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DYNAMIC CHARACTERISTICS OF POLYMERS IN THE VISCOUS-FLOW STATE IN THE REGION OF SOUND FREQUENCIES

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Although by the present time an enormous amount of material has been accumulated on the study of the dynamic properties of polymers in the glassy and highly elastic states (^{1}), very little is known about polymers in the flow state. The studies of dynamic properties described below were carried out on the following polymers: polyisobutylene P-20 (molecular weight, according to Flory, of the order of 10^5), high-pressure polyethylene (alkathene-2), low-pressure polyethylene (hostalen, grade GD), and block polystyrene (GOST 9440–60), in the frequency range from $2 \cdot 10^2$ to $2.2 \cdot 10^3$ Hz over a wide temperature interval. This choice of objects made it possible to investigate both highly crystalline and amorphous polymers. Measurements of the dynamic properties were carried out on a frequency rheometer operating on the principle of electromagnetic transducers (^{1}, ^{2}) and briefly described in (^{3}). The instrument operates in the temperature interval -50–$+170^\circ$ in the range of sound frequencies and makes it possible to measure the complex shear modulus $G^* = G' + iG''$, where G' is the real part of the complex shear modulus, characterizing the elastic properties of the material, and G'' is the imaginary part, characterizing the losses. At the same time it is possible to determine the dynamic viscosity $\eta_\mathrm{d} = G''/\omega$, where ω is the angular frequency, and the tangent of the angle of mechanical losses, $\operatorname{tg}\delta = G''/G'$.

To check the reliability of measurements of viscoelastic characteristics on the rheometer, the measurement of η_d was compared with the effective viscosity of polymers η_e, which is determined under static conditions by the usual methods of viscometry. From (^{4}) it is known that the dependences of η_e on the rate of deformation ($\dot{\gamma}$) and of η_d on (ω) can be superposed and represented in the form of a single dynamic-static characteristic of the viscosity properties of polymer systems. A comparison was made of the results of measuring the dynamic viscosity of alkathene-2 at frequencies $2 \cdot 10^2$–$2.2 \cdot 10^3$ and at a temperature of 150° with data obtained on a constant-pressure capillary viscometer (^{5}) at rates of deformation 10^2–10^3 s^{-1}. Within one or two decimal orders of variation in deformation rates and frequencies, depending on the shear stress, the viscosity is approximated in double-logarithmic coordinates by a straight line. Extrapolation in double-logarithmic coordinates (deformation rates and angular

Fig. 1. Dependence of the elastic modulus on frequency and of the tangent of the mechanical-loss angle on the reduced frequency for low-pressure polyethylene

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frequencies, on the one hand, and shear stresses, on the other) of the results of dynamic measurements to the region of lower frequencies and deformation rates and of the results of static measurements to the region of higher deformation rates shows that, in the interval of deformation rates and frequencies from 10^2 to 10^4 s^{-1}, the discrepancy between the results of these independent measurements does not exceed 50% in the values of the shear stress. As shown in ([6], [7]), the dynamic-static characteristic of the viscosity properties of polymer systems can be represented in generalized form by using the following reduced viscosity quantities (denoted by the subscript "p"): $\eta_{\mathrm{ep}} = \eta_{\mathrm{e}}/\eta_{\mathrm{n}}$ and $\eta_{\mathrm{dp}} = \eta_{\mathrm{d}}/\eta_{\mathrm{n}}$,

of the deformation rate $\dot{\gamma}_{\mathrm{p}} = \dot{\gamma}\eta_{\mathrm{n}}$ and the angular frequency $\omega_{\mathrm{p}} = \omega\eta_{\mathrm{n}}$, where η_{n} is the maximum Newtonian viscosity, obtained directly from experiment or by extrapolating the values η_{e} or η_{d}, respectively, to zero values of $\dot{\gamma}$ and ω. Using the reduced parameters, on the one hand, and the universal temperature-invariant characteristic of the viscous properties of polymers, on the other, one can obtain a universal generalized temperature-invariant characteristic of the viscous properties of polymer systems. Knowing this characteristic, one can compare with it the dependence $\eta_{\mathrm{dp}} = f(\omega_{\mathrm{p}})$ obtained on a frequency rheometer at different temperatures. This was done for polyisobutylene P-20 and high-pressure polyethylene in the temperature ranges 20–80 and 110-150° and at frequencies $3 \cdot 10^2$–10^3 and $2 \cdot 10^2$–$2 \cdot 10^3$ Hz, respectively, and also for low-pressure polyethylene and polystyrene in the temperature ranges, respectively, 140–150 and 150° and at frequencies $2 \cdot 10^2$–$2.2 \cdot 10^3$ Hz. The discrepancy between the experimental results obtained on the frequency rheometer and the universal temperature-invariant characteristic (8) was within the limits of validity of this characteristic (±100%). It follows from this that, using both direct measurements of dynamic viscosity and the generalized dynamic-static characteristic, one can find the dependence of the effective viscosity on the deformation rate (in isothermally established flows) at high values of it. This is very important, since, because of intense heat evolution in highly viscous media at large deformation rates, measurements of viscosity in established flows present, under such conditions, great and sometimes insurmountable difficulties.

Fig. 1. Dependence of the elastic modulus on frequency and of the tangent of the mechanical-loss angle on the reduced frequency for low-pressure polyethylene

For all the polymers investigated, dependences $G^* = f(\omega)$ at different temperatures were also obtained. In Fig. 1, in double logarithmic coordinates, the dependence $G' = f(\omega)$ is given for low-pressure polyethylene. Lines 1-6 corre-

Fig. 2

Figure 2: Fig. 2

spond to temperatures of 20, 40, 60, 80, 100, 120°, when the polymer is in the solid state; lines 7-9 describe the behavior of the polymer melt at temperatures of 135, 140, 150°. Attention is drawn to the higher temperature coefficient of the dependence $G'(\omega)$ for the polymer in the flowing state. The application of the method of reduced variables (temperature-frequency superposition ([1,6,7])), which is now widespread, makes it possible to extend the effective frequency interval in experimental measurements. In doing this, an auxiliary function $\alpha_\mathrm{T} = f(T)$ is introduced, where α_T is the temperature reduction coefficient to some arbitrarily chosen temperature T_0, and $G^*_\mathrm{p} = f(\omega\alpha_\mathrm{T})$, where G^*_p is the dependence, reduced to the temperature T_0, of the function $G^* = f(\omega, T)$ only on frequency. To characterize mechanical losses it is convenient to use the quantity tangent of the mechanical-loss angle $\mathrm{tg}\,\delta = f(\omega\alpha_\mathrm{T})$, which is shown in Fig. 1 in semilogarithmic coordinates for low-pressure polyethylene by the dashed line; curves 10 and 11 correspond to the polymer in the crystalline state and to its melt. In the present case, the reduction temperature for the polymer in the solid state was chosen as 120°, and for the melt $T_0 = 150°$.

In Fig. 2, for polystyrene, the dependence $G' = f(\omega)$ is given in double logarithmic coordinates, and the dependence $\mathrm{tg}\,\delta = f(\omega\alpha_T)$ in semilogarithmic coordinates. Lines 1-9 (for temperatures 20, 40, 60, 85, 106, 120, 130, 140, 150°) characterize the change in G' of polystyrene during the transition from the glassy state to the highly elastic state, and then to the viscous-flow state. Attention is drawn to the change in the value of G' in the temperature range 106-120°, since it is precisely here, at the frequencies used in the present work, that the transition from the glassy to the highly elastic state is observed. In this case the reference temperature was chosen to be 150°.

Fig. 2. Dependence of the elastic modulus on frequency and of the tangent of the angle of mechanical losses on reduced frequency for polystyrene

From the data presented in Figs. 1 and 2, as well as those obtained for alkathene-2, it is seen that at comparatively high frequencies the shear moduli for highly elastic deformations in the melts of these polymers are of the order of 10^6–10^7 dyn/cm^2. The moduli of highly elastic deformation determined in the present work agree well, in order of magnitude, with those values obtained according to (9) from the data of work (8) at high deformation rates. On the other hand, the above-mentioned values of G' are approximately 10-100 times higher than those obtained in static measurements (10) from the slope of the initial portion of the shear stress-deformation curves at low deformation rates (from 20 sec^{-1}). This indicates a strong dependence of the shear moduli on the deformation rate in polymer melts. In the range of deformation rates and frequencies varying from 10 to 10^4 sec^{-1}, it may be assumed, as a first approximation, that the tangent of the angle of inclination of the curve of the dependence of the modulus on

Fig. 3

Figure 3: Fig. 3

Fig. 4. Relaxation-time spectra for low-pressure polyethylene and polystyrene

Figure 4: Fig. 4. Relaxation-time spectra for low-pressure polyethylene and polystyrene

frequency is 0.6–0.7.

Fig. 3. Dependences of the reduced elastic modulus on reduced frequency and of the temperature shift coefficient on temperature for low-pressure polyethylene and polystyrene

It should be noted that the dependence $G'' = f(\omega)$ for low-pressure polyethylene and for polystyrene has qualitatively the same character as does

the dependence considered above, $G' = f(\omega)$. During the melting of such polymers as polyethylenes, the value of G' decreases considerably more strongly than G'', which also accounts for the sharp increase in this region of the tangent of the angle of mechanical losses.

Figure 3 gives, in semilogarithmic coordinates, the dependence of the temperature shift coefficient $a_T = f(T)$ for low-pressure polyethylene (curves 1, 2, respectively, for the solid polymer and its melts) and for polystyrene (3). Here, in double-logarithmic coordinates, the function $G''_{\mathrm{p}}(\omega a_T)$ is also given for low-pressure polyethylene (curves 4, 5, respectively, for the solid polymer and its melts, and for polystyrene, 6). As is seen from Fig. 3, application of the principle of temperature-frequency superposition made it possible to cover an experimental range in reduced frequencies of up to ten decimal orders of magnitude.

Fig. 4. Relaxation-time spectra for low-pressure polyethylene and polystyrene

Measurements of the complex shear modulus make it possible to find the distribution function of relaxation times, which characterizes the relaxation spectrum of a polymer according to (1, 11). In the present work the relaxation-time spectrum function H with respect to the logarithmic distribution of relaxation times τ was used. The calculation of the function $H(\tau)$ was carried out according to the first approximation by the method of Ninomiya and Ferry (12). Curves 1, 2, 3 give the function $H(\tau)$ for low-pressure polyethylene (respectively for the polymer in the solid state, at a temperature of 135°, and for its melts); curve 4 gives the function $H = f(\tau)$ for polystyrene. As is seen from Fig. 4, the function $H(\tau)$ in the case of low-pressure polyethylene cannot be represented in the form of a single continuous curve for the solid polymer and its melts, since the character of the change in the structure of a highly crystalline polymer as a result of the phase transition does not permit use of the reduced-variables method in the form in which it is described in (1) for the region of the phase transition.

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