

INFLUENCE OF VIBRATIONS (CYCLIC DEFORMATIONS
WITH LARGE AMPLITUDES) UPON THE VISCOELASTIC
PROPERTIES OF A POLYPROPYLENE MELT

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The article describes the relation between the cutoff of the long-time section of the relaxation spectrum and the shear rate for the case of continuous deformations. The correspondence between the amplitude of the rate of cyclic deformations and the deformation rate was determined for the case of continuous deformations in stationary flow.

The influence of cyclic deformations upon the viscoelastic properties of polymer systems has numerous interesting aspects and has been described in several papers in relation to polymers with fillers [1, 2] rubbers [3, 4], and polymer solutions [5]. It was shown in [6] that large-amplitude deformations of polyisobutylene change a fundamental characteristic of the polymer, namely its relaxation spectrum. The long-time section of the relaxation spectrum is cut off.

In analogy to the concept of initial viscosity, which is independent of the shear rate at small shear rates, the relaxation spectrum which is not affected by deformations will be termed initial relaxation spectrum. In analogy to the concept of effective viscosity, which depends upon the shear rate, the relaxation spectrum affected by deformations will be termed effective relaxation spectrum. It was established in [6] that, in the case of cyclic deformations, the effective relaxation spectrum is uniquely determined by the deformation rate which is equal to the frequency of the vibrations multiplied by the amplitude of the deformations. A unique correspondence of the form $\log \dot{\gamma} = \log \dot{\gamma}_{\max} + \log a$ exists between the deformation rate $\dot{\gamma}_{\max}$ and the shear rate $\dot{\gamma}$, where a denotes a constant which depends upon the type of the polymer considered. The long-time section of the effective relaxation spectrum resembles the long-time section of the initial relaxation spectrum. The calculation of the viscoelastic characteristics which are usually determined in investigations employing continuous deformations can be made with the linear theory of viscoelasticity, provided that the initial relaxation spectrum and the dependence of the long-time limit of the effective relaxation spectrum upon deformation rate or shear rate are known. The effective viscosity and the coefficient of normal stresses were calculated in this fashion.

The method of [6] has to be checked on a completely different polymer in order to generalize the method to linear polymers at temperatures above the vitrification and melting points. Moreover, the data of Tanner [7], which had been obtained with polyisobutylene solutions in cetane, were used for the generalization.

A torsion pendulum and a vibratory rheometer were used in the measurements of the dynamic characteristics. The measurements with the pendulum, which was used in the mode of freely attenuated oscillations, were made at frequencies between 0.1 and 1 Hz. The pendulum has been described in detail in [8]. The measurements with the vibratory rheometer, which was operated in the induced oscillation mode, were made at frequencies between 6 and 110 Hz and at various deformation amplitudes, as described in [6]. All measurements were made at 194°C.

The complex dynamic viscosity $\eta^* = \eta' - i\eta''$ was measured during cyclic deformations, where η' denotes the real component or the so-called dynamic viscosity, and η'' , the imaginary component. Measurements were made at various deformation amplitudes γ_0 and frequencies $\omega = 2\pi f$, where f denotes the

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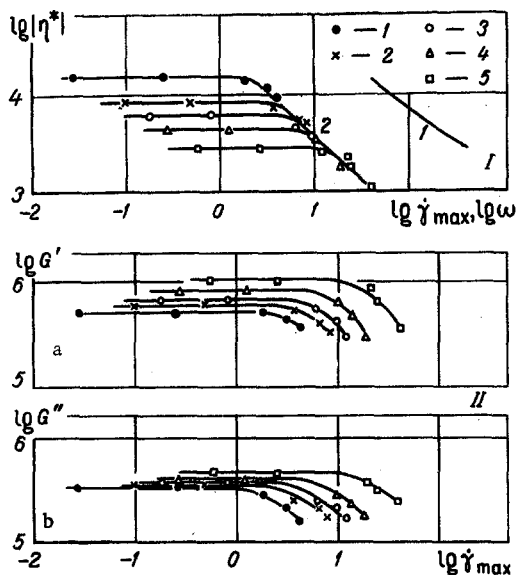


Fig. 1. I) Dependence of the absolute value of the complex dynamic viscosity upon the deformation rate for various frequencies (curve 2) and upon the frequency at small deformation amplitudes (curve 1); II) dependences of a) the modulus of elasticity and b) the modulus of losses upon the deformation rate for various frequencies: 1) $\omega = 40$; 2) 80; 3) 125; 4) 200; 5) 400. η^* expressed in p; ω , in sec^{-1} ; $\dot{\gamma}$, in sec^{-1} ; G' and G'' , in dyne/cm^2 .

$\dot{\gamma}_{\text{max}}$ has reached a critical value $\dot{\gamma}_{\text{max}}^{\text{CR}}$ at which the function $|\eta^*| = \Phi_1(\dot{\gamma}_{\text{max}})$ becomes the envelope. Figure 1, I shows also the dependence of the absolute value of the complex dynamic viscosity upon the frequency $|\eta^*| = \Phi_2(\omega)$ for $\dot{\gamma}_{\text{max}} < \dot{\gamma}_{\text{max}}^{\text{CR}}$. The envelope of the curves $|\eta^*| = \Phi_1(\dot{\gamma}_{\text{max}})$ can be combined with the curve $|\eta^*| = \Phi_2(\omega)$ by transposing the latter curve along the abscissa by the amount $\log a = 1.3$. This result can be explained as follows. The critical amplitudes and deformations γ_0^{CR} which correspond to the transition into the envelope depend only slightly upon the frequency (in the frequency range considered, the deviations from γ_0^{CR} amount to 9%). Since $\dot{\gamma}_{\text{max}} = \gamma_0 f = \gamma_0 \omega / 2\pi$, the values $\gamma_0^{\text{CR}} / 2\pi$ can be assumed constant in a first approximation. This means that $\dot{\gamma}_{\text{max}}^{\text{CR}}$ is proportional to ω and the envelope $|\eta^*| = \Phi_1(\dot{\gamma}_{\text{max}}^{\text{CR}})$ must be shifted along the abscissa relative to the function $|\eta^*| = \Phi_2(\omega)$ or $\eta(\dot{\gamma})$ by the amount $\log \gamma_0^{\text{CR}} / 2\pi = \log a$. Interestingly enough, in investigations in which polyisobutylene of low molecular weight was examined, the corresponding shift along the $\log \dot{\gamma}_{\text{max}}$ axis amounted to 1.9. This means that the quantity a depends upon the type of the polymer.

Figure 1, II(a, b) depicts the dependences of the components G' and G'' of the complex dynamic modulus upon the deformation rate for various oscillation frequencies. Two deformation ranges can be distinguished on the figure: there exists a region in which the moduli are independent of the deformation rate, and another region in which the absolute values of G' and G'' decrease with increasing $\dot{\gamma}_{\text{max}}$. The absolute values of G' and G'' increase with increasing frequency in both regions.

Figures 2a and 2b depict the frequency dependence of the components of the complex modulus. The G' and G'' values were obtained with the torsion pendulum in the frequency range $10^{-0.2} - 10^{0.8} \text{ sec}^{-1}$, and with the vibratory rheometer in the frequency range $10^{1.6} - 10^{2.6} \text{ sec}^{-1}$. The G'' values at low frequencies were obtained with the flow curve of polypropylene, because the equality $\tau = G''$ holds for low shear rates and frequencies, provided that we assume $\dot{\gamma} = \omega$. It follows from the $G''(\omega)$ dependence considered (curve 1 in Fig. 2b) that the transition region from low frequencies to higher frequencies is not well pronounced. Increasing frequencies imply that the values pass to the high-elasticity plateau, which is inclined, probably

frequencies of the oscillations. The γ_0 values were used to calculate the deformation rate $\dot{\gamma}_{\text{max}} = \gamma_0 f$. The η^* values were used to determine the complex shear modulus $G^* = \eta^* \times i\omega = G' + iG''$ and its components (with G' denoting the modulus of elasticity, and G'' , the modulus of losses).

The effective viscosity $\eta = \tau / \dot{\gamma}$ was measured along with the dynamic characteristics, where τ and $\dot{\gamma}$ denote the tangential stress and the shear rate, respectively.

"Moplen" polypropylene having an initial viscosity $\eta_{\text{max}} = 2.5 \cdot 10^6 \text{ p}$ at 194°C was the main object of the investigations. The characteristic viscosity of this polypropylene was 3.8 at 135°C in decalin. Moreover, Moplen polypropylene with a lower initial Newtonian viscosity was used for test calculations.

The viscosity values of polypropylene, which had been obtained upon continuous polypropylene deformations in the shear-rate interval between 10^{-2} and $10^{0.3} \text{ sec}^{-1}$, were taken from [9].

In our ensuing discussion, we assume that the frequency is equivalent to the shear rate in the case of continuous deformations. Apart from this, a quantitative correlation between the complex viscosity and effective viscosity is used, as well as a quantitative correlation between the modulus of the losses and the shearing stress.

Figure 1, I shows the dependence of the absolute value of the complex dynamic viscosity upon the deformation rate for various oscillation frequencies. The quantity $|\eta^*|$ is independent of $\dot{\gamma}_{\text{max}}$ at each given frequency, until

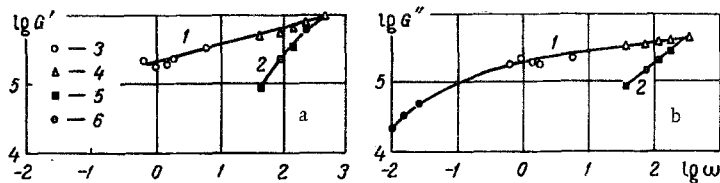


Fig. 2. Frequency dependences of a) the modulus of elasticity and b) the modulus of losses. 1) Small-deformation amplitudes; 2) deformation-rate amplitude $\dot{\gamma}_{\max} = 10 \text{ sec}^{-1}$; 3) torsion pendulum; 4 and 5) vibratory rheometer; 6) capillary viscosimeter. G' and G'' expressed in dyne/cm^2 , and ω , in sec^{-1} .

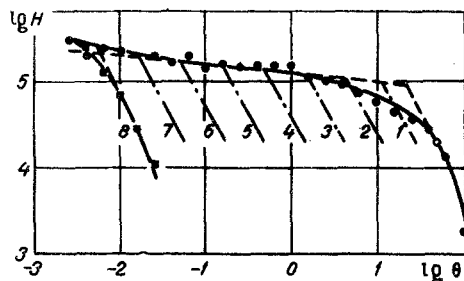


Fig. 3. Initial and effective relaxation spectra of polypropylene (the dashed line denotes the approximation of the initial spectrum; the dash-dot line indicates the approximation of the effective spectrum): 1) 0.063; 2) 0.2; 3) 0.63; 4) 2.0; 5) 6.3; 6) 20; 7) 63; 8) 200. H expressed in dyne/cm^2 ; θ , in sec .

due to polydispersion of the polymer. The modulus of elasticity figures (curve 1 in Fig. 2a) were obtained only in the plateau region. The vitrification range was not reached in this particular experiment. The vitrification range is situated at higher frequencies than we could reach in the present work. Curves 2 of Figs. 2a and 2b were obtained at a deformation rate of 10 sec^{-1} . A rather sharp cutoff of the functions $G'(\omega)$ and $G''(\omega)$ corresponds to that deformation rate. Since $\log a = 1.3$, the curves of Figs. 2a and 2b indicate the components $G'(\omega)$ and $G''(\omega)$ of the complex dynamic modulus, which are obtained when a cyclic deformation of small amplitudes is superimposed on a continuous deformation with a shear rate of 200 sec^{-1} .

The method of Ninomiya and Ferry [10] was used to calculate the initial relaxation spectrum $H_{in}(\theta)$ from the functions $G'(\omega)$ and $G''(\omega)$ which refer to the small-amplitude region of amplitude-independent G' and G'' . The initial relaxation spectrum is represented by the solid curve running through the filled circles in Fig. 3. The effective relaxation spectrum $H_e(\theta)$ was calculated from the data which are represented in Figs. 2a and 2b by curves 2, in analogy to the calculation of the initial spectrum. The effective relaxation spectrum is represented by the steep solid curve which runs through the filled squares. It follows from what has been said above that the effective relaxation spectrum must be equivalent to the polymer spectrum in the case of stationary flow, when the shear rate is 200 sec^{-1} .

The initial relaxation spectrum is related to the initial Newtonian viscosity $\eta_{\max} = \lim_{\dot{\gamma} \rightarrow 0} \eta$ by the expression

$$\eta_{\max} = \int_0^{\infty} H_{in}(\theta) d\theta. \quad (1)$$

The initial relaxation spectrum was approximated so that Eq. (1) rendered a spectrum corresponding to the greatest experimentally determined Newtonian viscosity. The approximation is represented in Fig. 3 by two sections of straight lines denoted by dashes. These lines characterize the long-time and average-time sections of the spectrum. The short-time section of the spectrum was not obtained, because the function $G''(\omega)$ was not given on the high-frequency side. The approximated initial relaxation spectrum can be described by the following functional dependences:

$$H_{in} = \begin{cases} 1.6 \cdot 10^7 \theta^{-1.75}, & 10^{1.34} < \theta < 10^{1.7}; \\ 1.2 \cdot 10^6 \theta^{-0.114}, & 0 < \theta < 10^{1.34}. \end{cases} \quad (2)$$

The η_{\max} value calculated from the approximated spectrum differs by 20% from the experimentally obtained value. This approximation could be considered adequate for the purposes of the present work.

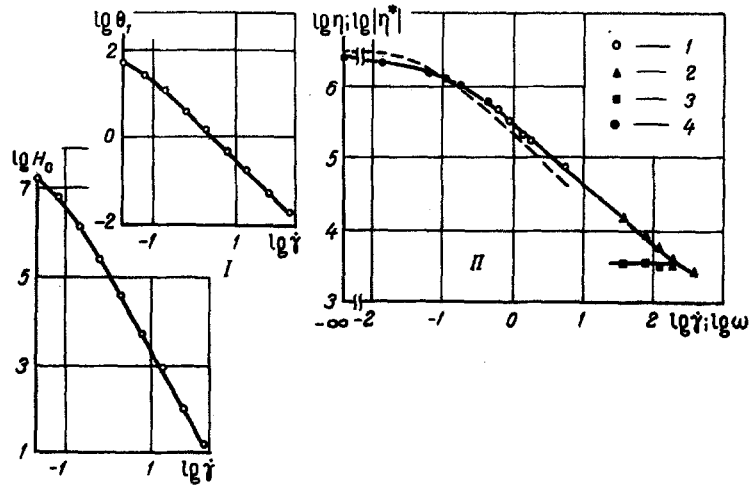


Fig. 4. I) Dependence of the parameters of the conditions determining the cutoff of the long-time part of the effective spectra and II) dependence of the effective viscosity upon the shear rate and dependence of the absolute value of the complex dynamic viscosity upon the frequency at small deformation amplitudes. 1) Torsion pendulum; 2, 3) vibratory rheometer; 4) capillary viscosimeter; the solid line denotes experimental data, and the dashed line, calculated results. H_0 expressed in dyne/cm²; Θ_1 , in sec; Ω , in p; and $\dot{\gamma}$ and ω , in sec⁻¹.

Let us determine the long-time sections of the cutoff or effective relaxation spectra for various $\dot{\gamma}$ values; we base our considerations upon the above relation between $\dot{\gamma}$ and $\dot{\gamma}_{\max}$. The long-time section of the function $H_e(\Theta)$ was approximated by a power function with a constant exponent (equal to -1.75), i. e., with the same exponent as the long-time section of the initial spectrum. The approximation for various $\dot{\gamma}$ values is indicated by the inclined dash-dot lines which intersect the initial relaxation spectrum at points determined by the relation $\log(1/\Theta) = \log \omega = \log \dot{\gamma}$. The cutoff limits of the $H_e(\Theta)$ spectrum at long relaxation times are given by points at which the function H on the dotted lines (Fig. 3) becomes equal to the smallest H value for the approximated initial relaxation spectrum (unfilled circles). Let us denote the longest relaxation times of the cutoff relaxation spectra by Θ_1 , and the relaxation time corresponding to the intersection points of the inclined dash-dot lines with the initial approximation spectrum, by Θ_2 . The equation of the straight lines which describe the long-time section of the effective relaxation spectra is $\log H(\Theta) = \log H_0(\dot{\gamma}) - 1.75 \log \Theta(\dot{\gamma})$. The approximation of the effective relaxation spectra can be stated in the form

$$H_e = \begin{cases} H_0(\dot{\gamma})\Theta^{-1.75}, & \Theta_2 < \Theta < \Theta_1; \\ 1.2 \cdot 10^5 \Theta^{-0.114}, & 0 < \Theta < \Theta_2. \end{cases} \quad (3)$$

The functions $H_0(\dot{\gamma})$ and $\Theta_1(\dot{\gamma})$ are shown in Fig. 4, I. The Θ_2 values satisfy the condition $H_0(\dot{\gamma})\Theta^{-1.75} = 1.2 \cdot 10^5 \Theta^{-0.114}$.

With proper consideration of the cutoff of the long-time part of the spectrum at increasing shear rates, i. e., with the known $H_e(\Theta)$ and with Eqs. (1) and (3), we can calculate the effective viscosity for various shear rates. Let us discuss the results of the calculations (see Fig. 4, II). The filled circles indicate the effective viscosity figures which were experimentally obtained during continuous deformations. The unfilled circles and filled triangles denote the experimentally measured absolute values of the complex dynamic viscosity. The filled squares indicate the absolute values of the complex dynamic viscosity measured during cyclic deformations with large amplitudes, the deformation being equivalent to a continuous stationary flow having the shear rate 200 sec^{-1} . The dashed curve indicates the $\eta(\dot{\gamma})$ dependence which was obtained with calculations according to the above-described method and with the data displayed in Fig. 4, II, i. e., when Eqs. (1) and (3) were taken into account in the calculations. It follows from Fig. 4, II that the cutoff which we introduced in our work for the long-time part of the spectrum can adequately account for the viscous properties of the polymer under non-Newtonian flow conditions. The discrepancy between the calculated

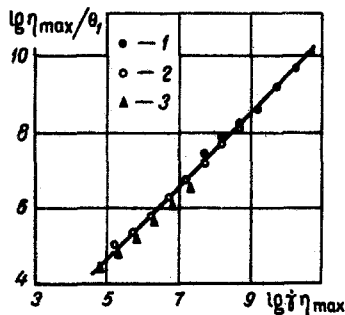


Fig. 5

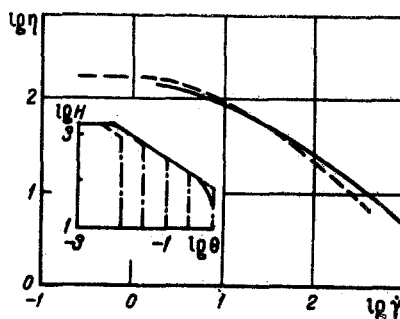


Fig. 6

Fig. 5. Universal representation of the relaxation time at which the effective relaxation spectra are cut off. 1) Polyisobutylene; 2 and 3) polypropylene. θ_1 and η_{\max} expressed in dyne/cm².

Fig. 6. Dependence of the effective viscosity of a polyisobutylene solution in cetane [7] upon the shear rate (the solid curve refers to experimental data; the dashed curve, to calculated values). η expressed in p.

and experimental $\eta(\dot{\gamma})$ values in the region of large $\dot{\gamma}$ values can be explained by the importance of the short-time part of the spectrum, which we did not determine at the shear rates considered.

For each critical value of the deformation rate and the corresponding frequency, the deformation work can be assumed to amount to

$$E_{\text{cr}} = 4\pi^3 |\eta^*| (\dot{\gamma}_{\max}^{\text{cr}})^2 \omega^{-1} \simeq 2.4 \cdot 10^5 \text{ erg/cm}^3. \quad (4)$$

This deformation work is five times greater than that obtained in the case of polyisobutylene [6].

Since θ_1 characterizes the relaxation time corresponding to the cutoff of the effective relaxation spectrum, we may expect that the function $\theta_1(\dot{\gamma})$ must be a characteristic parameter of the polymer. The $\theta_1(\dot{\gamma})$ dependences which were plotted in log-log coordinates with the data of [6] for polyisobutylene and for two polypropylenes the initial viscosities of which differed by the factor 20, are straight lines with identical slopes. Coincidence, which can be obtained by appropriately normalizing the straight lines, is of great interest. Coincidence results when the initial viscosity is chosen as the normalizing parameter. With this normalization, the quantity η_{\max}/θ_1 is an analog to the modulus for a Maxwellian element with the viscosity η_{\max} and the relaxation time θ_1 . When we use the concept of a reduced shear rate, we can plot the function $\eta_{\max}/\theta_1 = \Psi(\dot{\gamma}\eta_{\max})$ as shown in Fig. 5. Coincidence of the functions $\eta_{\max}/\theta_1 = \Psi(\dot{\gamma}\eta_{\max})$ for the various polydisperse polymers indicates that the cutoff of the relaxation spectra of these polymers extends to Maxwellian elements with equal moduli, when the reduced shear rate is the same. The equation of the function $\eta_{\max}/\theta_1 = \Psi(\dot{\gamma}\eta_{\max})$ can be written in the form:

$$\theta_1 = 2.8/\dot{\gamma}. \quad (5)$$

A universal relaxation spectrum exists for polydisperse linear polymers [11]. It has been shown in the present work that the cutoff of the relaxation spectra of linear polymers occurs always in the same form and as described by Eq. (5). In other words, there exists a unique relation between the shear rate in continuous deformations and the relaxation time corresponding to the cutoff of the relaxation spectrum. This behavior was predicted in [12, 13], and the present work has established the analytic form of the relation between the shear rate and the corresponding relaxation time for which a cutoff of the spectra is observed.

Thus, when only the initial relaxation spectrum of the polymers is known, Eq. (5) and the relations of the linear theory of viscoelasticity can be used to calculate the viscoelastic functions for various shear rates and for stationary flow conditions. Tanner's data [7] can be used to check the calculation method. Tanner made his measurements on a polyisobutylene solution in cetane. The initial relaxation spectrum and the cutoff relaxation spectra were determined in a rather wide interval of shear rates by superimposing a cyclic deformation with small amplitudes upon the quasi-stationary flow of the polyisobutylene solution in cetane. The initial relaxation spectrum which had been obtained by Tanner is indicated by the solid line in the insert of Fig. 6. The initial spectrum was approximated and cut off as shown by the dash-dot lines of

the figure. The cutoff and the above relationships were thereafter used to calculate the dependence of the effective viscosity upon the shear rate (dashed line). This dependence agrees strongly with the experimentally obtained dependence (solid curve). We note that Tanner's cutoff relaxation spectra result in the same dependence of the effective viscosity upon the shear rate.

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