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 \( \log \dot{\gamma} = \log \dot{\gamma}_{\text{max}} + \log a \) exists between the deformation rate \( \dot{\gamma}_{\text{max}} \) 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 \( \eta' \) denotes the real component or the so-called dynamic viscosity, and \( \eta'' \), the imaginary component. Measurements were made at various deformation amplitudes \( \gamma_0 \) and frequencies \( \omega = 2\pi f \), where \( f \) denotes the...
The effective viscosity \( \eta = \tau/\gamma \) was measured along with the dynamic characteristics, where \( \tau \) and \( \gamma \) denote the tangential stress and the shear rate, respectively.

*Moplen* polypropylene having an initial viscosity \( \eta_{\text{max}} = 2.5 \times 10^6 \) 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 \( 10^{0.3} \) 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, 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. The quantity \( |\eta^*| \) is independent of \( \gamma_{\text{max}} \) at each given frequency, until \( \gamma_{\text{max}} \) has reached a critical value \( \gamma_{\text{CR}} \) at which the function \( |\eta^*| = \Phi_1(\gamma_{\text{max}}) \) 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 \( \gamma_{\text{max}} < \gamma_{\text{CR}} \). The envelope of the curves \( |\eta^*| = \Phi_1(\gamma_{\text{max}}) \) 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 \( \gamma_{\text{CR}} \) which correspond to the transition into the envelope depend only slightly upon the frequency (in the frequency range considered, the deviations from \( \gamma_{\text{CR}} \) amount to 9%). Since \( \gamma_{\text{max}} = \gamma_0^\omega = \gamma_0 \omega/2\pi \), the values \( \gamma_0^\omega \) can be assumed constant in a first approximation. This means that \( \gamma_{\text{max}} \) is proportional to \( \omega \) and the envelope \( |\eta^*| = \Phi_1(\gamma_{\text{CR}}) \) must be shifted along the abscissa relative to the function \( |\eta^*| = \Phi_2(\omega) \) or \( |\eta^*| = \Phi_2(\gamma) \) by the amount \( \log \gamma_{\text{CR}}^\omega/2\pi = \log a \). Interestingly enough, in investigations in which polyisobutylene of low molecular weight was examined, the corresponding shift along the log \( \gamma_{\text{max}} \) 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 \( \gamma_{\text{max}} \). 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 \( 10^{-0.2} \) to \( 10^{0.8} \) sec\(^{-1} \), and with the vibratory rheometer in the frequency range \( 10^{1.6} \) to \( 10^{2.6} \) 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 \( \gamma = \omega \). 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