

Stress Relaxation in Molten Polymers. III

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1. The Parabolic Elasticity

From the consideration of the features of a large number of stress relaxation curves (relaxing stresses as functions of the time), observed with a Kepes consistometer when the viscous steady flow of a molten polymer was suddenly stopped, it was deduced^{1,2} that, by assuming nonlinear (i.e., non-Hookean) elasticity, analytical stress-time relations are found which are in a good agreement with the experimental ones.

In particular, the following stress-strain differential law was suggested (the law of the parabolic elasticity):

$$d\gamma/d\mathfrak{T} = \gamma_k \mathfrak{T}^{\alpha-1} / (\mathfrak{T} + \mathfrak{T}_k)^\alpha \quad (1)$$

where \mathfrak{T} is the relaxing shear stress, γ is the shear strain associated with the relaxation phenomenon (not to be confused with the measurable strain of the viscous flow), while \mathfrak{T}_k , γ_k , and α are constants characterizing the given real polymer at a given temperature.

It will be shown now that the elastic law (1), instead of being assumed, can be deduced from another general feature characterizing a large number of the experimental stress-time relationships. This feature consists in the following fact: a wide portion of the log-log plots of the stresses against the time is fairly linear, except at the shortest and at the longest times. Thus, the following stress-time equation can be assumed as valid in a broad field of stress and time:

$$\mathfrak{T} = K(t + t_0)^{-n} - \mathfrak{T}_0 \quad (2)$$

where t is the time (starting from the moment when the steady flow is stopped and the relaxation begins); deviations from the linearity of the log-log plots at the shortest times are accounted for by the constant t_0 (which depends, thus, on the initial stress \mathfrak{T}_{ss} , which is also the steady flow stress); similar deviations at the longest times are taken into account (also approximately) by the constant stress \mathfrak{T}_0 , which characterizes the given polymer at the given temperature, as well as the constants K and n , being independent of \mathfrak{T}_{ss} . The phenomenon, already pointed out in former work,^{1,2} called relaxation isochronism provides K , n , \mathfrak{T}_0 to be independent (at least in a first approximation) of the particular initial stress characterizing any single experiment.

From eq. (2) it is deduced that

$$t + t_0 = [K/(\mathfrak{T} + \mathfrak{T}_0)]^{1/n} \quad (3)$$

and

$$\begin{aligned} d\mathfrak{T}/dt &= -n(\mathfrak{T} + \mathfrak{T}_0)/(t + t_0) \\ &= -(n/k^{1/n})(\mathfrak{T} + \mathfrak{T}_0)^{1+(1/n)} \end{aligned} \quad (4)$$

On the other side, let us consider the general differential equation for stress relaxation:

$$\begin{aligned} \mathfrak{T} &= -\eta(d\gamma/dt) \\ &= -\eta(d\gamma/d\mathfrak{T})(d\mathfrak{T}/dt) \end{aligned} \quad (5)$$

where η is a viscosity coefficient (not to be *a priori* identified with any of the viscosities measured in the steady flow) withstanding the variations with the time of the ideal, nonmeasurable strain γ associated, in this theory, with the relaxation phenomenon. As in former work,^{1,2} η will be assumed to be constant, namely, stress- and time-independent. Considerations on this questionable working hypothesis were already made previously^{1,2} and will be subsequently developed in this paper.

By combining eqs. (4) and (5) we obtain:

$$d\gamma/d\mathfrak{T} = (K^{1/n}/\eta n)[\mathfrak{T}/(\mathfrak{T} + \mathfrak{T}_0)](\mathfrak{T} + \mathfrak{T}_0)^{-1/n} \quad (6)$$

The matching of eq. (2) with the experimental plots of the relaxation stresses against the time shows that the greatest values of the parameters \mathfrak{T}_0 (when they can be determined) are of the order of magnitude of $10\text{--}10^2$ dynes/cm.², namely, the \mathfrak{T}_0 are small, when compared with the \mathfrak{T}_{ss} ($10^4\text{--}10^5$ dynes/cm.²) and with a broad field of the measured stresses \mathfrak{T} . Thus, in a wide part of the relaxation curve (except at the longest times, when \mathfrak{T} becomes of the same order of magnitude as \mathfrak{T}_0) we can assume:

$$\mathfrak{T}/(\mathfrak{T} + \mathfrak{T}_0) \simeq 1$$

Then eq. (6) becomes equivalent to the elastic law (for parabolic elasticity) expressed by eq. (1), provided that:

$$\alpha = 1/n \quad (7)$$

$$\mathfrak{T}_k = \mathfrak{T}_0 \quad (8)$$

$$\gamma_k \mathfrak{T}_k^{\alpha-1} = K^{1/n}/n\eta \quad (9)$$

By defining a characteristic compliance J_k :

$$J_k = \gamma_k/\mathfrak{T}_k \quad (10)$$

and a characteristic relaxation time τ_k :

$$\tau_k = \eta J_k \quad (11)$$

from eqs. (7), (8), and (9) it follows that

$$\tau_k = (1/n)(K/\mathfrak{T}_0)^{1/n} \quad (12)$$

It must be remembered that eqs. (8) and (12) are valid as far as the stress-time law (2) is in agreement with the experimental stress relaxation data. Only the matching of eq. (2) with such data permits a choice between an elastic law of the type described by eq. (1) or one of the type described by eq. (6) (or possibly some other). In the (isochronic) linear region of \mathfrak{T} versus $\log t$ (namely, when $t \gg t_0$ and $\mathfrak{T} \gg \mathfrak{T}_0$), such a choice is not possible (at least within the limits of accuracy of the experimental data which are now at hand). Such accuracy, in many practical cases, is not sufficient to allow a sure determination of the parameter \mathfrak{T}_0 itself, hence of the related critical time defined by eq. (12), or of the ultimate time t_u :

$$t_u = (K/\mathfrak{T}_0)^{1/n} \quad (13)$$

namely, the time at which, according to eq. (2), the relaxing stress becomes zero.

It is seen, thus, that an elastic law of the type (1), or of an analytical type which, within a given range of the values of the data, cannot be distinguished from the parabolic type of eq. (1), is a consequence of the experimental feature that in many instances the log-log plots of the stresses against the time are linear.

2. A General Theory

All calculations suggested here and in the preceding papers of this series^{1,2} have the following drawbacks.

They are bound with some models, allowing the formulation of a stress-time equation

$$\mathfrak{T} = f(t)$$

defined for all values of the time t from zero up to infinity. This is a rather arbitrary extrapolation of the experimental data, ranging actually between some tenths of a second up to some hours. The upper limits of the time are determined by the stability of the measured substance more than by the patience of the observer. The investigation of a good number of real specimens showed that the ignorance of the actual course of the stress relaxation at very short (as at very long) times makes it impossible to state whether or not the relaxation area has an asymptotic value for indefinitely increasing initial stresses \mathfrak{T}_{ss} . Any conclusion arising from a particular type of stress-time equation appears, then, somewhat arbitrary.

The rather puzzling hypothesis, stressed before, of a constant viscosity is not essential. As far as only stress-time relationships (and related quantities, such as the relaxation areas A) are concerned, namely, when we are investigating quantities which are not defined by a separate consideration of the elastic and of the viscous components of the stress relaxation phenomenon, all calculations can be carried out considering, instead of an elastic law $d\gamma/d\mathfrak{T}$ and of a viscosity η separately, a particular law concerning the product

$$R(\mathfrak{T}, t) = \eta d\gamma/d\mathfrak{T} \quad (14)$$

where both factors η and $d\gamma/d\mathfrak{T}$ can be thought as functions of the stress (and, possibly, of a separate time variable).

In order to avoid as far as possible any arbitrary assumption or extrapolation and any consideration of models, it is shown that a general theory of stress relaxation can be deduced only by assuming the validity of eq. (5) in its more general meaning.

This meaning is the following: the relaxing stress \mathfrak{T} is withstood only by another stress of a viscous type, namely, a stress given by the product of a viscosity function $\eta(\mathfrak{T}, t)$ by the rate of a hypothetical, nonmeasurable internal shear. This rate of shear, in its turn, is assumed to be the product of an elasticity function $d\gamma/d\mathfrak{T}$ (a function, too, of the stress and the time) by the total derivative of the stress against the time, namely:

$$d\gamma/dt = (d\gamma/d\mathfrak{T}) \cdot (d\mathfrak{T}/dt)$$

The variables \mathfrak{T} and t are related to each other by the stress-time relationship, but in general we can suppose that the elasticity and the viscosity functions are time-dependent also in some other independent way.

When both sides of eq. (5) are multiplied by t and divided by \mathfrak{T} , we obtain after some rearrangement:

$$n(\mathfrak{T}, t) = -d(\log \mathfrak{T})/d(\log t) = t/R \quad (15)$$

Hence, the viscoelasticity function defined by eq. (14) will be:

$$R(\mathfrak{T}, t) = t/n(\mathfrak{T}, t) \quad (16)$$

The function R has the dimensions of time; the function n (a number), defined by eq. (15), can be quite easily derived by graphic differentiation of the experimental log-log plots of stress against time, and both R and n can be, in their turn, plotted against the time or the stress.

It is immediately seen that, in the case of a simple Maxwell body (or Voigt body), the R function degenerates in a constant: the classical relaxation time of the body considered.

Let us consider now a plot of the stress \mathfrak{T} against R . The feature of the relaxation isochronism provides such plot to be a general function characterizing the given polymer at the given temperature, defined in the whole isochronic region and independent of the initial stress (except at the shortest times, namely at the highest stresses).

It is suggested now that this plot be taken as a characterizing element for the given real system. A number of experimental instances of this means of polymer characterization will be given subsequently.

The following formulas can be easily derived and proved to be useful:

$$d\mathfrak{T}/dt = -\mathfrak{T}/R \quad (17)$$

$$A = \int_0^{\gamma^{\max}} \mathfrak{T} dt = \int_0^{\mathfrak{T}^{\max}} R d\mathfrak{T} \quad (18)$$

$$d\gamma = (t/n\eta) d\mathfrak{T} \quad (19)$$

$$W = \int_0^{\gamma^{\max}} \mathfrak{T} d\gamma = \int_0^{\mathfrak{T}^{\max}} R \cdot (\mathfrak{T}/\eta) \cdot d\mathfrak{T} \quad (20)$$

While the quantities defined by eqs. (17) and (18) can be calculated from the relaxation data, those defined by eqs. (19) and (20), based on a separation of the elastic components from the viscosity components, require an independent knowledge of the elasticity law or of the viscosity law. This is a general confirmation of the statement already made² that the relaxation phenomena alone, as far as they are dealt with only on the basis of eq. (5), are not sufficient to allow a calculation of the stored elastic energy W , namely, that different values of this energy can be associated with a given course of the relaxing stress as a function of the time.

The analytical procedures suggested here shall be matched, in subsequent work in this series, with the experimental data of a number of practical instances, in order to evaluate their effectiveness as a means of polymer characterization.

References

1. Mussa, C., and V. Tablino, *J. Appl. Polymer Sci.*, **6**, S21 (1962).
2. Mussa, C., and V. Tablino, *J. Appl. Polymer Sci.*, **7**, 1391 (1963).

Synopsis

The parabolic law, according to the equation $d\gamma/d\mathfrak{C} = \gamma_k \mathfrak{C}^{\alpha-1}/(\mathfrak{C} + \mathfrak{C}_k)^\alpha$, of the elasticity in the relaxation phenomena of molten polymers can be deduced from the consideration of the feature that the experimental stress relaxation curves show log-log plots which are often linear in a broad field. A general analysis, only on the basis of the viscoelastic equation $\mathfrak{C} = -\eta(d\gamma/dt)$ permits calculation of relaxation functions, which are suggested as possible means of polymer characterization.

Résumé

La loi parabolique, selon la formule $d\gamma/d\mathfrak{C} = \gamma_k \mathfrak{C}^{\alpha-1}/(\mathfrak{C} + \mathfrak{C}_k)^\alpha$, pour l'élasticité associée aux phénomènes de relaxation dans les polymères fondus peut être déduite à partir de la caractéristique expérimentale suivante: les diagrammes doublement logarithmiques des courbes de relaxation expérimentales sont souvent linéaires dans un domaine étendu. Une analyse en termes généraux fondée uniquement sur la hypothèse de la validité de la formule viscoélastique, $\mathfrak{C} = -\eta(d\gamma/dt)$ permet d'établir des fonctions de relaxation qui peuvent servir à caractériser les polymères.

Zusammenfassung

Das parabolische Elastizitätsgesetz-Formel $d\gamma/d\mathfrak{C} = \gamma_k \mathfrak{C}^{\alpha-1}/(\mathfrak{C} + \mathfrak{C}_k)^\alpha$, bei den Relaxationserscheinungen geschmolzener Polymerer kann aus dem experimentellen Befund abgeleitet werden, dass die Spannungsrelaxationskurven im doppellogarithmischen Diagramm oft über einen grossen Bereich linear verlaufen. Eine allgemeine, nur auf der Viskoelastizitätsgleichung $\mathfrak{C} = -\eta(d\gamma/dt)$ beruhende Analyse ermöglicht die Formulierung von Relaxationsfunktionen, die zur Charakterisierung von Polymeren dienen können.

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