

## Stress Relaxation in Molten Polymers. II

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In previous work<sup>1</sup> there has been suggested an evaluation of the elastic energy stored within a molten polymer in a viscous steady flow. Such evaluation was based on the consideration of the energy  $W_M$  defined by:

$$W_M = (1/2)\dot{\gamma}_{ss} \int_0^{\infty} \mathfrak{C} dt = (1/2)\dot{\gamma}_{ss} A$$

where  $\dot{\gamma}_{ss}$  is the rate of shear during viscous steady flow and  $\mathfrak{C}$  is the shear stress during relaxation; the integral  $A$  is extended throughout the whole relaxation time. Attention has been drawn to this integral, which was termed the relaxation area. It was shown that  $W_M$  is the elastic energy stored within an "equivalent" system of Maxwell bodies coupled in parallel and defined by the following conditions: (a) it relaxes in the same way as the real polymer; (b) it exhibits the same viscosity under the same steady flow conditions.

Although this method was found to be practically useful in comparative investigations on elastic effects arising when molten polymers are processed, it will be shown now that a different evaluation of such effects can be suggested, which yields a closer agreement with the experimental features of stress relaxation phenomena.

The criteria on which the method of evaluation suggested here is based are the following.

(1) The stress relaxation after cessation of viscous steady flow of a molten polymer is considered quite apart from the steady flow itself, because the wriggling macromolecular motions occurring within the polymer melt during stress relaxation are different from the macroscopic and measurable motions of the polymer in the bulk during the steady flow.

Analytically, in stress relaxation, the "nonmeasurable" shear strains  $\gamma$  (and their rates  $\dot{\gamma}$ ) are different from those appearing in the steady flow formulas; also the viscosities governing the two phenomena cannot be identified *a priori*.

(2) The shapes and the features which were found experimentally to characterize the stress relaxation curves (the stress-time relations) observed in a large number of instances are assumed as a basis for the analytical characterization.

(3) The relaxation phenomena alone are not sufficient to permit an absolute evaluation of the energies concerned; it is clear that the same

relaxation curve is shown by systems of widely different overall dimensions: for instance, the same relaxation curve can be given by a system of strong springs and high viscosity dashpots or by weak springs and low viscosity dashpots; it is evident that the energies are different in the two cases.

### Features of the Relaxation Curves

The most typical feature has been called in a former work<sup>2</sup> "relaxation isochronism." It consists in the following: the stress, when the relaxation begins, falls rapidly from the initial value  $\mathcal{T}_{ss}$  (the steady flow stress) to lower ones, then it continues to decrease with a stress-time law which is practically independent of the initial value  $\mathcal{T}_{ss}$  of the stress when the latter is higher than a given limit.

Much more, it was already pointed out by Kepes<sup>3</sup> that there is a definite trend towards an inversion of the expected stress-time dependence, namely, at a given low value of the relaxation stress, the corresponding time for a relaxation curve starting from a given high initial stress is somewhat smaller than the time given by a relaxation curve starting from a lower initial stress. In other words, the relaxation curves corresponding to different initial stresses intersect each other (see Fig. 1). We share the opinion of Kepes<sup>3</sup> that such inversion of the run is but a second-order effect, bound with (possibly nonreversible) transformations of the polymeric melt brought about by the highest shear stresses, and occurring during the flow

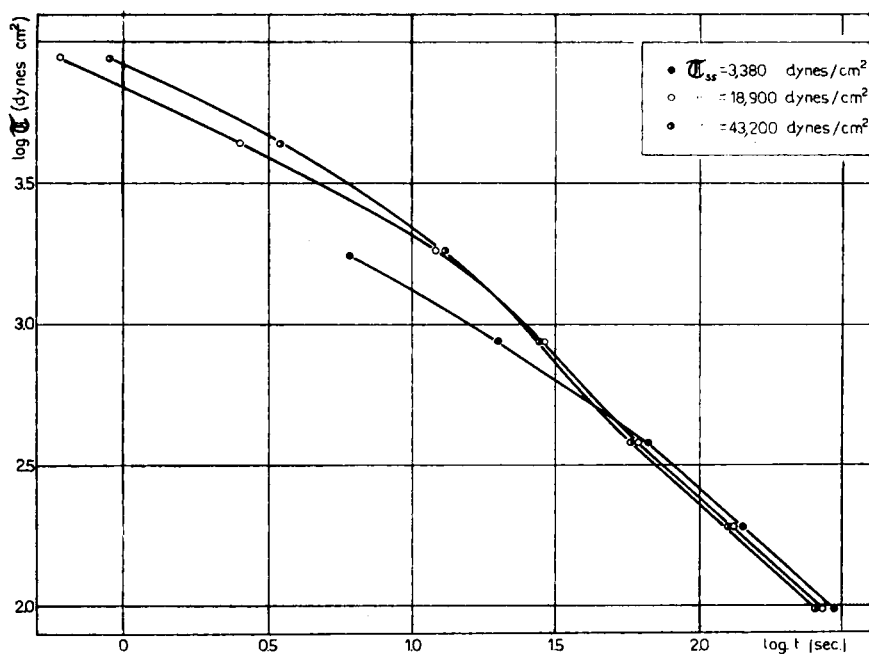


Fig. 1. Log-log plot of relaxation curves for sample LPP I at 200°C. by different initial stresses,  $\mathcal{T}$ .

as well as during long-term relaxation (times as long as some hours have been recorded). Therefore, in the following this inversion will be neglected as a secondary perturbing and poorly reproducible effect.

The much better defined effect called relaxation isochronism will be considered here as fundamental, in order to state an analysis of the stress relaxation of molten polymers. From a quantitative point of view, it has been found that, within the limits of accuracy of the present calculation, the new relaxation parameters which will be defined by this analysis are practically unaffected when a single mean isochronic relaxation curve is assumed instead of the slightly different experimental ones.

Another feature is to be pointed out: the time lag between two relaxation curves beginning from different  $\mathfrak{C}_0$ s in most cases was found to be of the same order of magnitude at widely different relaxation stresses. Within the accuracy limits into which the relaxation isochronism is valid, such time lag can be considered as constant. Then, the relaxation isochronism itself appears no more as an absolute feature: two stress-time curves appear as isochronic when the time lag existing between them (which is relevant only at the highest stress values) becomes small when compared with the total relaxation time. As will be seen later, the isochronism, the constancy of the time lag between different relaxation curves and, therefore, the very parameters defined on this basis will appear as limiting features which are the more valid, the higher are the initial stresses.

In Figure 1 are shown some typical stress-time curves (in a log-log plot, in order to cover the broad field of times and stresses). The isochronic region is evident, as well as the inversion phenomenon.

The relaxation isochronism is clearly related to the non-Hookean character of the elasticity which is effective in such phenomena.

The classical analytical proceedings of rheology involve the assumption of linear (Hookean) elasticity; such assumption can be made as far as small strains and comparatively low stresses are considered. Actually, the strains involved after cessation of an indefinite steady flow are the highest possible, hence they cannot be assumed to be small.

As it was pointed out by Claesson,<sup>4</sup> the existence of a relaxation isochronism can be dealt with as a lack of "memory" of the viscoelastic elements taking part, firstly, to the steady flow, then, to the stress relaxation. In fact, the initial value of the stress existing in the molten mass during the steady flow is no longer wholly "remembered" when it has been higher than a given limit.

We will now try to define some nonlinear stress-strain laws which can provide isochronic or quasi-isochronic relaxation curves possibly closer to the experimental ones.

### Stress-Strain Laws of Nonlinear Elements

When  $\gamma$  are the shear strains and  $\mathfrak{C}$  are the shear stresses, it is assumed that the stress-strain curves of the elastic elements in the polymer melt

must conform to the general condition that the derivative  $d\gamma/d\mathfrak{C}$  is a decreasing function of the stress.

We will consider now two particular types of such functions.

The first type is defined by the general formula:

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

where  $\gamma_k$  and  $\mathfrak{C}_k$  are characteristic strains and stresses defining, together with the exponent  $\alpha$ , a particular kind of nonlinear elasticity.

The resulting strain is:

$$\gamma = [\gamma_k / (1 - \alpha)] \{ [(\mathfrak{C} / \mathfrak{C}_k) + 1]^{1-\alpha} - 1 \} \quad (2)$$

For  $\alpha = 1$  this is:

$$\gamma = \gamma_k \ln[(\mathfrak{C} + \mathfrak{C}_k) / \mathfrak{C}_k] \quad (3)$$

and, for  $\alpha > 1$ ,  $\gamma$  tends towards an asymptotic value

$$\gamma_\infty = \gamma_k / (\alpha - 1) \quad (4)$$

It is convenient to define a characteristic compliance  $J_k$ :

$$J_k = \gamma_k / \mathfrak{C}_k = \lim_{\mathfrak{C} \rightarrow 0} (d\gamma/d\mathfrak{C}) \quad (5)$$

Nonlinear elements of this type are defined by the three parameters  $\gamma_k$ ,  $\mathfrak{C}_k$ ,  $\alpha$ . This will be called here the "parabolic" type. We can also take into account a less general type, characterized by a faster trend towards an asymptotic value  $\gamma_k$  of the strain. It is defined by the equation:

$$d\gamma/d\mathfrak{C} = (\gamma_k - \gamma) / \mathfrak{C}_k \quad (6)$$

The corresponding stress-strain curve is:

$$\gamma = \gamma_k [1 - \exp \{ -\mathfrak{C} / \mathfrak{C}_k \}] \quad (7)$$

Such an element, which is defined only by two parameters ( $\gamma_k, \mathfrak{C}_k$ ) is termed here an element of the exponential type.

We will come back now to the examination of the experimental data, in order to state some general rules allowing a choice of the elastic nonlinear elements and of their grouping.

### Grouping of Nonlinear Elements

In classical rheological investigations of noncrosslinked polymers, a system of elementary Maxwell bodies grouped in parallel is adopted; this procedure gives rise to a rather arbitrary partition of the stress among the elementary bodies; this partition contradicts the physical intuition, suggesting a unique stress spread throughout the whole molten polymer. On the other hand, a system of linear Maxwell bodies coupled in series is equivalent to a single element, while a system of nonlinear bodies coupled in series has no simple single equivalent.

The general differential equation of the free relaxation is assumed to be the following:

$$\mathfrak{T} = -\eta d\gamma/dt \quad (8)$$

We will consider now a system of  $i$  elastic elements (linear and nonlinear) coupled in series with each other and with a single dashpot having an equivalent viscosity  $\eta_e$ . For such a system, eq. (8) becomes:

$$\mathfrak{T} = -\eta_e \sum_i d\gamma_i/dt \quad (9)$$

The same equation holds also for a system of  $i$  elastic elements coupled in series, with any one of which a different individual viscosity  $\eta_i$  is associated in such a way that the stress (which is equal for all elements), is related with the strain  $\gamma_i$  of any single  $i$ th element by the relationship:

$$\mathfrak{T} = -\eta_i d\gamma_i/dt$$

provided that it be:

$$1/\eta_e = \sum_i 1/\eta_i$$

Assuming that the viscosities, the stress-strain laws and their derivatives are time-independent (more exactly, that they do not have the time as an independent variable) by defining:

$$F_i(\mathfrak{T}) = \int \eta_e (d\gamma_i/d\mathfrak{T}) (d\mathfrak{T}/\mathfrak{T}) \quad (10)$$

and by integration of eq. (9) under the condition that  $\mathfrak{T}$  is equal to  $\mathfrak{T}_{ss}$  for  $t = 0$  we obtain eq. (11):

$$t = \sum_i [F_i(\mathfrak{T}_{ss}) - F_i(\mathfrak{T})] \quad (11)$$

Let us consider, now, two different relaxation curves starting from two different initial values of the stress:  $\mathfrak{T}'_{ss}$  and  $\mathfrak{T}''_{ss}$ . At any given value  $\mathfrak{T}$  of the relaxing stress the corresponding times  $t'$  and  $t''$  must be related by eq. (12), easily derived from eq. (11):

$$\Delta t = t' - t'' = \sum_i [F_i(\mathfrak{T}'_{ss}) - F_i(\mathfrak{T}''_{ss})] \quad (12)$$

This formula means that, in the case of elastic elements coupled in series, when the associated viscosities and the stress-strain laws are time-independent, the relaxation curves corresponding to different initial stresses are obtained from each other simply by shifting one of them by a time lag  $\Delta t$  which, according to eq. (12), is a function of the initial stresses alone.

As said before, if we suppose the present analysis to be valid as a limit for increasing initial stresses, the experimental relaxation curves do follow, at least in a semiquantitative way, the condition stated here, when the limits of reproducibility of the data and the experimental and calculative accuracy are taken into account.

As a consequence of these considerations, we have chosen a system of elastic elements coupled in series. One of such elements can be linear, while the others must be nonlinear.

The type of nonlinearity will be selected according to the following considerations:

By constant (namely, stress-independent) viscosities, the relaxation area is given by the general formula:

$$A = \int_0^{\infty} \mathcal{T} dt = \eta_0 \sum_i \gamma_{ss_i} \quad (13)$$

where  $\gamma_{ss_i}$  are the maximum strains (corresponding to the initial stress reached during the steady flow).

Thus, eq. (13) means that when the relaxation areas for increasing values of the initial stress and for constant  $\eta_0$ , tend to a finite limit, the strains, too, must tend to a finite limit, namely we must choose an asymptotic stress-strain law, such as the one of the parabolic type with  $\alpha > 1$  or the exponential one of eq. (7).

It was found in our experiments that the relaxation areas show a trend towards an asymptotic behavior when they are plotted as a function of the initial stresses. We cannot exclude, nevertheless, the existence of a comparatively little relevant increase of the relaxation area with rising initial stress. Such an increase corresponds to an apparently linear elastic component associated with the lowest values of the relaxation times (some fractions of a second), hence with the lowest values of the compliance: apparently, the compliance of the wholly stretched polymer chains.

We have preferred to adopt the exponential type of nonlinear elastic behavior, because (a) the analytical proceedings are simpler, and it is always preferable to choose the system introducing the smallest number of parameters and (b) the exponential model corresponds more closely to the idea of elastic elements having a nearly constant elastic modulus up to a given limit of the strain, then, beyond this limit, behaving as practically inextensible.

### Analysis by Means of Exponential Bodies in Series

The integration of eq. (8) taking into account eqs. (5), (6), and (7) gives, in the case of a single nonlinear exponential element, and assuming a constant viscosity:

$$t = \tau_k [E_i(-\mathcal{T}/\mathcal{T}_k) - E_i - (\mathcal{T}_{ss}/\mathcal{T}_k)] \quad (14)$$

where  $\tau_k = \eta/J_k$  is a characteristic relaxation time,  $x = \mathcal{T}/\mathcal{T}_k$  is a reduced stress,

$$x_{ss} = \mathcal{T}_{ss}/\mathcal{T}_k \quad (15)$$

and  $E_i(x)$  is the exponential integral function.

Taking into account  $i$  elementary bodies grouped in series, eq. (16) is obtained:

$$t = \tau_H \ln (\mathfrak{C}_{ss}/\mathfrak{C}) + \sum_i \tau_i [E_i(-\mathfrak{C}/\mathfrak{C}_{ki}) - E_i(-\mathfrak{C}_{ss}/\mathfrak{C}_{ki})] \quad (16)$$

where

$$\tau_i = \eta_e \gamma_{ki} / \mathfrak{C}_{ki} = \eta_e J_{ki}$$

The term with  $\tau_H = \eta_e J_H$  is a possible contribution from a Hookean spring with the lowest compliance  $J_H$ ;  $\tau_i, \mathfrak{C}_{ki}/\gamma_{ki}$  are the unknown parameters of the non-Hookean elements. The parameters  $\tau_i$  and  $\mathfrak{C}_{ki}$  can be determined by matching eq. (16) with the experimental data following a procedure by trial and error (beginning from the lowest relaxation times).

A discrete relaxation spectrum ( $\tau_i, \mathfrak{C}_{ki}$ ) is obtained in this way. The matching of the formulas with the experimental data shows that a continuous spectrum, when it may be calculated, will probably provide a better fit.

A first rough analysis in discrete spectra of some experimental instances will be given now, in order to investigate the possible meanings of the analytical method outlined here.

### Experimental Examples

We consider here the same samples examined in the preceding work,<sup>1</sup> namely: (A) a low pressure polyethylene (LPP I) of intrinsic viscosity 1.30 dl./g. (measured in tetralin at 135°C.); (B) a low pressure polyethylene (LPP II) of intrinsic viscosity 1.70 dl./g. (in tetralin at 135°C.); (C) a high pressure polyethylene (HPP) having a melt index 2 and an intrinsic viscosity of 1.05 dl./g. (in xylene at 75°C.) for which the long-branching index (according to Beasley<sup>5</sup>) was evaluated<sup>6</sup> to be  $\beta = 0.34$ , corresponding to an heterogeneity ratio  $M_w/M_n = 3.3$ ; (D) a specimen of natural rubber (NR) (unvulcanized) having an intrinsic viscosity of 1.80 dl./g. (in toluene, 25°C.) after a heat treatment (24 hr. at 12°C.). As was pointed out by us,<sup>1</sup> such heat treatment was followed by slight crosslinking.

The results of our analysis are summarized in Table I. Samples LPP I and HPP are characterized by a  $\tau_H$  and by two nonlinear elements. In the case of sample LPP II, a third nonlinear element was found to be necessary, while for natural rubber (NR) the determination of the linear component ( $\tau_H$ ) was not possible, and two nonlinear elements were found to be sufficient.

The relaxation areas were calculated by means of eq. (17):

$$A = \tau_H \mathfrak{C}_{ss} + \sum_i \tau_i \mathfrak{C}_{ki} \quad (17)$$

and were compared with the ones calculated graphically from the experimental plot.

We have tried also to obtain an absolute evaluation of the stored elastic energy, by introducing a further working hypothesis, namely, that the

TABLE  
 Experimental Values of the

Sample	Temp., °C.	$\tau_H$ , sec.	$\tau_1$ , sec.	$\mathfrak{C}_{k_1}$ , dynes/ cm. <sup>2</sup>	$\tau_2$ , sec.	$\mathfrak{C}_{k_2}$ , dynes/ cm. <sup>2</sup>
Low pressure polyethylene, sample I (LPP I)	160	0.6	39	2,100	210	260
	180	0.5	25	2,050	105	200
	200	0.4	14	2,000	65	180
Low pressure polyethylene sample II (LPP II)	160	0.8	380	6,400	1,600	1,400
	180	0.6	230	6,200	920	1,300
	200	0.4	170	6,000	860	1,200
High pressure polyethylene (HPP)	160	0.8	350	5,800	8,000	200
	180	0.7	160	4,000	6,500	200
	200	0.6	110	2,500	5,500	200
Natural rubber (NR)	160	—	560	8,000	8,000	1,500
	180	—	550	7,000	5,500	1,500
	200	—	540	6,000	3,500	1,500

equivalent viscosity  $\eta_e$  is equal to the Newtonian viscosity  $\eta_N$  deduced from the flow curves of the samples at any given temperature.

The stored elastic energy, under this assumption, is expressed by eq. (18):

$$W_N = (1/\eta_N) [(1/2)\mathfrak{C}_{ss}^2 \tau_H + \sum_i \tau_i \mathfrak{C}_{k_i}^2] \quad (18)$$

The general formula giving the elastic energy stored within the assumed system is:

$$W = (1/\eta_e) [(\tau_H \mathfrak{C}_{ss}^2 / 2) + \sum_i \tau_i \mathfrak{C}_{k_i}^2] \quad (19)$$

It is seen that, in order to calculate  $W$ , it is necessary to know the viscosity  $\eta_e$  or the characteristic compliances  $J_H, J_i$ .

Such quantities cannot be deduced from the stress relaxation experiments alone.

In order to check how much the present analysis corresponds to the actual relaxation behavior of the real samples, the experimental relaxation curves are confronted with the ones which can be calculated on the basis of the data of Table I. In Table II this comparison is made in some instances. It is seen that the higher the initial stresses, the better is the agreement of the theoretical and the experimental data.



## I

## Stress Relaxation Parameters

$\tau_i$ , sec.	$\mathfrak{C}_{ki}$ , dynes/ cm. <sup>2</sup>	$A$ , poises $\times 10^{-5}$		$W_N$ , ergs/cm. <sup>3</sup>	$\eta_N$ , poises $\times 10^{-5}$	$A/\eta_N$
		Calc.	Meas.			
—	—	1.62	1.67	$2 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $1.24 \times 10^3$	1.5	1.08
		0.90	0.91	$2 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $0.91 \times 10^3$	1.2	0.75
—	—	0.52	0.53	$2 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $0.58 \times 10^3$	1	0.52
13,000	150	67.3	68.1	$0.25 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $12 \times 10^3$	16	4.2
12,000	150	45.1	45.4	$0.30 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $12 \times 10^3$	10	4.5
11,000	150	37.4	37.4	$0.32 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $12 \times 10^3$	6.5	5.5
—	—	37.3	38.2	$1 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $30 \times 10^3$	4	9.3
—	—	20	20.8	$1.7 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $14 \times 10^3$	2	10
—	—	14.1	14.8	$2.5 \times 10^{-6}\mathfrak{C}_{ss}^2 +$ $7.5 \times 10^3$	1.2	11.8
		165	164.5	$43 \times 10^3$	12.5	13.2
		121	120.1	$43 \times 10^3$	9	13.4
		85	86.1	$43 \times 10^3$	6.3	13.5

### Considerations about the Results of the Suggested Analysis

A comparative examination of the data of Table I allows the following remarks.

(1) The time constants (relaxation times) are all decreasing functions of the temperature. The relaxation times are the product of a viscosity by a compliance; thus the first factor (which, in its turn, is an exponential function of the reciprocal absolute temperature) is obviously overwhelming.

(2) The contribution of the linear element ( $\tau_H$ ) is always negligible; the relaxation phenomenon is ruled primarily by nonlinear elastic factors.

(3) The characteristic stresses  $\mathfrak{C}_{ki}$  are also nonincreasing functions of the temperature;  $\mathfrak{C}_{ki}$  is practically constant for linear chains, as those of the LPP's, while it varies more markedly for long-branched (HPP) and crosslinked (NR) samples; for elements of a higher order (corresponding to  $\tau_2$  and  $\tau_3$ ) the characteristic stresses do not change with the temperature; apparently, they are bound with a kind of elasticity which is more structural than entropic.

(4) For LPP II and HPP the products ( $\tau_i\mathfrak{C}_{ki}$ ) are nearly constants, for LPP I they decrease with increasing  $\tau_i$  while for NR they increase.

(5) The calculated and measured relaxation areas practically coincide; this is a result, not a fact. Such an agreement must be considered as a

TABLE II  
Stress Relaxation for Sample LPP I at 160°C.

Stress, dynes/cm. <sup>2</sup>	Time, sec.	
	Meas.	Calc.
43,200	0	0
8,700	0.9	0.9
4,390	3.5	3.2
1,730	13	13
870	28	28.5
384	60	72
192	130	130
96	266	265
18,900	0	0
8,700	0.6	0.58
4,390	2.5	2.52
1,730	12	12.7
870	29	29.8
384	61	74
192	132	150
96	271	260
3,380	0	0
1,730	6	8.6
870	20	25.6
384	66	70.3
192	142	146
96	291	255

necessary (not sufficient) condition in order to state whether the analysis in elementary components is correct.

(6) For initial stresses of a practical range, the most important contribution is represented by the constant term (the asymptotic energy). Two distinct types of behavior are shown; for shorter chains (LPP I and HPP) the asymptotic energy decreases with increasing temperature. Since the stored energy, in the linear approximation, is proportional to the reciprocal elastic modulus, this fact means, that for shorter chains the elasticity has a prevailing entropical character. For longer (LPP II) and crosslinked (NR) chains, it is noteworthy that the asymptotic energy is practically constant; this fact can be explained as a consequence of a prevailing positional character of this kind of elasticity.

(7) In the last column of Table II is reported the ratio between the relaxation area  $A$  (having the same dimensions as viscosity) and the corresponding Newtonian viscosity  $\eta_N$  of the polymer. It is suggested that this ratio be termed the *elasticity number*. This number is particularly interesting because (a) it gives a marked quantitative distinction of the degree of elasticity of the investigated polymers, in good agreement with their technological behavior and (b) because it results directly from objective and measurable data, with a minimum of analytical transformations.

For poorly elastic polymers (LPP I) the elasticity number is low and decreases with the temperature (as the asymptotic energy); for the other, more elastic polymers the much larger elasticity numbers are nondecreasing functions of the temperature, showing a trend toward constancy.

(8) The energy  $W_N$  and the elasticity number  $A/\eta_N$  are subjected to a drawback which limits their accuracy: the Newtonian viscosity  $\eta_N$  is not well defined by high melt viscosities. Highly viscous polymers at low rates of shear show a viscosity indefinitely increasing with decreasing  $\dot{\gamma}$ , namely they behave similarly to a Bingham body; in our opinion such behavior occurs when  $\dot{\gamma}$  is lower than the reciprocal time constant of the rebuilding of the pseudorecticular structure which is responsible for this behavior as well as of the existence of a yield point of polymer melts. As a consequence, sometimes (in our instances, see samples LPP II and NR) the flow curves do not show a well-defined Newtonian region, and the evaluation of the Newtonian viscosity will be somewhat arbitrary, as far as these phenomena are not better understood.

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### Synopsis

A new analytical method is suggested for the evaluation of the stress relaxation phenomena arising when a viscous flow of molten polymers is suddenly stopped. This method is based on the consideration of the relaxation isochronism and of other most typical features of the experimental stress-time relationships. Such features can be deduced by means of an analysis in elementary non-Hookean bodies in series having a stress-time law of a particular analytical type. Such an analysis is applied to four samples of high and low pressure polyethylenes and natural rubber. The new parameters defined in this way are discussed in order to state some correlations with the structural features. Attention is drawn on the importance of an elasticity number defined as the ratio of the relaxation area to the corresponding Newtonian viscosity.

### Résumé

Une nouvelle méthode analytique est suggérée pour évaluer les phénomènes de relaxation qui ont lieu lorsqu'un écoulement visqueux stationnaire est brusquement arrêté. La méthode est basée sur l'observation des caractéristiques plus typiques des relations expérimentales entre le temps et la tension de relaxation, comme l'isochronisme de relaxation. Ces caractéristiques peuvent être déduites par une analyse considérant des corps élastiques élémentaires non-Hookeens groupés en série, ayant une loi élastique d'un type analytique particulier. Cette analyse est appliquée à quatre échantillons de polyéthylène à haute et basse pression et au caoutchouc naturel. On montre un nombre élastique défini par le rapport de l'aire de relaxation à la viscosité Newtonienne correspondante.

### **Zusammenfassung**

Eine neue Methode zur Auswertung der Relaxationserscheinungen bei geschmolzenen Polymeren wird vorgeschlagen. Die Methode beruht auf der Betrachtung des Relaxations-Isochronismus, sowie anderer Eigenschaften der empirischen Zeit-Spannungs-Beziehungen. Solche Eigenschaften können aus einer Analyse elementarer nicht-linearer Körper abgeleitet werden, die durch ein Dehnungs-Spannungs-Gesetz eines besonderen analytischen Typus charakterisiert sind. Vier Proben von Hoch- und Niederdruckpolyäthylen und natürlichem Kautschuk werden in dieser Weise analysiert; die so erhaltenen Relaxationsparameter werden in ihren Beziehungen zu den Struktureigenschaften diskutiert. Die Elastizitätszahl, nämlich das Verhältnis der Relaxationsfläche zur Newton'schen Viskosität ist von besonderem Interesse.

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