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Abstract

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RHEOLOGY OF POLYMERS. ON THE UNIVERSALITY OF A TEMPERATURE-INVARIANT CHARACTERISTIC OF THE VISCOSITY OF POLYMERS IN THE CONDENSED STATE

The dependence of the effective viscosity η_e of polymer systems on the rate of deformation D may be represented in the form of the function $\eta = \eta_H F(D\theta)$, where η_H is the greatest Newtonian viscosity (at $D \to 0$), and θ is the characteristic relaxation time ([1,2]). The form of the function $F(D\theta)$ in different theories varies. We have shown ([3]) that, irrespective of the form of $F(D\theta)$, the effective viscosity may be represented as the product of two functions, one of which depends only on temperature and the other only on the rate of deformation. Using the concepts of reduced viscosity $\eta_p = \eta_e/\eta_H$ and reduced rate of deformation $D_p = D\eta_H$, one may obtain an invari–

Fig. 1. Universal temperature-invariant viscosity characteristic.
1 –high-pressure polyethylene (according to ([3])): a–170°, –190°, –210°, –230°;
2 –polypropylene (according to ([3])): a–190°, –210°, –230°, –250°, –270°;
3 –polystyrene (according to ([3])): a–170°, –190°, –210°, –230°;
4 –polyethylene I (according to ([4])): a–108°, –125°, –140°, –174°, –206°, –230°;
5 –polyethylene II (according to ([4])): a–112°, –125°, –175°, –190°, –250°;
6 –polyethylene (according to ([5])): a–130°, –150°, –170°, –190°, –210°;
7 –polyvinyl butyral (according to ([4])): a–119°, –125°, –139°, –155°;
8 –natural plasticized rubber (according to ([6])): a–50°, –60°, –80°, –100°, –120°, –140°;
9 –polyisobutylene (our data): a–5°, –0°, –10°, –20°, –40°, –60°, –80°, –100°;
10 –synthetic rubber "goroprene" (our data): a–40°, –60°, –80°, –120°.

···function $\eta_p(D_p)$ invariant with respect to temperature and, correspondingly, the curve of the dependence of the reduced viscosity on the reduced rate of deformation, invariant with respect to temperature.

Figure 2

Figure 2: Figure 2

Figure 1 shows that, when the data from which temperature-invariant flow curves of linear polymers are constructed are plotted on a single graph in the coordinates $D_{\text{p}}, \eta_{\text{p}}$, for polymers differing greatly in the flexibility of their macromolecules, a narrow band is formed. The greatest scatter of experimental points is observed in the middle part of this band, where, however, the maximum deviation from the curve averaging the dependence does not exceed 250%. In constructing Fig. 1, we used previously published data for high-pressure polyethylene, polypropylene, polystyrene ([3]), for polyisobutylene with molecular weight $2 \cdot 10^4$ (according to Staudinger) on the basis of measurements in a constant-pressure capillary viscometer and in a cone–plate rotational viscometer, for the synthetic rubber "Coroprene" (from experiments in a capillary viscometer), as well as literature data for three grades of polyethylene ([4,5]), polyvinyl butyral ([4]), and natural plasticized rubber ([6]). The field of points in Fig. 1 corresponds to 51 curves $\eta_{\text{p}}(D_{\text{p}})$ for various polymers at different temperatures. The continuous curve in the field of points in Fig. 1 gives the averaged universal temperature-invariant characteristic of polymers in the condensed state. It is characteristic that experimental viscosity data for cellulose acetate, a polymer possessing very rigid molecules, also fall within the same band (these points are not shown in Fig. 1).

Fig. 2. Comparison of the experimental universal viscosity characteristic with existing formulas (for the designations of the curves, see the text)

It follows from ([3]) that

$$\eta = \eta_{\text{n}} F\left(D_{\text{p}} \frac{\theta'}{\eta_{\text{n}}}\right).$$

The quantities marked with a prime refer to a certain reference temperature, the choice of which, owing to the smallness of the temperature-density correction, is immaterial. Let us take $\theta/\eta_{\text{n}} = 1/G$, where G depends only weakly on temperature. The suggestion that G is the shear modulus of polymers at low rates of deformation, when the flow process has not yet affected their structure, may undoubtedly be of interest.

From the comparison of the temperature-invariant curves of various polymers presented in Fig. 1, it follows that, when reduced parameters are used, the viscous properties of linear polymers can be described, to a first approximation, by one universal dependence, invariant both with respect to temperature and with respect to the kind of polymer. From the universality of the temperature-invariant characteristic of the viscosity of polymers there follow two most important conclusions: first, the independence of the form of the function $F(D_{\text{p}}/G)$ from the nature of linear polymers and, second, the fact that G depends only

weakly not only on temperature but, most importantly, also on the nature of linear polymers in the viscous-flow state. What has been said is valid to within the scatter of experimental measurements relative to the averaged universal characteristic of the viscous properties of polymers and for the temperature interval represented by the data of Fig. 1.

The construction of flow curves of polymer solutions in reduced coordinates revealed the following tendency. At low polymer content in the system, the flow curves differ sharply in form and position from the universal viscosity curve. As the polymer content in the system increases, the viscosity curves in reduced coordinates approach the universal curve more and more closely, both in form and in position; moreover, the region of the lowest Newtonian viscosity shifts toward larger values of D_{p}.

The universal characteristic of the viscosity properties of polymers presented in Fig. 1 was compared with several equations known from the literature for the dependence $\eta = \eta_{\text{p}} \cdot F(\theta D)$. Assuming, as before, that $\theta = \eta_{\text{n}}/G$, various formulas known from the literature can be represented using the variables η_{n} and D_{p}.

Figure 2 gives a comparison of the universal viscosity characteristic of polymers with equations proposed for describing the dependence of viscosity on the rate of deformation. Here curve 1 gives the universal characteristic of the viscosity properties of polymers found above. Bueche found that his theoretical formula does not describe the viscosity curve of polymer systems sufficiently well. He therefore proposed two empirical functions: for solutions and for polymer melts ([7]). The first of these,

$$\frac{1}{\eta_{\text{p}}} = 1 + CD_{\text{p}}^{1/2}$$

corresponds in Fig. 2 to curve 2 (parameter $C = 5 \cdot 10^{-3}$). The second:

$$\frac{1}{\eta_{\text{p}}} = 1 + CD_{\text{p}}^{3/4}$$

corresponds to curve 3 ($C = 1 \cdot 10^{-4}$). Curve 4 was constructed according to the Eyring formula ([8]). In the case of the use of reduced variables, this formula takes the form

$$\eta_{\text{p}} = \frac{1}{CD_{\text{p}}} \ln \left[CD_{\text{p}} + \sqrt{(CD_{\text{p}})^2 + 1} \right],$$

where $C = 1 \cdot 10^{-5}$. Curve 5 was constructed according to the Gurevich formula ([9]), which was used in the form:

$$\frac{\lg \eta_{\text{p}}}{\eta_{\text{p}}} = -CD_{\text{p}}.$$

Here $C = 4 \cdot 10^{-6}$. Curve 6 was constructed according to the de Witt formula ([10])

$$\frac{1}{\eta_{\text{p}}} = 1 + CD_{\text{p}}^2$$

with $C = 1 \cdot 10^{-12}$.

It is evident from Fig. 2 that none of the proposed formulas for the dependence $\eta_{\text{a}}(D)$ describes the true universal characteristic of the viscosity properties of polymers over a sufficiently broad range of variation of the variables.

Curve 1 may be approximated, for example, by the following empirical equation

$$1/\eta_{\text{p}} = 1 + 0.4\left|D_{\text{p}}/C\right|^{0.355} + \left|D_{\text{p}}/C\right|^{0.71}$$

with $C = 1.32 \cdot 10^5$ dyn/cm^2. It should be noted that the constant C, to within a constant factor, is equal to the shear modulus G. Other approximate analytical forms of representing the universal viscosity characteristic are, of course, also possible.

The existence of a universal characteristic of the viscosity properties of linear polymers is explained by the cooperative character of the process of deformation of macromolecules in flow and indicates that the influence of the rate of deformation on molecular interaction and on the destruction of supramolecular structures in polymers in the viscous-flow state, irrespective of their nature, has, at least qualitatively, the same character. In existing theories of the viscosity of polymer systems, a similar assumption is made ([11]). It is assumed that the statistical factor reflecting the interrelation of the motion of molecular-kinetic

units, identical for all linear polymer molecules. However, such an assumption becomes invalid for dilute polymer solutions, whose viscosity depends mainly on the interaction of high-molecular-weight substances with the low-molecular-weight solvent.

The influence of intermolecular interaction on viscosity was previously taken into account formally in Bueche' s theory ([1]). Bueche also found ([12]) that one of the empirical equations he proposed can be used to describe the viscous properties of certain polymer systems ([7]).

Knowledge of a universal characteristic of the viscous properties of linear polymers makes it possible to carry out approximate calculations of their effective viscosity over a wide range of deformation rates and temperatures, if the values of the highest Newtonian viscosity are known for them. The invariance of the

relation between reduced viscosity and reduced deformation rate with respect to temperature and to the nature of the polymer is of important theoretical significance, since it indicates that, in reduced states, deformable linear polymers behave identically regardless of their nature. The highest Newtonian viscosity η_n is indeed a measure of the difficulty of cooperative displacement of segments, and this manifests itself over a wide range of deformation rates. Therefore, the reduced state is characterized by the effective stresses at which a definite state of linear polymers in the visco-fluid state is attained.

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