UNIVERSAL SUPERELASTICITY CHARACTERISTIC FOR POLYMER SYSTEMS

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The superelastic strain is represented in universal form as a function of the product shear rate times maximum relaxation time in the relaxation spectrum for a polymer system. A relation is established between the superelastic strain and the relaxation spectrum as well as the change of the latter due to the shear rate.

The viscoelastic properties of plastic polymers within the ranges of linear and nonlinear mechanical behavior have been represented in [1] as functions of the dimensionless argument $\dot{\gamma}\theta_{\mathrm{in}}^{\mathrm{max}}$ and this has made it possible to construct a universal relaxation characteristic for a large class of polymer systems, indicating how the relaxation spectrum varies with an increasing shear rate. The fact that one value of relaxation time $\theta_{\mathrm{in}}^{\mathrm{max}}$ is sufficient for determining the specific properties of a polymer system indicates the universality of the viscoelastic properties of a large class of polymer systems and suggests the feasibility of a universal representation of various viscoelastic characteristics. This hypothesis will be tested here in the case of two important characteristics of polymer systems, namely the effective viscosity η and the superelastic strain γ_{e} as functions of the shear rate.

We first consider the $\eta(\dot{\gamma})$ relations derived for several polymer systems. The problem of generalizing the viscous properties of polymers has been considered in many earlier studies, most outstanding among them [2-10]. It appeared logical to express the characteristic relaxation time θ_0 in terms of such parameters as the molecular weight and the concentration of the polymer substance in a system, on the basis of one or another molecular model. At the same time, as correctly shown in [7, 8], it would not be possible in this manner to establish universal characteristics for polymer systems as long as the effect of the molecular parameters on the properties of such systems may be other than predicted by theory. On the other hand, a method has been proposed in [9, 10] for universally describing the viscous properties of block polymers in terms of the argument $\dot{\gamma}\eta_{\mathrm{in}}$, with η_{in} denoting the maximum coefficient of Newtonian viscosity. Evidently, such a description may be valid if $\theta_{\mathrm{in}}^{\mathrm{max}} \sim \eta_{\mathrm{in}}$, i.e., if the properties of systems are compared with like superelastic properties. In the most general method of constructing the referred viscous characteristics for polymer systems, therefore, the effect of their viscous and elastic properties must be accounted for independently, namely by having the argument of the viscoelasticity functions include experimentally determinable quantities characterizing these properties. This can be done by expressing $\theta_{\mathrm{in}}^{\mathrm{max}}$ in terms of the ratio η_{in}/G_0, where G_0 denotes the initial modulus of superelasticity. An equivalent expression for $\theta_{\mathrm{in}}^{\mathrm{max}}$ is [1, 2]

$$\theta_{in}^{\max} = 2\eta_{in}/G_0 = 2\zeta_{in}/\eta_{in} = 2\theta_0, \tag{1}$$

with ζ_{in} denoting the initial coefficient of normal stresses. Indeed, it has been shown in [2] that in this case one can easily construct concentration-invariant viscosity characteristics for solutions of various polymers, which could not be done by other methods of calculating the relaxation time. On the basis of the results in [9, 10], where those authors have been able to establish universal $\eta/\eta_{\mathrm{in}} = f(\dot{\gamma}\eta_{\mathrm{in}})$ characteristics for polymer melts by comparing their temperature-invariant viscosity characteristics, we will now construct the $\eta/\eta_{\mathrm{in}} = f(\dot{\gamma}\theta_{\mathrm{in}}^{\mathrm{max}})$ characteristics for several polymer systems [2, 12-17] (Fig. 1). Obviously,

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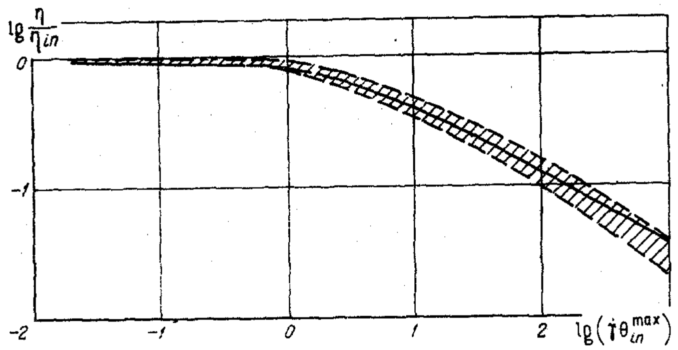

Fig. 1. Viscosity ratio η/η_{in} as a function of the referred strain rate $\dot\gamma\theta_{in}^{max}$. Solid line represents the temperature-invariant viscosity characteristic of polydisperse polymers [10] with the assumption that $G_0 = 2 \cdot 10^5$ dyn/cm^2. The shaded area represents the spread of test values for the following systems: polyisobutylene P-20 [12] at 22°C, 40°C, 60°C, 80°C, 100°C, polybutadiene ($M_w = 2.4 \cdot 10^5$, $M_w/M_n = 1.1$) in methylnaphthalene (according to Berezhnaya) 10% volume at 22°C, polystyrene in toluene [13, 14] 15% volume, 20.1% volume at 30°C, polystyrene in chlorated diphenyl [15] 13% volume, 16% volume at 27°C, polydimethylsiloxane ($M_w = 9.71 \cdot 10^4$, $M_w/M_n = 1.18$) [16] at 20°C, polyethylene [17] at 150°C. Initial viscosity $\eta_{in} = 8 \cdot 10^4$, $2.5 \cdot 10^6$ P.

in this case the viscous properties can be represented in the form of a temperature- and concentration-invariant characteristic common to the various polymer systems under study. The temperature-invariant viscosity characteristic of polydisperse polymers [9, 10] is also shown in Fig. 1, by a solid line with the initial modulus of superelasticity for these substances G_0 assumed equal to $2 \cdot 10^5$ dyn/cm^2. As to the polymer systems the test data for which have been plotted in Fig. 1, their η_{in} values differ by up to a factor of 10^6 and their G_0 values differ by up to a factor of 10^2. Judging by the trend of the curve in Fig. 1, polymer systems behave like Newtonian fluids when $\dot\gamma\theta_{in}^{max} < 0.7$, while at high values of the argument the effective viscosity becomes a power function of the shear rate:

$$\eta/\eta_{in} \approx (2.4 - 4.5)(\dot\gamma\theta_{in}^{max})^{-0.7} \tag{2}$$

(in referred coordinates).

The use of dimensionless coordinates η/η_{in}, $\dot\gamma\theta_{in}^{max}$ for representing the viscosity test data for the various polymer systems in Fig. 1 is a further step in the refinement of the procedure for constructing temperature-invariant viscosity characteristics which has been proposed in [9, 10] and extended in [2]. As has been noted in [1], however, the $\eta/\eta_{in} = f(\dot\gamma\theta_{in}^{max})$ curve is not universal and, according to Fig. 1, can be constructed only for polymers with a sufficiently wide molecular-weight distribution and for solutions of various monodisperse polymers.

On the same premises, we will not consider a universal representation of superelastic properties for various polymer systems. The general trend in the development of superelastic strains in various polymer systems can be seen in Fig. 2, where the magnitudes of reversible strain have been plotted against the dimensionless shear rate (parameter $\dot\gamma\theta_{in}^{max}$). According to this diagram, the ratio of the inner time scale to the response rate determines the ability of a material to develop superelastic strains. A universal characteristic of relaxation properties has been established in [1] in the form of relation $\theta_e^{max}/\theta_{in}^{max} = f(\dot\gamma\theta_{in}^{max})$, with θ_e^{max} denoting the maximum relaxation time in an effective relaxation spectrum, i.e., in a relaxation spectrum modified by strain. The question arises then as to how the change in the relaxation spectrum is related to the appearance of superelasticity in various polymer systems under an increasing load. An answer to this question is provided in Fig. 3 by the graph of superelastic strain as a function of $\theta_e^{max}/\theta_{in}^{max}$, the latter characterizing the change in relaxation properties of the polymer

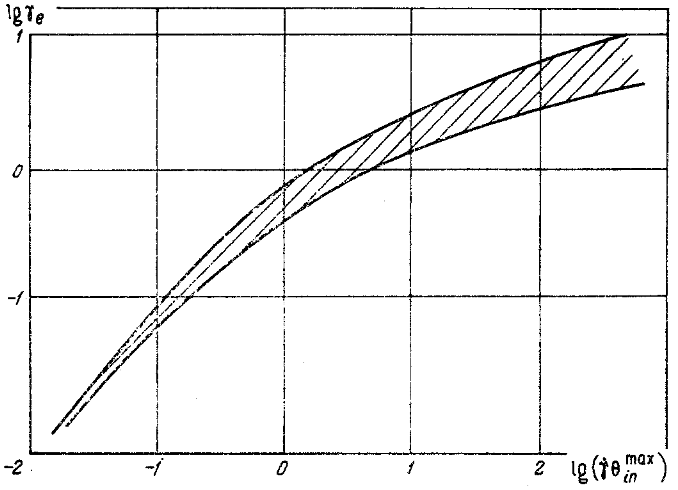

Fig. 2. Superelastic strain γ_e as a function of the referred strain rate $\dot{\gamma}\theta_{in}^{max}$. The shaded area represents the spread of test data. The polymer systems are the same as in Fig. 1 and also polybutadiene ($M_w = 2.04 \cdot 10^5$, $M_w/M_n = 1.1$) (according to Berezhnaya), polystyrene in diethylphthalate [18] 60% volume at 22°C, polyisobutylene in vaseline oil [19] ($M_w = 1.4 \cdot 10^6$, 4.15% volume; $M_w = 1.5 \cdot 10^7$, 2% volume; $M_w = 2.8 \cdot 10^6$, 3% volume) at 25°C, polybutadiene (according to Berezhnaya) ($M_w = 1.52 \cdot 10^5$, $M_w/M_n = 1.1$) at 22°C polybutadiene ($M_w = 2.4 \cdot 10^5$, $M_w/M_n = 1.1$) in methylnaphthalene (according to Berezhnaya) 30% volume and 50% volume.

systems within the nonlinear range of mechanical behavior. The quantity γ_e alone is a dimensionless characteristic of superelasticity in a system at a given shear rate $\dot{\gamma}$ and, therefore, the ordinate axis in Figs. 2 and 3 does not have to be normalized in any way.

Evidently, γ_e as a function of $\dot{\gamma}\theta_{in}^{max}$ or $\theta_e^{max}/\theta_{in}^{max}$ constitutes a universal superelasticity characteristic of polymer systems which is invariant with respect to temperature, to concentration, and to the nature of the polymer (within the class of polymers included in this study). For low values of the argument $\dot{\gamma}\theta^{max}$ (< 0.7), the test data fit on a straight line (not shown in Fig. 2) described by the simple equation

$$\gamma_e = \frac{1}{2}\,\dot{\gamma}\theta_{in}^{max}.$$

Inasmuch as this range of argument values corresponds to Newtonian flow, the straight line on the left-hand side in Fig. 2 actually represents Hooke's law under shear: $\gamma_e = \tau/G_0$. The existence of a universal relation between superelastic strain and ratio $\theta_e^{max}/\theta_{in}^{max}$ proves directly that the superelastic strains as well as the viscosity and the coefficient of normal stresses are well related to the relaxation spectrum of a polymer system and to its changes.

Thus, a large class of polymer systems is subject "on the average" to the following trends: within the range of Newtonian flow there may develop superelastic strains of the order of 0.3 relative units; the viscosity and the modulus of superelasticity remain constant here. Deviations from Hooke's law under shear begin within the same range of $\dot{\gamma}\theta_{in}^{max}$ values within which viscosity anomalies begin to develop.

Of special interest is the range of high shear rates, where, according to Fig. 2, the power-law relation between γ_e and $\dot{\gamma}\theta_{in}^{max}$

$$\gamma_e \simeq (0.56 - 1.2)\,(\dot{\gamma}\theta_{in}^{max})^{0.3} \tag{3}$$

applies.

The ranges of argument $\dot{\gamma}\theta_{in}^{max}$ where (2) is valid and where (3) is valid almost overlap. For this reason, these formulas may be treated together and, consequently, within the range of sufficiently high

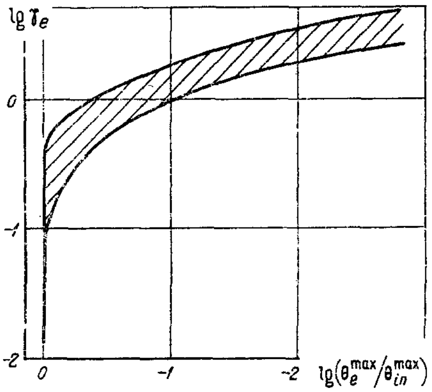

Fig. 3. Superelastic strain (γ_e) as a function of $\theta_e^{max}/\theta_{in}^{max}$. The polymer systems are the same as in Figs. 1 and 2.

argument values

$$G_\infty = \tau/\gamma_e \approx (1-4)\,G_0. \tag{4}$$

This means that the modulus of superelasticity at higher shear rates cannot increase infinitely for the various systems in this study but, instead, attains the asymptotic value G_∞ not over four times higher than the initial value G_0. This, apparently, can be regarded as reaching the superelastic-state plateau, where the modulus ceases to vary with the rate (frequency) of external loading.

The numerical value of this ultimate modulus G_∞ depends on the initial state of the system, inasmuch as G_0 and G_∞ are related according to formula (4).

The results of this study, together with the results in [1], yield some conclusions concerning the universal laws which govern the viscoelastic properties of polymers within the nonlinear range of mechanical behavior. As has been assumed earlier, some molecular models have one maximum relaxation time for a polymer system. This maximum relaxation time is expressed in terms of two measurable parameters: the initial viscosity and the initial coefficient of normal stresses, which represent, respectively, the first and the second moment of a relaxation spectrum for polymer systems. With an increasing external load on the system, defined by the ratio of the characteristic loading time $1/\dot{\gamma}$ and the proper relaxation time of a system θ_{in}^{max}, there occurs a change in the relaxation spectrum which can be described as a shift of the peak relaxation time toward lower values. This change occurs identically for various polymer systems [1], indicating that the form of their relaxation spectra are all equivalent within the plastic range and that the trend of the spectrum changes is the same and, on the whole, dependent on the shear rate. Such a change in the relaxation spectra for various polymer systems, as a function of the shear rate, predetermines the similarity of the viscoelastic properties of those polymer systems and provides a basis for establishing a few simple (although only approximate, inasmuch as the properties of individual systems deviate from the average relaxation characteristic) relations for stresses developing during steady flow, for relaxation characteristics of polymers, and for superelastic strains as functions of the state-of-strain characteristic – the dimensionless shear rate.

In conclusion, we note the basic limitations of these results. Obviously, they are not valid when the original assumptions are violated, i.e., when polymer systems are considered whose relaxation spectra differ appreciably from those described by these universal characteristics. These characteristics do not apply, for instance, to low-molecular polymers or dilute solutions and, generally, to polymer systems not going through a superelasticity plateau. One may also surmise that these methods of universally describing the viscoelastic and the superelastic properties of polymer systems cannot be applied to polymers with a high filler content.

NOTATION

θ_0	is the characteristic relaxation time;
θ_{in}^{max}	is the maximum relaxation time in the initial relaxation spectrum;
η	is the effective viscosity;
τ	is the shear stress;
$\dot{\gamma}$	is the shear rate;
η_{in}	is the maximum Newtonian viscosity;
ζ_{in}	is the maximum coefficient of normal stresses;
ζ	is the coefficient of normal stresses;
γ_e	is the superelastic strain;
G_0	is the initial modulus of superelasticity;
G_∞	is the modulus of superelasticity at high shear rates.

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