

Elasticity of Molten Polymers from Stress Relaxation Data

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INTRODUCTION

Little experimental work has been published on the stress relaxation phenomena arising when a steady viscous flow of a molten polymer is suddenly stopped. Moreover, an analytical evaluation of the relaxation data based on the determination of the relaxation spectra by means of inverse Laplace transforms has the following drawbacks: (a) it requires long calculations, and actually the accuracy and reproducibility of the experimental data, as well as their extent, are not sufficient for a complete analysis, nor are they adequate to the importance of the analytical procedure; (b) it is based on the use of linear models, such as the Voigt or the Maxwell bodies, while in general the actual physical systems are far from being linear. Consequently, at a given temperature, the relaxation spectrum depends on the stress to which the specimen is subjected; therefore, the polymer characterization becomes even more complicated.

The writers have done a great deal of experimental work on molten polymers using a Kepes consistometer,^{1,2} an instrument which appears to be particularly fit for stress relaxation investigation. On this experimental basis, an evaluation of the elastic components of molten polymers will be suggested here, which can be carried out without the determination of the relaxation spectra.

THE VISCOELASTIC PARAMETERS

Attention has been already drawn by Ferry³ to the opportunity of considering the elastic energy stored within a molten macromolecular system as a consequence of a steady viscous flow. In this way, the following parameters are defined.

1. The steady flow viscosity $\eta_0 = \tau_0/\dot{\gamma}_0$, where τ_0 = stress, $\dot{\gamma}_0$ = rate of shear (here and in the following the subscript zero means quantities related to the steady flow).

2. A stored elastic energy (per cubic centimeter):

$$W = \int_0^{\gamma_0} \tau d\gamma \quad (1)$$

In a Hookean elastic system, where the strain γ is proportional to the stress τ , a steady state compliance J_w can be defined, such that

$$W = J_w \tau_0^2 / 2 \quad (2)$$

when

$$\gamma = J_w \tau \quad (3)$$

(3) A relaxation time:

$$\lambda_w = J_w \eta_0 \quad (4)$$

It is immediately seen that the ratio of the stored elastic energy W , defined by eq. (2), to the power $P = \dot{\gamma}_0 \tau_0 = \eta_0 \dot{\gamma}_0^2$ dissipated in the steady viscous flow is

$$W/P = J_w \eta_0 / 2 = \lambda_w / 2$$

We can define, in this way, a single *energetically equivalent Maxwell body* composed of a Hookean spring with a compliance modulus J_w , coupled in series with a dashpot with a Newtonian viscosity η_0 ; such a body stores the same amount of elastic energy under the same steady viscous flow defined by a uniform rate of shear $\dot{\gamma}_0$ corresponding to the stress $\tau_0 = \eta_0 \dot{\gamma}_0$.

In general such quantities are expected to be dependent on the flow conditions, namely temperature and rate of shear, and hence on the steady state stress τ_0 .

An actual determination of J_w and of λ_w is possible only if the stored elastic energy W can be calculated. An evaluation of such energy will be tried here on the basis of the experimental stress relaxation graphs $\tau = f(t)$ representing the relaxation stresses as functions of the time t . It is to be remembered that for real viscoelastic macromolecular systems the ordinates corresponding to an abscissa "t" of two functions $\tau = f(t)$ starting from two different values of τ_0 are not proportional to each other. Furthermore, the stress relaxation functions, as well as the flow curve in the steady flow, depend, in general, on the previous rheological history of the specimen. But it is supposed here

that such dependence can be neglected, namely, that there is a one-to-one correspondence between the relaxation stresses and the times "t," as well as between the steady stresses τ_0 and the corresponding shear rates $\dot{\gamma}_0$. Actually, this hypothesis is not very restrictive: it means that the steady flow is continued until an asymptotic steady state is reached which is no longer dependent on the previous history of the specimen; the only condition is that during the long-lasting steady flow the specimen does not undergo any chemical or structural change such as oxidation, degradation, or cross-linking.

CALCULATION OF THE STORED ELASTIC ENERGY

Let us first consider the general differential equation of a relaxation process in the absence of outer forces:

$$\tau + \eta(d\gamma/dt) = 0 \quad (5)$$

where η is the viscosity which is effective in the relaxation process. It cannot be supposed, a priori, that this viscosity is equal to the one measured in the steady flow; furthermore, this viscosity in general is not a constant but may vary as a function of the rate of shear. The stress-strain relationship, too, can be different from the simple linear eq. (3).

The stored elastic energy is given by

$$W = \int_0^{\gamma_0} \tau d\gamma = \int_0^{\gamma_0} \tau(d\gamma/dt)dt \quad (6)$$

where γ_0 is the steady state strain.

Then, taking into account eq. (5), we have

$$W = - \int_0^{\gamma_0} \tau \dot{\gamma} dt = \int_0^{\gamma_0} (\tau^2/\eta) d\gamma \quad (7)$$

To calculate W it is necessary to know the stress-strain relationship and the relationship connecting the viscosity to the rate of shear.

Let us now consider, in the graph of the experimental stress relaxation function $\tau = f(t)$, the area A limited by the graph itself and the coordinate axes. This area is:

$$A = \int_0^{\infty} \tau dt = - \int_0^{\infty} \eta \dot{\gamma} dt = \int_0^{\gamma_0} \eta d\gamma \quad (8)$$

With constant viscosity, it will be

$$A = \eta \gamma_0 \quad (9)$$

This area A will be called the "relaxation area." It has the dimensions of a viscosity and when multiplied by a rate of shear (a reciprocal time), it has the dimensions of a stress (or of an energy per unit volume).

In a similar manner, the functions $A(t)$ and $A(\tau)$ can be defined; when the stresses diminish to zero by $t \rightarrow \infty$, it is seen immediately that

$$W = \int_0^{\tau_0} A(\tau) d(\tau/\eta) \quad (10)$$

and, for constant viscosity, that

$$W = (1/\eta) \int_0^{\tau_0} A(\tau) d\tau \quad (11)$$

As was foreseen, in order to calculate the stored elastic energy it is necessary to know the internal apparent viscosity η (or the relationship between stress and rate of shear) during the relaxation phenomena.

A general procedure based on trial and error can be outlined as follows.

A particular relationship connecting η and $\dot{\gamma}$ is assumed (e.g., the same that results from the flow curve of the steady state). By means of eq. (7) or (10), a number of values of the energy W are calculated from the different experimental stress relaxation graphs corresponding to different values of the initial stress τ_0 , and a function $W(\tau)$ is stated, connecting the stored energy to the stress.

But

$$dW/d\tau = (dW/d\gamma)(d\gamma/d\tau)$$

and, since it is

$$dW/d\gamma = \tau$$

it will be

$$d\gamma/d\tau = (1/\tau)(dW/d\tau) \quad (12)$$

By integration of eq. (12) and under the boundary condition that when $\tau = 0$, γ is 0 also, a stress-strain relationship $\gamma(\tau)$ can (at least in principle) be obtained. By using this last relationship and the formerly assumed one concerning $\eta(\dot{\gamma})$, the differential eq. (5) can, in principle, be resolved, and a stress relaxation function $\tau = f(t)$ is obtained, which must be the same as the experimentally determined one.

If the calculated and the experimental stress relaxation function do not agree, the viscosity function $\eta(\dot{\gamma})$ is changed, new energy values W are calculated as above, and a new elastic function $\gamma(\tau)$ is determined. A new stress relaxation function is obtained. The trials are repeated until the experimental and the calculated relaxation functions do agree.

Such a procedure shows a number of drawbacks: it is not always practically feasible, it is too long, and it is difficult to obtain a set of W values sufficient to give a good determination of the elastic

function; furthermore, arbitrary factors are still present in the calculation of the absolute energy values.

It appears, then, that the procedure outlined above is not convenient. Other methods of evaluation of the stored elastic energy will be outlined in the following; they are less objective, but much more easily carried out.

The quantities obtained by means of such methods cannot yet be assumed to be the true values of the elastic energy; nevertheless, they can be considered parameters of elasticity which, as will be shown in some experimental instances, appear to have some practical meaning in the characterization of polymers.

LINEAR APPROXIMATION

Let us suppose that, at a given temperature, through the calculation of the relaxation spectra, a set of linear elementary Maxwell bodies coupled in parallel has been defined, each consisting of a spring having a compliance J_i and of a dashpot having a Newtonian viscosity η_i , hence a relaxation time $\lambda_i = J_i\eta_i$; this system, at a given value of the initial stress τ_0 , relaxes in the same way as the molten polymer.

In the steady state each elementary Maxwell body shall withstand a stress τ_{0i} while its spring will extend corresponding to a strain $\gamma_{0i} = J_i\tau_{0i} = \dot{\gamma}_0\lambda_i$. It is obvious that

$$\sum_i \tau_{0i} = \tau_0 \quad \text{and} \quad \sum_i \eta_i = \eta_0$$

where $\eta_0 = \tau_0/\dot{\gamma}_0$ is the steady state viscosity of the real polymer.

During the relaxation, the stress τ_i of each element must relax according to the law

$$\tau_i = \tau_{0i} \exp \left\{ -t/\lambda_i \right\}$$

and the total stress,

$$\tau = f(t) = \sum_i \tau_{0i} \exp \left\{ -t/\lambda_i \right\} \quad (13)$$

coincides with the stress relaxation function which was actually found. It is immediately seen that the total elastic energy stored within the system of Maxwell bodies is given by

$$W_M = \dot{\gamma}_0 A/2 \quad (14)$$

where A is the relaxation area defined by eq. (8).

The same result is obtained in the case of a continuous distribution of elementary Maxwell bodies characterized by a relaxation function,

$$H(\lambda) = \lambda G(\lambda) = \eta(\lambda)$$

defined within the limits λ_1 and λ_2 , where it is

$$\tau(\lambda) = \dot{\gamma}_0 \eta(\lambda) = \dot{\gamma}_0 H(\lambda)$$

Then the elastic energy is

$$\begin{aligned} W_M &= \int_{\lambda_1}^{\lambda_2} W(\lambda) d\lambda = (1/2) \int_{\lambda_1}^{\lambda_2} [\tau^2(\lambda)/G(\lambda)] d\lambda \\ &= (1/2) \dot{\gamma}_0^2 \int_{\lambda_1}^{\lambda_2} \lambda H(\lambda) d\lambda \end{aligned}$$

but

$$\begin{aligned} A &= \int_0^\infty \tau dt = \int_0^\infty dt \int_{\lambda_1}^{\lambda_2} \tau(\lambda) d\lambda \\ &= \dot{\gamma}_0 \int_0^\infty dt \int_{\lambda_1}^{\lambda_2} H(\lambda) \exp \left\{ -t/\lambda \right\} d\lambda \\ &= \dot{\gamma}_0 \int_{\lambda_1}^{\lambda_2} \lambda H(\lambda) d\lambda \end{aligned}$$

Hence

$$W_M = \dot{\gamma}_0 A/2$$

Thus, the elastic energy stored within a system of elementary linear Maxwell bodies, which relaxes in the same way as the real polymer (at a given value τ_0 of the initial stress) and exhibits, in the steady flow, the same viscosity η_0 (at the same rate of shear $\dot{\gamma}_0$), can be calculated from the relaxation area without one's knowing the relaxation spectrum or the relaxation function. In general, the real system is not linear; i.e., neither are the springs Hookean nor the dashpots Newtonian. Hence, at different values of the stress τ_0 , the corresponding systems of the τ_{0i} and of the λ_i are different.

Actually, it was found in most experimental instances that at different τ_0 values the λ_i values change but little while the corresponding τ_{0i} are not proportional to each other, those corresponding to the largest λ_i being nearly independent of the τ_0 (when this latter is over a given limit).

A more detailed analysis of the evolution of the τ_{0i} and λ_i is not within the aims of the present work.

The following procedure is suggested.

From the relaxation areas, the values of the W_M are calculated by means of eq. (14) for different temperatures and different initial stresses τ_0 . We can thus define a single energetically equivalent Maxwell body, consisting of a dashpot of viscosity η_0 and of a Hookean spring of compliance:

$$J_w = 2W_0/\tau_0^2 = (\dot{\gamma}_0 A/\tau_0^2) \quad (15)$$

storing the same amount of elastic energy as the system of Maxwell bodies relaxing in the same way as the real polymer. According to eq. (4) we can also define the ratio of the stored elastic energy to the power dissipated in the steady flow:

$$W_M/P = \lambda_w/2 = J_w \eta_0/2$$

which is the half of the relaxation time of the energetically equivalent Maxwell body.

In most instances, at a given temperature, the log-log plot of J_w versus τ_0 was found to be fairly on a straight line. This fact suggested a further step in the analysis.

NONLINEAR MODELS

Let us suppose that, during the relaxation phenomena, the stress-strain relationship is not linear but is represented by an equation such as

$$\gamma = K\tau^\alpha \quad (16)$$

The stored elastic energy, under the hypothesis of constant viscosities, will then be given by:

$$W' = (\alpha/\alpha + 1)K\tau_0^{(\alpha+1)} = (\alpha/\alpha + 1)\dot{\gamma}_0 A \quad (17)$$

where τ_0 is the maximum stress (thus the initial stress in the relaxation phenomena).

The quantity defined by eq. (15) becomes:

$$J_w' = 2W'/\tau_0^2 = (2\alpha/\alpha + 1)K\tau_0^{(\alpha-1)}$$

Hence the slope of the log-log plot of J_w against τ_0 (which was actually found to be in most instances a straight line) will give the value of the exponent α , and a *power correction factor*

$$\xi = 2\alpha/\alpha + 1 \quad (18)$$

can be determined from such plots.

We can calculate the "corrected" values of the J_w , namely:

$$J_w' = (2\alpha/\alpha + 1)(\dot{\gamma}_0 A/\tau_0^2) = \xi J_w$$

Such "corrected" values, too, cannot be assumed to be the true values of the stored elastic energy. Nevertheless, the parameters α or ξ will be assumed to characterize the degree of linearity of the elastic components in a molten polymer. The elasticity is linear when $\alpha = 1$ or $\xi = 1$. We also can define a *nonlinearity exponent* of elasticity, $(1 - \alpha)$, which is zero for linear polymers and is measured by the slope of the log-log plot of J_w versus τ_0 .

The analytical procedure outlined above has been applied to many different polymers, mostly of the olefinic and diolefinic type. It was found that the consideration of the J_w , λ_w , and α has proved to be useful in the polymer characterization. The results concerning some samples of high- and low-pressure polyethylenes and of natural rubber are given in Table I.

EXPERIMENTAL

The measurements were made with a Kepes viscosimeter of the cone-plate type, at shear rates ranging from 5×10^{-4} up to 3 sec.^{-1} , at 160, 180, and 200°C. The samples were whole polymers such as the following:

High-pressure polyethylene (HPP) having a melt index of 2 and an intrinsic viscosity (measured in xylene at 75°C.) of 1.05 dl./g.; the inhomogeneity ratio (M_w/M_n) has been evaluated, by fractionation, as 3.3.

A low-pressure polyethylene (LPP I) of intrinsic viscosity (in tetraline at 135°C.) 1.30 dl./g.

Another low-pressure polyethylene (LPP II)

TABLE I

Samples	Intrinsic viscosities, dl./g.	Melt viscosities ^a , $\times 10^{-3}$, poise	$J_w^b 10^4$, cm. ² /dynes	λ_w^b , sec.	Nonlinear exponent of elasticity, ^c $(1 - \alpha)$	Pseudo-plasticity exponent ^c n
High-pressure polyethylene (HPP)	1.05	200	5.4	42	+0.60	0.40
Low-pressure polyethylene, sample I (LPP I)	1.30	100	0.6	2	+0.50	0.40
Low-pressure polyethylene, sample II (LPP II)	1.70	800	3.5	80	+0.05	0.50
Natural rubber (NR)	1.80	800	27	370	-0.50	0.60

^a The melt viscosities are measured at 180°C., under a constant rate of shear of 0.01 sec.⁻¹.

^b The values of J_w and λ_w are those obtained at 180°C. and for an initial steady-state stress of 5×10^4 dynes/cm.².

^c The values of $(1 - \alpha)$ and n are those observed at 180°C.

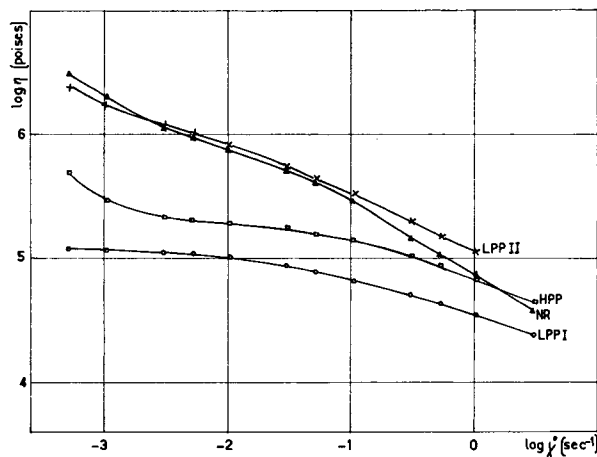


Fig. 1. Flow curves at 180°C.

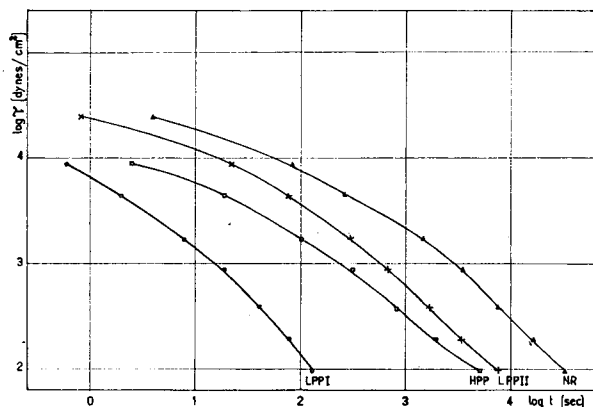


Fig. 2. Relaxation times at 180°C.

having an intrinsic viscosity (in tetraline at 135°C.) of 1.70 dl./g.

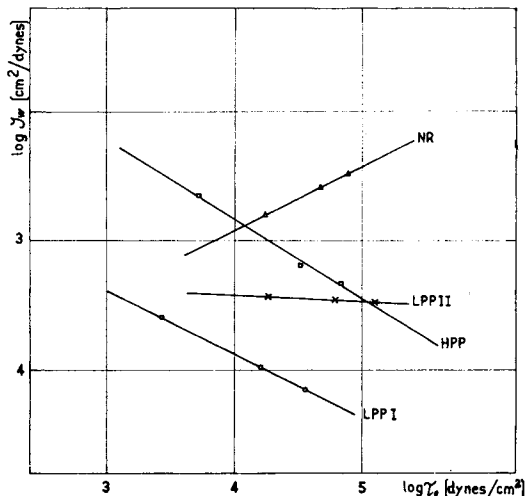
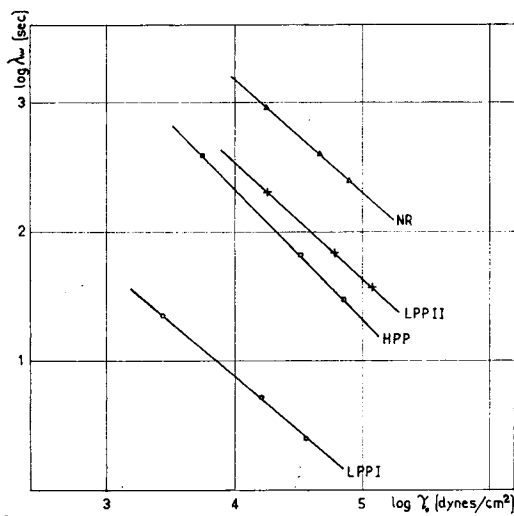
A specimen of natural rubber (NR) (unvulcanized) having an intrinsic viscosity (in toluene at 25°C.) of 3.27 dl./g.

In the case of the natural rubber, for a good reproducibility of the experimental results, it was found that the specimen had to be kept under vacuum at 120°C. for 24 hr. After this time the intrinsic viscosity dropped to only 1.80 dl./g. Since this decrease of intrinsic viscosity was not accompanied by a decrease in melt viscosity, the specimen apparently had undergone a slight cross-linking.

The flow curves of the specimens at 180°C. are given in Figure 1.

Stress relaxation measurements have been made, starting from different values of the steady-state stresses. Some examples are given in Figure 2, of the measured relaxation times (at 180°C.).

The relaxation areas were calculated, and the

Fig. 3. Parameters J_w at 180°C.Fig. 4. Parameters λ_w at 180°C.

J_w and λ_w parameters at 180°C. were obtained; they are plotted in Figures 3 and 4.

From the data in Table I it can be shown that the elastic components in the molten HPP are much larger than those of LPP I since, by melt viscosities of the same order of magnitude the J_w of the former is about 10 times larger than that of the latter. The difference of the characteristic times λ_w is larger; namely, by equal values of the steady-flow stress, the elastic energy stored within HPP appears to be about 20 times larger than within LPP I. Similarly, although the melt viscosities are nearly equal, the natural rubber shows J_w and λ_w much larger than LPP II. However, there is a qualitative difference; namely, the natural rubber has a negative value of the elastic nonlinearity exponent.

The greater elasticity of the HPP is probably related to long branching, a characteristic feature of this polymer (the branching parameter, according to Beasley, has been evaluated as 0.28 in the case of sample HPP).

It will be investigated in subsequent work whether the greater elasticity of the rubber and its negative elastic nonlinearity exponent can be interpreted as a consequence of the crosslinkages.

Thus it appears that this kind of evaluation of the stress relaxation phenomena, based on the consideration of the stress relaxation areas, can give some information of the structural properties of polymers.

References

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Synopsis

When a steady viscous flow of a molten polymer is suddenly stopped, the stress τ can be recorded as a function of the time t . By means of inverse Laplace transforms, a system of linear Maxwell bodies relaxing in the same way can be defined. It is shown that the elastic energy W_M stored within this system is equal to $\dot{\gamma}_0 A/2$, where $\dot{\gamma}_0$ is the rate of shear of the steady flow and where

$$A = \int_0^{\infty} \tau dt$$

is the "stress relaxation area." Thus, for a calculation of W_M the inverse Laplace transforms are not needed. Then, the following parameters are defined: (1) the shear compliance J_w , (2) the relaxation time λ_w of a single Maxwell body storing the same energy W_M under the same steady viscous flow (λ_w is also equal to the double of the ratio of W_M to the power dissipated in the steady flow), and (3) a "nonlinearity exponent of elasticity" given by the slope of the log-log plots of the J_w against the initial stresses. Stress relaxations in low- and high-pressure polyethylenes and natural rubber have been measured by means of a cone-plate consistometer. The above-defined parameters are calculated and discussed as possible means of characterizing the polymer structure.

Résumé

La tension de relaxation τ qui se manifeste lorsque l'écoulement continu visqueux d'un polymère fondu est soudainement arrêté peut être enregistrée en fonction du temps t . Par des transformations inverses de Laplace on peut définir

un système de corps linéaires de Maxwell à relaxation similaire. On démontre que l'énergie élastique W_M accumulée dans ce système est égale à $\dot{\gamma}_0 A/2$, où $\dot{\gamma}_0$ est le gradient de la vitesse de déformation (dans l'écoulement continu) et

$$A = \int_0^{\infty} \tau dt$$

est "l'aire de relaxation." On voit que pour calculer W_M il n'est pas nécessaire de recourir aux transformations inverses de Laplace. On peut définir de cette façon les paramètres suivants: (1) le module de déformation J_w ; (2) la constante de temps λ_w d'un seul corps de Maxwell qui peut accumuler la même énergie W_M suite au même écoulement visqueux; ce λ_w est égal à deux fois le rapport entre W_M et la puissance dissipée au cours de cet écoulement; (3) un "exposant de non-linéarité de l'élasticité" donné par la pente du diagramme de $\log J_w$ en fonction du \log de la tension initiale. On a mesuré des tensions de relaxation (avec un consistomètre cône-plan) pour des polyéthylènes à basse et à haute pression et pour du caoutchouc naturel. Les paramètres définis ici ont été calculés, et on discute leur utilisation pour la caractérisation de la structure des polymères.

Zusammenfassung

Wenn das stationäre, viskose Fließen eines geschmolzenen Polymeren plötzlich unterbrochen wird, können die entstehenden Relaxationsspannungen als Zeitfunktionen = $f(t)$ dargestellt werden. Mittels reziproker Laplace-Transformationen, kann ein System linearer Maxwell-Körper angegeben werden, deren Relaxationsspannungen denselben zeitlichen Verlauf aufweisen. Es wird gezeigt, dass die in diesem System gespeicherte elastische Energie W_M gleich $\dot{\gamma}_0 A/2$ ist, wo $\dot{\gamma}_0$ der Geschwindigkeitsgradient der Dehnung durch viskoses Fließen und

$$A = \int_0^{\infty} \tau dt$$

die "Relaxationsfläche" ist. Es kann also W_M ohne Laplace-Transformationen berechnet werden. Die folgenden Parameter können definiert werden: (1) der Nachgiebigkeitsmodul J_w , (2) die Relaxationszeit λ_w eines einzelnen Maxwell Körpers, in welchem dieselbe elastische Energie W_M infolge des gleichen stationären viskosen Fließens gespeichert wird; weiter ist λ_w gleich dem Verhältnis von W_M zu der in der Zeiteinheit durch das viskose Fließen verbrauchten Energie, und (3) ein "Exponent der Nicht-Linearität der Elastizität," der durch die Neigung der doppeltlogarithmischen Auftragung von J_w gegen die anfängliche Spannung bestimmt ist. Die Relaxationsspannung von Hoch- und Niederdruckpolyäthylenen sowie von natürlichem Kautschuk wurde mittels eines Kegel-Platte-Konsistometers gemessen. Die Anwendung der hier definierten, berechneten Parameter zur Charakterisierung der Polymeren wird besprochen.

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