UNIVERSAL RELAXATION CHARACTERISTIC OF POLYMER SYSTEMS

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On the basis of test data pertaining to continuous and cyclic deformation of polymer systems, a method is proposed for determining the maximum relaxation time. A universal relation is derived for the maximum relaxation time as a function of the shear rate.

A basic characteristic of polymer systems is their relaxation spectrum, which determines all manifestations of their viscoelastic properties. The concept of a relaxation spectrum [1, 2] pertains to the linear range of mechanical behavior, where, for instance, the frequency characteristics of the dynamic modulus components do not depend on the amplitude of deformations and where neither the effective viscosity $\eta = \tau/\dot{\gamma}$ nor the coefficient of normal stresses $\xi = \sigma/2\dot{\gamma}^2$, both measured under steady-state conditions, depend on the shear rate. At the same time, the properties of fluid polymers which appear as a viscosity anomaly and as an anomalous shear rate characteristic of the coefficient of normal stresses are quite nonlinear. These effects, according to the phenomenological theory of thixotropic viscoelasticity [3, 4], may be regarded as due to a weakening of the effect which long relaxation times have on the observed viscoelastic characteristics – a weakening which becomes more significant as the deformation rate increases. This theory has been verified experimentally under steady flow conditions [5-8] and then extended to the case of large-amplitude harmonic vibrations [9, 10], where a sufficiently large amplitude of the deformation rate effects a change in the relaxation spectrum just as the shear rate does under steady-state conditions.

In the light of this experimental evidence, there arises the question as to the extent to which the initial relaxation spectrum $H_i(\theta)$ corresponding to small loads on a system (i.e., to the linear range of mechanical behavior) determines the mechanical behavior in the nonlinear range, i.e., as to which parameters of the initial spectrum predetermine the changes in the material when the latter is subjected to increasing external loads. This question ties in closely with the efforts by many authors [12-20] to develop methods of representing the nonlinear characteristics of polymer systems in universal terms. Some of these methods were discussed in [21].

The beginning of research on this subject can apparently be traced to [13], where a molecular theory was developed to interpret the flow of polymer systems and where the first guidelines were established for generalizing the viscous characteristics of polymers. An important parameter is the relaxation time θ_0 regarded as characteristic, defined on the basis of certain molecular properties of a polymer system, and referred to the linear range of its mechanical behavior. According to this theory, the ratio η/η_i of effective viscosity to initial (maximum) viscosity of a Newtonian fluid should be a function of the dimensionless quantity $\dot{\gamma}\theta_0$ which is universal for all polymers regardless of their molecular weight and temperature. Thus, it is proposed here to express the nonlinear properties of a system in terms of parameter θ_0, which characterizes the properties of the original system. A universal viscosity curve was constructed in [14] on the basis of this theory, with the value of parameter θ_0 determined by fitting – an important procedure for a more accurate description of test data. Although this theory had been developed for monodisperse polymers, the universal functional relation between η/η_i and $\dot{\gamma}\Theta_0$ was obtained for polymers with a wide molecular-weight distribution.

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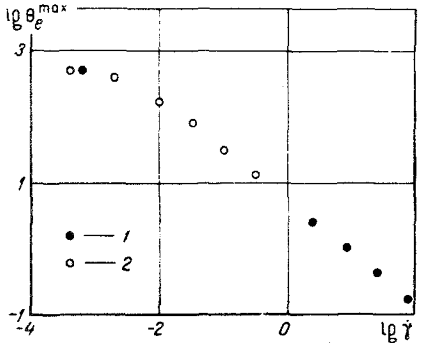

Fig. 1

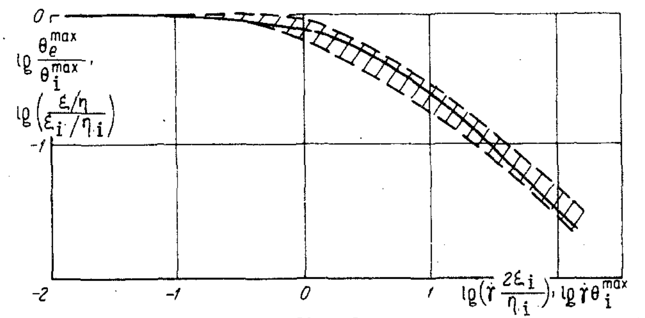

Fig. 2

Fig. 1. Maximum relaxation time as a function of the shear rate: based on the relaxation spectrum (1); based on steady flow modes (2).

Fig. 2. Universal relaxation characteristic for polymers, based on steady flow modes. Solid line represents Eq. (15). Shaded area represents the scatter of test points for: polyisobutylene [24] at 22°C, 40°C, 60°C, 80°C, 100°C, polystyrene solution in decalene [22] at 25°C and volume concentration 18%, 29%, 38%, 46.6%, 57.3%, polybutadiene*(M_w = $1.52 \cdot 10^5$, $M_w/M_n = 1.1$) at 22°C, polybutadiene ($M_w = 2.4 \cdot 10^5$, $M_w/M_n = 1.1$) solution in methylnaphthalene (also according to the data obtained by Malkin and Berezhnaya) at 22°C and volume concentrations 10%, 30%, 50%, polymethylmethacrylate solution in diethylphthalate [7] at 30°C and weight concentration 5%, polyisobutylene solution in tetralene [29] at 25°C and weight concentration 12%, polystyrene solution in toluene [7, 26] at 30°C and weight concentration 9.34%, 15%, 20.1%, polystyrene solution in chlorinated diphenyl [28] at 27°C and weight concentration 13%, 16%, polydimethylsiloxane [27] (M_w = $4.68 \cdot 10^5$, $M_w/M_n = 1.29$; $M_w = 9.71 \cdot 10^4$, $M_w/M_n = 1.18$) at 20°C, polyethylene [6] at 150°C and $\eta_i = 1.4 \cdot 10^4$, $8.0 \cdot 10^4$, $2.5 \cdot 10^6$ p.

The attempt in [18] to construct a universal viscosity curve for polystyrene melts with various molecular-weight distributions has revealed that the curve in [14] is not universal in the case of a molecular-weight variation. The results in [18] indicate that a universal viscosity curve can be constructed only for a group of polymers with the same molecular-weight distribution. It is to be noted that a universal viscosity relation is not sensitive to changes in the degree of branching. This follows from [25], where the viscous properties of both linear and branching monodispersed polystyrene have been analyzed with the aid of test data from [18].

By introducing into the argument of $\dot{\gamma}\theta_0$ an empirical parameter which depends on the molecular-weight distribution, the authors of [12] have succeeded in generalizing the viscous characteristics for polyethylene melts of diverse molecular structures and molecular-weight distributions, which must obviously be viewed as a special case, considering that the shape of the flow curve changes when the molecular-weight distribution changes.

An important method of generalizing the viscous characteristics of block polymers is by the temperature-invariant viscosity curve proposed in [19, 20]. It has been shown that, for industrial specimens of polymers with wide molecular-weight distributions, such a generalization is possible by a η/η_i versus $\dot{\gamma}\eta_i$ relation.

A molecular theory has been developed in [15, 16] pertaining to the flow of amorphous polymers, where the parameter which characterizes a polymer system includes the characteristic relaxation time at a zero shear rate. This parameter is of the same order of magnitude as the characteristic relaxation time in the theory according to [11]. The ratio of the characteristic relaxation time at a given shear rate to the characteristic relaxation time at a zero shear rate is equal to η/η_i. As will be shown here subsequently, however, this conclusion does not agree with test data. At high shear rates the theory yields a relation between η and $\dot{\gamma}^{-3/4}$ which agrees with the empirical equation proposed in [14]. A later study in [15] has yielded $\eta \sim \dot{\gamma}^{-9/11}$. It follows from [15, 16] that a universal representation of the viscosity characteristic is obtained in the same coordinates as in the theory according to [13].

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* According to data obtained by Malkin and Berezhnaya at the Laboratory of Polymer Rheology, Institute of Petrochemical Synthesis, Academy of Sciences of the USSR.

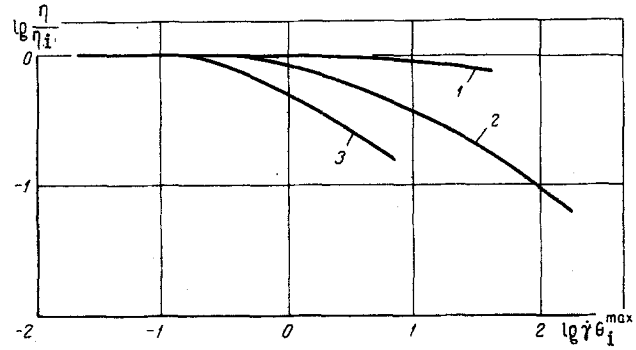

Fig. 3. Viscosity ratio η/η_i as a function of the referred deformation rate $\dot{\gamma}\theta_i^{max}$: for polybutadiene (according to the data obtained by Malkin and Berezhnaya) ($M_w = 1.52 \cdot 10^5$, $M_w/M_n = 1.1$) at 22°C (1), for polystyrene solution in decalene [22] at 25°C and volume concentration 57.3% (2), for polyisobutylene solution in tetralene [29] at 25°C and weight concentration 12% (3).

In [17] there have been developed concepts of a molecular cluster in concentrated polymer solutions and of interaction between molecular segments which depends on the shear rate. The universal representation of viscosity in this theory is almost the same as in [13-16].

An independent method of evaluating the characteristic relaxation time has been proposed in [22], where it has also been shown that by letting $\theta_0 = \eta_i/G_i$ (G_i denoting the initial value of the viscoelasticity modulus), i.e., by expressing θ_0 in terms of measured test quantities only, one can arrive at a temperature-invariant and concentration-invariant generalization of the viscoelastic characteristics of polymer solutions in η/η_i, $\dot{\gamma}\theta_0$ coordinates.

The main drawback of all these methods is that only viscous properties, without elastic properties, are used as functions for generalizing the behavior of polymer systems. Elastic properties can also be accounted for, however, if the maximum relaxation time is used which covers both kinds of properties.

The object of this here study was to find a method of calculating the maximum relaxation time from the results of research on polymer systems under steady flow conditions at various shear rates and under cyclic small-amplitude deformation, and then to generalize the test data published in the technical literature. The behavior of polymer systems will thus be generalized in terms of the relaxation spectrum and its variation due to deformation.

At sufficiently low frequencies ω of harmonic vibrations, as is well known, the imaginary component G" and the real component G' of the dynamic modulus are proportional to the frequency ($G'' \sim \omega$) and to that frequency squared ($G' \sim \omega^2$) respectively. Therefore, there must be a maximum relaxation time θ_i^{max} for which $H_i(\theta) = 0$ at $\theta > \theta_i^{max}$. Obviously, θ_i^{max} may be regarded as the first relaxation characteristic of polymer systems. We will show, first of all, how θ_i^{max} can be expressed in terms of the initial Newtonian viscosity η_i and the initial normal stress coefficient ξ_i. According to [1, 2, 23], these two quantities are expressed in terms of $H_i(\theta)$ as follows:

$$\eta_i = \int_0^{\theta_i^{max}} H_i(\theta)\, d\theta, \tag{1}$$

$$\xi_i = \int_0^{\theta_i^{max}} H_i(\theta)\, \theta d\theta. \tag{2}$$

We will assume that η_i, ξ_i, and θ_i^{max} in Eqs. (1) and (2) are functions of the temperature. The form of function $H_i(\theta)$ is then, by virtue of the temperature-frequency superposition principle [1], independent of the temperature while η_i and ξ_i are functions of θ_i^{max}.

It is easy to show now that the quantities η_i, ξ_i, and θ_i^{max} are all interrelated. In order to prove this, we differentiate expressions (1) and (2) with respect to θ_i^{max}:

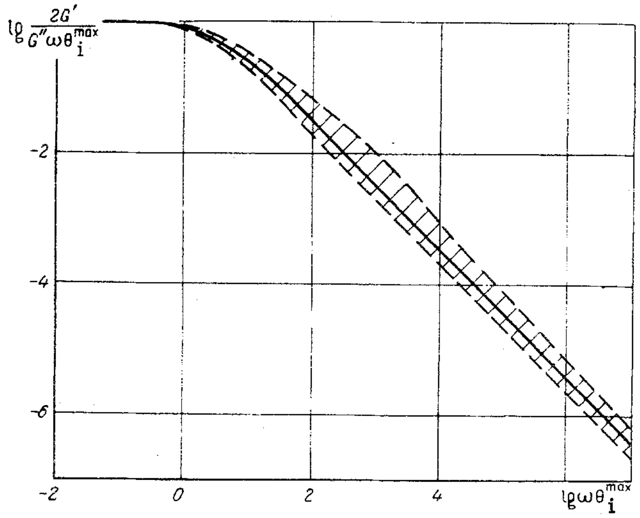

Fig. 4. Generalized relaxation characteristic of polymer systems, based on cyclic small-amplitude deformations. Solid line represents Eq. (16). Shaded area represents the scatter of test points for: polyisobutylene NBS solution in decalene [30] at 25°C and weight concentration 20%, polystyrene S-III [31] at 190°C, polyisobutylene solution in cetane [31] at 25°C and weight concentration 2%, polymethylmethacrylate [32] ($M_W = 1.91 \cdot 10^5$, $M_W/M_n = 1.26$; $M_W = 5.21 \cdot 10^4$, $M_W/M_n = 1.39$) at 220°C, mixture of polymethylmethacrylates [32] ($M_W = 1.43 \cdot 10^5$, $M_W/M_n = 1.23$ and $M_W = 8.01 \cdot 10^4$, $M_W/M_n = 1.59$) at 220°C, polyisobutylene ($M_W = 8.4 \cdot 10^5$) solution in mineral oil [33] at 25°C and weight concentration 2%, polystyrene ($M_W = 2.67 \cdot 10^5$) solution in arochlorine [34] at 25°C and weight concentrations 10%, 20%, polystyrene [38] ($M_W = 5.18 \cdot 10^6$) at 200°C, polyisobutylene P-20 [9] at 22°C, polyisobutylene ($M_W = 10^6$) solution in cetane [5] at 25°C and weight concentration 8.7%, 5.4%, polystyrene [35] ($M_W = 5.81 \cdot 10^5$, $M_W/M_n = 1.06$; $M_W = 5.87 \cdot 10^4$, $M_W/M_n = 0.94$; $M_W = 8.9 \cdot 10^3$, $M_W/M_n = 1.01$) at 160°C, polyisobutylene ($M_W = 1.1 \cdot 10^6$) solution in mineral oil [37] at 25°C and weight concentration 4%.

$$\frac{d\eta_i}{d\theta_i^{max}} = H_i(\theta_i^{max}), \tag{3}$$

$$\frac{d\xi_i}{d\theta_i^{max}} = H_i(\theta_i^{max})\,\theta_i^{max}. \tag{4}$$

Dividing (4) by (3), we have

$$\frac{d\xi_i}{d\eta_i} = \theta_i^{max}. \tag{5}$$

According to [24], η_i, ξ_i, and G_i are related by the simple equation

$$\xi_i = \eta_i^2/G_i. \tag{6}$$

Inserting ξ_i from (6) into Eq. (5) and then differentiating, we easily obtain

$$\theta_i^{max} = \frac{2\eta_i}{G_i} = \frac{2\xi_i}{\eta_{in}}. \tag{7}$$

The use of the dimensionless deformation rate $\dot{\gamma}\theta_i^{max}$ provides for a new way of generalizing the viscoelastic characteristics of polymer systems in the nonlinear range.

In order to proceed, we will first seek out any general laws according to which the relaxation properties of polymer systems vary as functions of the parameter $\dot{\gamma}\theta_i^{\max}$. It has been shown in [3-10] that an increase in the load intensity on a system can be represented by a model where a higher deformation rate causes the upper edge of the relaxation spectrum to shift farther. The spectrum edge is here the "maximum" (at a given shear rate) relaxation time, while the effective viscosity and the coefficient of normal stress are defined as follows:

$$\eta = \int_0^{\theta_e^{\max}} H_e(\theta)\, d\theta, \tag{8}$$

$$\xi = \int_0^{\theta_e^{\max}} H_e(\theta)\, \theta d\theta. \tag{9}$$

Let us differentiate (8) and (9) with respect to $\theta_e^{\max}$:

$$\frac{d\eta}{d\theta_e^{\max}} = \int_0^{\theta_e^{\max}} \frac{\partial H_e(\theta)}{\partial\theta_e^{\max}}\, d\theta + H_e\left(\theta_e^{\max}\right), \tag{10}$$

$$\frac{d\xi}{d\theta_e^{\max}} = \int_0^{\theta_e^{\max}} \frac{\partial H_e(\theta)\,\theta}{\partial\theta_e^{\max}}\, d\theta + H_e\left(\theta_e^{\max}\right)\theta_e^{\max}. \tag{11}$$

Assuming that the derivative $\partial H_e(\theta)/\partial\theta_e^{\max} = 0$, i.e., that the effective relaxation spectrum does not depend on $\theta_e^{\max}$, we can write

$$\frac{d\xi}{d\eta} = \theta_e^{\max}. \tag{12}$$

It has been shown in many studies that, within a definite range of shear rates, $\sigma \sim \tau^2$ not only within the linear range but also beyond its limits. At higher shear rates this relation ceases to be quadratic. Consequently, in the general case we have

$$\xi = f(\dot{\gamma})\,\eta^2, \tag{13}$$

where $f(\gamma)$ is some function weakly dependent on the shear rate and equal to $1/G_i$ at small values of $\dot{\gamma}$. With the aid of (12) and (13) we obtain

$$\theta_e^{\max} \simeq \frac{2\xi}{\eta}. \tag{14}$$

The dependence of $\theta_e^{\max}$ on the shear rate is shown in Fig. 1 for polyethylene, according to the data in [9]. Here are also shown the values of $2\xi/\eta$ at various shear rates, according to the data in [24]. According to Fig. 1, the values determined on the basis of formula (14) and directly from the relaxation spectra are in close agreement. Consequently, the effective relaxation spectrum does not depend on $\theta_e^{\max}$ The same conclusion is also drawn from the results which will be shown here subsequently.

The magnitude of the maximum relaxation time $\theta_e^{\max}$ can be found, if relations $\eta(\dot{\gamma})$ and $\xi(\dot{\gamma})$ are known while $\theta_i^{\max} = \lim\limits_{\dot{\gamma}\to 0}\theta_e^{\max}$. A variation in the relaxation spectrum can be represented in a dimensionless form: $\theta_e^{\max}/\theta_i^{\max}$ as a function of $\dot{\gamma}\theta_i^{\max}$, shown in Fig. 2, according to the test data in [6, 7, 22, 24, 26-29]. For comparison with this relation, in Fig. 3 is also shown η/η_i as a function of $\dot{\gamma}\theta_i^{\max}$ for the same polymers as in Fig. 2. In the latter case it is not possible to construct a single curve for polymers with very different molecular-weight distributions. It follows directly from Figs. 2 and 3 that, generally, $\eta/\eta_i \neq \theta_e^{\max}/\theta_i^{\max}$. We note, however, that for polymer systems $\eta/\eta_i = \theta_e^{\max}/\theta_i^{\max}$ only up to values of $\dot{\gamma}$ at which the proportionality $\sigma \sim \tau^2$ is exact within the range of nonlinear behavior.

An important fact revealed in Fig. 2 is the existence of a single relaxation spectrum characteristic for polymer systems. This characteristic can be described by the following empirical equation:

$$\theta_e^{\max}/\theta_i^{\max} = \frac{1}{1 + 0.3\dot{\gamma}\theta_i^{\max}}. \tag{15}$$

In conclusion, we note that from the analogy established between the frequency characteristics of dynamic functions and the shear rate characteristics of stresses one can derive a formula analogous to (15) on the basis of test data pertaining to cyclic small-amplitude deformations of polymers.

In order to construct such a frequency characteristic of dynamic functions, we will consider the function $2G'/G''\omega$ referred to θ_i^{max} versus the dimensionless frequency $\omega\theta_i^{max}$. The choice of this function is dictated by the requirement that $2G'/G''\omega \to \theta_i^{max}$ as $\omega\theta_i^{max} \to 0$. It is not difficult to show that this requirement is indeed met. The relation between $2G'/G''\omega\theta_i^{max}$ and $\omega\theta_i^{max}$, according to the test data in [5, 9, 30-38], is shown in Fig. 4. The solid line on this diagram represents the equation

$$2G'/G''\omega\theta_i^{max} = \frac{1}{1+0.3\,\omega\theta_i^{max}}. \qquad (16)$$

Obviously, the right-hand side here is the same as in Eq. (15), if $\omega = \dot{\gamma}$. It follows therefore that

$$2G'/G''\omega = \theta_e^{max} \text{ for } \omega = \dot{\gamma}. \qquad (17)$$

Equation (14) yields the following relation between θ_e^{max}, which characterizes the change in the relaxation spectrum due to a heavier load on the system, and the stress ratio

$$\sigma/\tau = \theta_e^{max}\dot{\gamma}. \qquad (18)$$

Formula (15) simplifies considerably the calculation of normal stresses according to the known $\tau(\dot{\gamma})$ relation and the known value of θ_i^{max}. Formulas (15) and (18) combined do obviously fully define the relation $\sigma(\dot{\gamma})$ when the relation $\tau(\dot{\gamma})$ is known.

The results obtained here are valid for polymer systems such as thermoplastics as well as nonvulcanized elastomers and their concentrates, but not for dilute solutions of low-molecular polymers with viscoelastic properties.

NOTATION

η	is the effective viscosity;
τ	is the shear stress;
γ	is the shear rate;
ξ	is the coefficient of normal stresses;
σ	is the first difference between normal stresses;
θ_0	is the characteristic relaxation time;
ξ_i	is the maximum coefficient of normal stresses;
η_i	is the maximum Newtonian viscosity;
θ_i^{max}	is the maximum relaxation time in the initial relaxation spectrum;
$H_i(\theta)$	is the initial relaxation spectrum;
θ_e^{max}	is the maximum relaxation time in the effective relaxation spectrum;
$H_e(\theta)$	is the effective relaxation spectrum;
θ	is the relaxation time;
G'	is the elasticity modulus;
G''	is the loss modulus;
G_i	is the initial superelasticity modulus;
ω	is the angular frequency.

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