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Abstract

Full Text

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Rheology of Polymers. A Temperature-Invariant Characteristic of Anomalously Viscous Systems

The most detailed studies of the question of a temperature-invariant representation of data on the mechanical properties of polymers are due to Ferry and co-workers (ˆ1). They showed that the results of dynamic tests for a wide variety of elastomers can be represented in the form of a single common curve. This was achieved by parallel shifting–to superposition–of experimental curves obtained at different temperatures.

The first attempt to represent in invariant form the dependences of viscosity on flow regime belongs to Arveson (ˆ2), who studied the flow of lubricants. He, and later also Brunstrum et al. (ˆ3), showed purely empirically that, for the lubricants they studied, the curves of reduced viscosity versus rate of deformation are well superposed on one another under a parallel shift along the rate-of-deformation axis. Here the reduced viscosity was understood as the ratio of the viscosity of the lubricant under experimental conditions to the viscosity of the dispersion medium at the same temperature. However, Filippov (ˆ4), studying the flow of polyethylene melts, came to the conclusion that it is impossible to superpose experimental data into one common curve if a sufficiently wide range of rates of deformation is considered (up to 6–7 decimal orders).

Fig. 1. Experimental and invariant curves of the dependence of the "effective" viscosity of polyethylene on the rate of deformation.
1 –130°, 2 –150°, 3 –170°, 4 –190°, 5 –210°, 6 –230°.

Finally, Shott and Kagan (ˆ5) succeeded in superposing the curves of the dependence of viscosity on rate of deformation (over an interval of 2–2.5 decimal orders, obtained by them at three temperatures) for one of the polyethylenes studied. In doing so, however, they proceeded from fundamentally incorrect

Fig. 2

Figure 2: Fig. 2

considerations regarding the form of the dependence of effective viscosity on rate of deformation.

Let us represent the viscosity of a polymer system η, at a certain temperature T and rate of deformation D, in the form of a function: $\eta = \eta_{\text{n}} f(\tau, D)$. Here η_{n} denotes the greatest Newtonian viscosity of the system at the same temperature; and τ is the generalized relaxation time, as well as a dimensionless

time, but depends on the spectrum of relaxation times, i.e., $\tau = \varphi(\tau_1, \tau_2, \dots, \tau_n)$. In the simplest case the entire spectrum can be characterized by a single relaxation time. With regard to the form of the function φ, we note that it must be a homogeneous function of the first degree. This follows evidently from dimensional considerations.

The function f is dimensionless (since it is simply the ratio of two viscosities), while its arguments have dimensions reciprocal to one another. It also follows from dimensional considerations that f must be a function of the product of the arguments.

Fig. 2. Experimental and invariant curves of the dependence of the effective viscosity of polystyrene on the rate of deformation.
1—170°; 2—190°; 3—210°; 4—230°

V. A. Kargin and G. L. Slonimskii proposed a molecular-mechanical model that gives a good description of the main features of deformation of amorphous-liquid linear polymers (6). From this model, in particular, it follows that the k-th relaxation time τ_k is linearly related to the coefficient of viscous resistance. If, furthermore, following the works (1,7), we assume that τ_k is inversely proportional to the density ρ and the absolute temperature T, then one may write

$$\tau_k = a_k \frac{\eta_{\text{n}}(T)}{\rho T}.$$

It follows from this that the ratio of the relaxation time at a given temperature to that at a certain temperature taken as the reference temperature (all quantities referring to this temperature are hereafter denoted by a prime) is equal to:

$$\frac{\tau_k}{\tau'_k} = \frac{\eta_{\text{n}}(T)}{\eta'_{\text{n}}(T)} \frac{\rho' T'}{\rho T}. \tag{1}$$

If the values of τ_k determined by this formula are substituted into the function φ, then, obviously, by virtue of the homogeneity noted above we obtain the formula for reducing τ to the temperature T':

Fig. 3. Experimental and invariant curves of the dependence of the effective viscosity of polypropylene on the rate of deformation. 1 –190°; 2 –210°; 3 –230°; 4 –250°; 5 –270°; 6 –290°.

Figure 3: Fig. 3. Experimental and invariant curves of the dependence of the effective viscosity of polypropylene on the rate of deformation. 1 –190°; 2 –210°; 3 –230°; 4 –250°; 5 –270°; 6 –290°.

$$\tau = \tau' \frac{\eta_{\mathrm{n}}(T)}{\eta'_{\mathrm{n}}(T)} \frac{\rho' T'}{\rho T}.$$

Substitution of this expression into the general formula for viscosity leads to the expression:

$$\eta = \eta_{\mathrm{n}} f\left[D\eta_{\mathrm{n}}(T)\frac{\rho' T'}{\rho T}\frac{\tau'}{\eta'_{\mathrm{n}}(T)}\right]. \tag{2}$$

For a definite choice of the reference temperature T', the quantity

$$\frac{\tau'}{\eta'_{\mathrm{n}}(T)},$$

entering formula (2), will be constant; therefore η may be regarded as a function of the form:

$$\eta = \eta_{\mathrm{n}} f\left(D\eta_{\mathrm{n}}\frac{\rho' T'}{\rho T}\right).$$

Thus it is possible to replace the very complicated argument in the original expression by a single argument composed only of quantities directly observed in experiment. If we now denote η/η_{n} by η_{p} (reduced viscosity, a dimensionless quantity), and the argument of the function $D\eta_{\mathrm{n}}\frac{\rho' T'}{\rho T}$ by D_{p} (reduced shear rate, having, however,

dimension of the shear stresses), then we obtain: $\eta_{\mathrm{p}} = f(D_{\mathrm{p}})$—a single-valued functional dependence invariant with respect to temperature.

Thus, the proposed method is based on the following basic assumption: there is a linear relationship between τ_k and η_{n}, as follows from the works (^{6}). This, in particular, means that when the temperature changes,

Fig. 3. Experimental and invariant curves of the dependence of the effective viscosity of polypropylene on the rate of deformation.
1 –190°; 2 –210°; 3 –230°; 4 –250°; 5 –270°; 6 –290°.

all relaxation times change proportionally. This assumption coincides to a considerable degree with the assumption made by Ferry (^{1}) in developing his theory of the dependence of the viscoelastic properties of elastomers on temperature.

Often the dependence of viscosity on deformation rate is obtained over wide intervals of variation of the latter, which, in order to present this dependence in an acceptable form, presupposes the use of logarithmic coordinates. Then it is obvious that the temperature-invariant dependence of the experiment will be the dependence of $\log \eta_\mathrm{p}$ on $\log D_\mathrm{p}$. Let us also note that usually, for melts, the quantity $\frac{\rho' T'}{\rho T}$, for any choice of the reduction temperature T', differs only slightly from unity (as a rule, by no more than 6–8%), i.e., the values of $\log \frac{\rho' T'}{\rho T}$ lie within ± 0.03, which, for measurements over a range of several decimal orders in shear rates (usually from 3 to $7 \div 8$), is a negligible quantity. In some cases the term $\frac{\rho' T'}{\rho T}$ may be disregarded. Then the reduced rates of deformation may be calculated by the simplified formula:

$$D_\mathrm{p} = D\eta_\mathrm{n}(T) \quad \text{or} \quad \log D_\mathrm{p} = \log D + \log \eta_\mathrm{n}.$$

This means that the choice of the reduction temperature is not essential, since in practice the curves $\log \eta_\mathrm{p} = F(\log D_\mathrm{p})$ should coincide sufficiently well even without taking the temperature-density correction into account.

On the basis of the proposed method, flow curves were processed for the following polymer materials: high-pressure polyethylene, alkathene 2 (density at 20° 0.92; characteristic viscosity in tetralin at 75° 0.95; number-average molecular weight $3.2 \cdot 10^5$; degree of branching 3.7%), block polystyrene (density at 20° 1.054; weight-average molecular weight $3 \cdot 10^5$) and isotactic polypropylene (density at 20° 0.89; characteristic viscosity in decalin at 135° 3.5; content of atactic fraction 9%). The flow curves of these materials were obtained on a gas capillary constant-pressure viscometer (^{8}). The viscosity values were determined

with errors not exceeding ±5%. The effective viscosity of the molten polymer was calculated by the Weissenberg method, taking inlet effects into account (^{9}).

Figures 1, 2, and 3 present curves of the dependence of the effective viscosity of the materials studied on the rate of deformation over a wide temperature range. The same experimental data are also shown there in transformed form in accordance with equation (2). The values of the highest Newtonian viscosities used in the calculation are presented in Fig. 4. As is evident from these figures, the experimental data given, with a sufficient degree of accuracy, fall for each polymer on a single invariant curve. The only exceptions were those viscosity values obtained near the melting temperature (curves 1 in Figs. 1 and 3). Apparently, this is connected with the fact that at these temperatures it was not possible to obtain reliable values of η_n.

Fig. 4. Dependence of the highest Newtonian viscosities of polyethylene (1), polystyrene (2), and polypropylene (3) on temperature

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The results obtained confirm the validity of the proposed method for transforming experimental data into an invariant generalized dependence and show that reliable determination of the magnitude of the highest Newtonian viscosity is of primary importance for characterizing anomalously viscous systems.

The coordinate-reduction method described can be used as a method for checking the agreement of experimental data with one another, or for calculating viscosity values over a considerably wider range of rates of deformation than could be obtained experimentally.

To obtain complete data on the change in viscosity as a function of flow regime over a wide range of temperatures and rates of deformation, it is sufficient to obtain a flow curve at any one temperature, and also to determine the highest Newtonian viscosities at three or four temperatures in the interval of interest to the investigator; then, using the reduced-coordinate method, one can calculate the effective viscosities at various temperatures and rates of deformation. The need to determine η_n at three or four temperatures is connected with the fact that, as is evident from Fig. 4, the dependence $\log \eta_\mathrm{n}$ on $1/T$ is often nonlinear. Straightening the curves for the dependence $\log \eta_\mathrm{n} = f(1/T)$ can probably be achieved by using double-logarithmic coordinates.

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Note: Figure translations are in progress. See original paper for figures.