\phi=-\infty}^{\phi=t} \Phi(t-\phi) \mathbf{e}(\phi) d\phi = \sum_n \left[\frac{(-1)^{n+1}}{(n-1)!} \int_0^t s^{n-1} G(s) ds \right] \mathbf{B}_n \quad (8b)$$

and eq. (4):

$$\int_{-\infty}^t \Phi(t-\phi) \mathbf{e}(\phi) d\phi = \sum_n \frac{(-1)^{n+1}}{(n-1)!} \times \left[\int_0^\infty \tau^{n-1} H(\tau) \int_0^{t/\tau} s^{n-1} e^{-s} ds d\tau \right] \mathbf{B}_n \quad (8c)$$

Similarly, for the higher integrals:

$$\int_{-\infty}^t \int_{-\infty}^t \psi(t-\phi_1, t-\phi_2) \mathbf{e}(\phi_1) \mathbf{e}(\phi_2) d\phi_1 d\phi_2 = \left[\int_t^\infty \int_t^\infty \psi(s_1, s_2) ds_1 ds_2 \right] \mathbf{E}^2 + \sum_m \sum_n \frac{(-1)^{m+n+2}}{[2n!][2m!]} \times \left[\int_0^t \int_0^t s_1^m s_2^n \psi(s_1, s_2) ds_1 ds_2 \right] [\mathbf{B}_m \mathbf{B}_n + \mathbf{B}_n \mathbf{B}_m] \dots \quad (9)$$

If we consider deformation periods t which are of the same order or larger than the time required for stresses to sufficiently relax in instantaneous stress relaxation experiments, it follows that eq. (1) may be written as (compare White³³ and Langlois and Rivlin⁴³):

$$\mathfrak{d} = -p\mathbf{I} + \sum_s \mathbf{M}_s \quad (10)$$

with

$$\mathbf{M}_1 = \omega_1 \mathbf{B}_1 \quad (11a)$$

$$\mathbf{M}_2 = \omega_2 \mathbf{B}_1^2 + \omega_3 \mathbf{B}_2 \quad (11b)$$

$$\mathbf{M}_3 = \omega_4 [\text{tr} \mathbf{B}_1^2] \mathbf{B}_1 + \omega_5 (\mathbf{B}_1 \mathbf{B}_2 + \mathbf{B}_2 \mathbf{B}_1) + \omega_6 \mathbf{B}_3 \quad (11c)$$

The coefficient $\omega_{j(n)}$ of the \mathbf{B}_n matrix is from eqs. (8) and (11):

$$\omega_{j(n)} = \frac{(-1)^{n+1}}{2n!} \int_0^\infty s^n \Phi(s) ds \quad (12a)$$

$$= \frac{(-1)^{n+1}}{(n-1)!} \int_0^\infty s^{n-1} G(s) ds \quad (12b)$$

$$= (-1)^{n+1} n \int_0^\infty \tau^{n-1} H(\tau) d\tau \quad (12c)$$

For narrow molecular weight distributions, we have from eq. (5)

$$\omega_{j(n)} \sim (-1)^{n+1} H_0 \tau_m^n \quad (12d)$$

The coefficient $\omega_{k(m+n)}$ of the matrix groups of type $(\mathbf{B}_m \mathbf{B}_n + \mathbf{B}_n \mathbf{B}_m)$ is

$$\omega_{k(m+n)} = \frac{(-1)^{m+n+2}}{4n!m!} \int_0^\infty \int_0^\infty s_1^m s_2^n \psi(s_1, s_2) ds_1 ds_2 \quad (13)$$

From eqs. (10) and (11), it follows that the coefficient ω_1 is the zero shear viscosity, η , and ω_3 is related to the steady-state shear compliance^{32,33} by:

$$\omega_3 = J_e \eta^2 \quad (14)$$

Let us now look at the opposite case in which the stress decay would be small in the time scale of the process. We would then write:

$$\sigma = -pI + \sum_n \left[\frac{(-1)^{n+1}}{(n-1)!} \int_0^{\Delta t} s^{n-1} G(s) ds \right] \mathbf{B}_n + \dots \quad (15)$$

The most important rheological properties would seem to be integrals of the type given by eq. (15).

In a laminar shearing motion¹¹

$$\begin{aligned} v_1 &= \Gamma x_2 \\ v_2 &= v_3 = 0 \end{aligned} \quad (16)$$

$$\mathbf{B}_1 = \begin{vmatrix} 0 & \Gamma & 0 \\ \Gamma & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

$$\mathbf{B}_2 = \begin{vmatrix} -2\Gamma^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (17)$$

with for $n > 2$, $\mathbf{B}_n = 0$

We have upon substituting into eq. (15):

$$\sigma_{12} = \sigma_{21} = \left[\int_0^{\Delta t} G(s) ds \right] \Gamma + \dots \quad (18a)$$

$$\sigma_{11} - \sigma_{22} = +2 \left[\int_0^{\Delta t} sG(s) ds \right] \Gamma^2 + \dots \quad (18b)$$

As the modulus decay is slow and might be expressed by

$$G(s) = G(0) - \epsilon s + \dots \quad (19)$$

we may integrate eqs. (18) to yield

$$\sigma_{12} = \sigma_{21} = [G(0) - (\epsilon \Delta t / 2) + \dots] \Gamma \Delta t \quad (20)$$

$$\sigma_{11} - \sigma_{22} = [G(0) - 2/3 \epsilon \Delta t + \dots] (\Gamma \Delta t)^2$$

As $\Gamma \Delta t$ may be recognized as the shearing strain, we see that the stresses in eq. (20) have the exact form of the theory nonlinear elasticity with a decaying modulus.²³

Dimensional Analysis

We now turn to the problem of specifying the processing behavior of raw elastomers in actual plant equipment. While in some special instances, we may be able to solve the actual boundary value problem, such as flow in a viscometer, this is in general not possible. However, by analyzing the terms in the equations of motion it is possible to find certain characteristic dimensionless groups which will specify the deformation behavior regardless of the exact details of the boundary value problem solution. This method of characterizing the equations of motion by dimensional analysis was first applied to Newtonian fluids by Reynolds⁸ and to heat transport by Nusselt.⁹ More recently, it has been applied to classes of viscoelastic fluids^{33,44} which are more special than those considered here. We shall first consider the case in which the deformation periods are of the same order as the time required for the relaxation kernels to decay (i.e., the Rivlin-Ericksen asymptote). The equations of motion are:

$$\rho D\mathbf{v}/Dt = \nabla \cdot \boldsymbol{\sigma} \quad (21a)$$

$$\rho D\mathbf{v}/Dt = -\nabla p + \sum_n \nabla \cdot \mathbf{M}_n \quad (21b)$$

Placing these equations in dimensionless form with characteristic velocity U , length L , and pressure P yields the groups: $LU\rho/\mu$, $PL/\mu U$, $\omega_{j(n+1)}U/\omega_{j(n)}L$, and $\omega_{k(m+n)}/\omega_{j(m+n)}$. These dimensionless quantities are respectively: the ratio of inertial to viscous forces (Reynolds Number), the ratio of pressure forces to viscous forces, the ratio of the $(n+1)$ acceleration tensor to the n th acceleration tensor, and cross ratios of forces due to kinematic matrices of the same order in velocity. Here μ is a shearing viscosity which may be chosen to be say the zero shear viscosity η . In a viscometric flow it might be taken as the laminar shear viscosity. For most if not all elastomer processing operations, inertial forces will be negligible and the Reynolds Number may be neglected. The $\omega_{j(n+1)}u/\omega_{j(n)}L$ is a generalization of the Weissenberg Number introduced in earlier papers.^{33,34} For $n=1$ this group becomes:³³

$$-\omega_{j(2)}U/\omega_{j(1)}L = -\omega_3U/\eta L = J_e\eta^2/\eta L = J_e\eta U/L \quad (22)$$

Turning to the general case we find that if the elastomer has a narrow molecular weight distribution, then from eq. (6) and eq. (12d):

$$-\omega_{j(n+1)}U/\omega_{j(n)}L \sim \tau_m U/L \quad (23)$$

For broad molecular weight distributions where the relaxation spectrum is not well understood:

$$\frac{\omega_{j(n+1)}U}{\omega_{j(n)}L} = \frac{1}{n} \frac{\int_0^\infty s^n G(s) ds}{\int_0^\infty s^{n-1} G(s) ds} \frac{U}{L} \quad (24a)$$

$$= \frac{n}{(n-1)} \frac{\int_0^\infty \tau^n H(\tau) d\tau}{\int_0^\infty \tau^{n-1} H(\tau) d\tau} \frac{U}{L} \quad (24b)$$

From inspecting eq. (24b) or considering the implications of presuming

$$G(s) = G_m e^{-s/\tau_m} + \sum_i G_i e^{-s/\tau_i} \quad \tau_m > \tau_i \quad (25)$$

we can see that eq. (23) may well be a reasonable representation even when the distribution of molecular weight is wide.

We now turn to the group of terms, $\omega_{k(m+n)}/\omega_{j(m+n)}$. These are simply generalizations of the viscoelastic ratio numbers discussed in earlier papers.^{33,44} These groups and those due to other kernels such as $\Sigma(s_1, s_2)$ will characterize properties such as non-Newtonian flow and direction of normal stresses.

In the case that the deformation time is small in comparison with the rate of modulus decay, we have instead dimensionless groups of form:

$$\frac{\int_0^t s^n G(s) ds}{\int_0^t s^{n-1} G(s) ds} \cdot \frac{U}{L}, \quad \frac{PL}{\left[\int_0^t G(s) ds \right] U} \quad (26)$$

It should be seen that these dimensionless groups may be specified by the Rivlin-Ericksen asymptote quantities and the ratio of the deformation residence time t to the natural time (e.g., maximum relaxation time) τ of the material. This ratio may be recognized to be Reiner's "Deborah Number."⁴⁵ It is then the Weissenberg and the Deborah Numbers which mainly specify the short time processing characteristics of elastomers.

Not only may dimensionless groups arise from the equations of motion themselves but also from the boundary conditions, the most important of which is the question of slippage or adhesion at boundaries. Mooney^{6,46} has pointed to the existence of slippage by elastomers under processing conditions.

Determination of Processability

The problem of determining the processing behavior of elastomers in factory equipment is a difficult one which has always plagued the rubber industry. Different aspects of this problem have been described by Mooney,^{6,46-48} Dinsmore and Juve,⁴⁹ and White and Tokita.⁵ Basically, what is required is the specification of these elastomer properties which will determine how the rubber compounds will behave in Banbury mixers, mills, calenders, tubers, etc. as they move throughout the factory. Most researchers have attempted to solve this problem in an entirely empirical manner and as one might expect have achieved little success. On the other hand, beginning in the 1930's some researchers, notably Mooney⁵⁰ tried to apply existing knowledge of the mechanics of materials to solve this problem. The basis of Mooney's studies was a shearing disk viscometer. This rotational instrument has proven to be quite adaptable and Mooney and others^{6,47,48,51} show how it may be used to measure non-Newtonian viscosity, scorch life, slippage and elastic recovery. The Mooney viscometer is still a subject of continuing research and improvement.^{5,52,53}

In the remainder of this section, we shall outline the application of the theory of viscoelasticity to the prediction of elastomer processing behavior in specific processing equipment. We have already shown that the rheological behavior of elastomers may be specified by a series of dimensionless groups which contain kinematic variables and material properties. If we consider a processing operation in which a particular compounded stock behaves in a satisfactory manner, then our processability tests for future materials should be the determination of these dimensionless groups so that they will have similar values to the good processing stock. As the machinery speeds and dimensions will be maintained constant we must thus only compare the material properties in these dimensionless groups which may be seen to be

$$\eta, \tau_m, \omega_k(m+n)/\omega_j(m+n), \dots, \int_0^t s^n G(s) ds \quad (27)$$

The temperature variation of these properties must also be considered.

If we must determine an infinite number of physical properties and their variation with temperature we are of course no better off than before. However, by carefully observing the meaning of the properties we see that they may be broken down into three categories. The first category is the viscosity. While the coefficient ω_1 is simply the absolute zero shear viscosity, higher terms such as ω_4/ω_6 seem to represent largely contributions to the non-Newtonian flow behavior. The entire contribution of these terms may then be measured on a multispeed Mooney viscometer. If we are comparing different lots of a particular uncompounded elastomer, say, a polybutadiene or SBR, then it is found that while the absolute viscosity may vary there is little change in the non-Newtonian viscosity-shear rate curve. For this reason, we need only specify the absolute viscosity, through, say, the 4-min. large disk Mooney viscosity (ML-4), when comparing different lots.

The second category is elastic memory which is specified by our dimensional analysis through the maximum relaxation time τ_m . It was originally hoped that all necessary measurements could be made on the multispeed Mooney viscometer and we noted that τ_m may be shown to be equivalent to elastic recovery at a specific shear rate as shown below (compare White³³)

$$\tau_m \simeq \frac{\int_0^{\tau_m} \tau H(\tau) d\tau}{\int_0^{\tau_m} H(\tau) d\tau} = J_e \eta \quad (28)$$

$$\tau_m \simeq (\phi_e/\sigma) \cdot (\sigma/\Gamma) \simeq (\phi_e/\Gamma)$$

where ϕ_e is an elastic recovery angle and σ the shearing stress. We have found, however, that the measurement of elastic recovery at a specific shear rate is a rather insensitive test of memory. We, then, set out to measure τ_m directly from stress relaxation experiments. From eq. (25) we find τ_m to be:

$$\lim_{(\text{large } t)} \frac{d \log G(t)}{dt} = - \frac{1}{\tau_m} \quad (29)$$

We now rewrite this as:

$$\lim_{(\text{large } t)} \left[\frac{d \log G(t)}{d \log t} \right] = - \frac{t}{\tau_m} \quad (30)$$

We may thus determine τ_m by finding the time value on a logarithmic plot of $G(s)$ when the slope is minus one. Alternatively the time value at which $G(t)$ decays to 10^4 dyne/cm.² is a sensitive approximate method. This measurement of τ_m has turned out to be far more satisfactory than the elastic recovery values. It should be noted that the same stress relaxation experiment which yields τ_m may be used to compute the absolute modulus.

In this analysis of processability, one must however be wary of stability problems such as fracture tearing. This seems to be often related to the

viscoelastic character of materials, especially in vulcanizates,⁵⁴ but a one-to-one correspondence in processing raw materials has not been found. As argued by Bagley⁵⁵ and White,³³ melt fracture in polymer melts seems to be closely related to viscoelastic phenomena. However, the well-known Ziegler polybutadiene mill crumbling problem does not seem to have so simple an explanation.^{56,57} The other phenomena, such as mechanochemical breakdown and strain-induced crystallinity which was waved aside earlier should be reintroduced and weighed. Generally though when all is said and done, and one must treat series of gum elastomers and compounds not differing in composition too considerably day in and day out, specification of τ_m and ML-4 solves most problems.

Molecular Structure and Rheological Properties

The main structural characteristics of polymers which affect rheological properties, τ_m , or ML-4 are: (1) polymer chain regularity; (2) glass temperature as a measure of chain stiffness and polarity; (3) absolute molecular weight; (4) molecular weight distribution; (5) branching. We now briefly discuss these in turn. The main significance of polymer chain regularity is that it influences crystallization tendencies. Thus, high-*cis* polyisoprenes and polybutadienes crystallize on cooling or stretching, unlike the same polymers with more random microstructures.^{22,23}

Glass temperature T_g , has a significant effect on rheological properties of polymers. Generally, we have found that linear narrow distribution polymers having the same molecular weight have the same value of τ_m at equivalent $(T - T_g)$. As the temperature behavior of τ_m is given by the Williams-Landel-Ferry (WLF) equation^{26,27,58} which relates such dependence to $(T - T_g)$, an equivalence of τ_m at one temperature means an equivalence at all $(T - T_g)$. Furthermore we note that the higher the glass temperature, the higher the τ_m .

In linear, narrow-distribution polymers, τ_m increases with about the 3.5 power of the molecular weight,^{27,35-39} and the Mooney viscosity with about the first power.⁵⁹ The weaker dependence of the latter should be expected from the viscosity-shear rate-molecular weight studies of Porter and Johnson⁶⁰ and Collins and Bauer.⁶¹

Increasing the width of molecular weight distribution of linear polymers increases elastic memory and τ_m . The classic paper by Leaderman et al.⁶² shows this point rather well (see also Ferry²⁶). Width of distribution is a major factor which must be watched in comparing day-to-day production especially of emulsion polymerized synthetic rubber.

Increasing long chain branching at constant molecular weight acts to increase elastic memory and τ_m if one is above a characteristic molecular weight approximately 10^5 . This is apparent from the work of Kraus and Gruver,⁶³ and has also been shown in our laboratory.

As an example of the above considerations, we will compare the rheological characteristics of three 25% styrene random copolymers of butadiene (SBR). These elastomers, all of which have an ML-4 of about 50,

are (A) 5°C. emulsion (cold) copolymer, (B) 50°C. emulsion (hot) copolymer, (C) butyllithium copolymer. As indicated by our own experiments and those described in the literature for butadiene homopolymers⁶⁴⁻⁶⁶ and styrene copolymers,⁶⁷ we find that SBR B has a very wide molecular weight distribution and considerable long-chain branching, while SBR A has wide distribution and significant (though less than SBR B) long-chain branching. SBR C has a narrow molecular weight distribution and little or no long-chain branching. Both SBR A and SBR B have glass transition temperatures of -55°C . while SBR C has a value of about -80°C . Measurement of the maximum relaxation time at 30°C . for these polymers of eq. (30) yields the results shown in Table I.

TABLE I

	$\tau_m \times 10^{-3}$
SBR A	40
SBR B	700
SBR C	0.5

The high value of τ_m for SBR B relative to SBR A is due to long-chain branching and molecular weight distribution. The low value of τ_m for SBR C is due to the narrowness of the distribution, the absence of long-chain branching and a lower glass temperature. It is worthwhile to note that Wolstenholme⁵³ has recently compared the laminar shear flow viscosities of SBR A and SBR C and found that SBR C exhibits less deviations from Newtonian behavior. Tokita and White⁵⁷ have compared the mill behavior of SBR A and SBR C and found the butyllithium polymer to exhibit severe crumbling and bagging over a considerable temperature range unlike emulsion copolymers. This latter phenomenon indicates the need to generalize the theory outlined in this paper to consider raw elastomer tear and failure properties.

Conclusions

We have defined a series of unit operations for elastomer processing. We have further applied the theory of nonlinear viscoelasticity to obtain specifications for processability and discussed relationships between rational properties and molecular structure.

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Résumé

Les opérations de traitement d'élastomères sont discutées et classifiées comme opérations unitaires. La théorie de la viscoélasticité non-linéaire est appliquée au traitement du caoutchouc amorphe non-vulcanisé et l'importance du temps de relaxation maximum, τ_m , est mise en évidence.

Zusammenfassung

Verarbeitungsprozesse für Elastomere werden diskutiert und in Grundprozesse eingeteilt. Die Theorie der nichtlinearen Viskoelastizität wird auf die Verarbeitung von unvulkanisiertem, amorphen Kautschuk angewendet und die Wichtigkeit der maximalen Relaxationszeit, τ_m , wird betont.

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