

VISCOSITY OF THIXOTROPIC MATERIALS IN DEPENDENCE ON TIME

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Approximative relations were derived for viscosity of liquids with rheotropic behaviour in dependence on time, based on the theory of non-elastic flow. A method is proposed for determination of the upper limit of all relaxation times from experimental dependence $\eta(t)$ based on box distribution of relaxation times under certain simplifying assumptions.

Behaviour of materials with the viscosity dependent on time such as thixotropic, rheopexic materials *etc.* at shear strain is characterized by the shape of rheograms *i.e.* by formation of hysteresis loops. According to the shape of these loops it is possible in majority of cases to determine the type of material in respect to the dependence of viscosity on time. But if these curves have a more complex character *e.g.* when their certain parts correspond both to the increasing and decreasing velocity gradient, *i.e.* when they are not monotonic or if they cross each other, it is necessary to apply the consecutive measurement of stress relaxation with which it can be determined whether the material concerned is not a viscoelastic one^{1,2}. An experimental study of rheologic behaviour of non-elastic materials with the viscosity dependent on time, the time dependence of the instantaneous viscosity at various values of the velocity^{3,4} gradient is usually determined.

Here an effort has been made to find a formal description of viscosity in dependence on time for the constant velocity gradient. For determination of the relaxation time is either used a model with discrete distribution of relaxation times or a model of box distribution. Applicability of the proposed method has been verified for three samples of block copolymers propylene oxide-ethylene oxide.

THEORETICAL

The theory of time dependent non-elastic flow⁵ has been applied for the analysis of stationary laminar shear. According to this theory the value of the instantaneous apparent viscosity in time t given by

$$\eta(t) = \tau(t)/D, \quad (I)$$

is in general determined by the specific form which depends both on the type of motion as well as on the distribution function of relaxation times of the studied material. The description of the stationary shear taking place is given by the function

$$f[I_2(t'), I_3(t'), X] \equiv f(I'_2, I'_3, X), \quad (Ia)$$

where t' is a certain fixed time, X is characterizing the geometry of the equipment in which the shear takes place, $I_2 \equiv D_{ij}D^{ij}$, $I_3 \equiv \det D_{ij}$, $D_{ij} \equiv \frac{1}{2}(u_{ij} + u_{ji})$. Mostly it is possible to substitute for the function $f(I'_2, I'_3)$ the polynomial in I'_2, I'_3 . For the laminar stationary shear ($I_3 = 0$) it is possible to substitute for the function $f(I'_2)$ the product

$$f(I'_2) = f(I) \varepsilon(t'), \quad (2)$$

where $\varepsilon(t')$, defined by the equations

$$(t') = 0 \quad \text{for} \quad -\infty < t' < 0, \quad (3a)$$

$$(t') = I \quad \text{for} \quad 0 \leq t' < \infty, \quad (3b)$$

is the Heviside's step function and $f(I)$ is determined for the given experiment by the invariants of the tensor of velocity deformation I'_2, I'_3 . To solve this problem analytically it is necessary to model the actual distribution function of relaxation times by as simple function as possible. The simplest case suitable for actual liquids with the viscosity dependent on time is represented by the Dirac's function

$$\delta(\theta - \theta_0) = 0, \quad \theta \neq \theta_0, \quad (4a)$$

$$\int_{-\infty}^{+\infty} \delta(\theta - \theta_0) d\theta = 1, \quad (4b)$$

where $R(\theta) = 0$ for $\theta \neq \theta_0$, $R(\theta) = R_0$ for $\theta = \theta_0$.

Then

$$\eta(t) = \eta_0 - A(1 - e^{t/\theta_0}), \quad (5)$$

where $\eta_0 \equiv \eta(t = 0)$; $A > 0$ is constant for the given experiment. The curves $\eta(t)$ are monotonically descending and are asymptotically approaching at certain value η_∞ which is the lower the higher is the shear velocity. By taking the limit for $t \rightarrow \infty$ in Eq. (5) the constant $A = \eta_0 - \eta_\infty$ is determined. Eq. (5) then gets its final form

$$\eta = \eta_0 - (\eta_0 - \eta_\infty) e^{-\beta t}, \quad \beta \equiv 1/\theta_0. \quad (6)$$

The simple dependence $\eta(t)$ determined by Eq. (6) will not be satisfactory for description of viscosity in dependence on time of actual materials. The plot according to Eq. (6) is usually situated above the experimentally determined curve $\eta(t)$ and differences between the actual and theoretical values are the greater the more complex is the internal structure of the compound studied. For block copolymers propylene oxide-ethylene oxide a more complex behaviour has been found than that described by the Dirac's model. Nevertheless, this model has been applied as the first approximation. The value β was being determined so that limiting values η_0 and η_∞ for the model compound were the same as for the actual compound and the value η_∞ had been practically reached for both compounds in about the same time interval.

To obtain a better mathematical description of the time dependence it is necessary to characterize the matter by a more general distribution *i.e.* by a continuous distribution of relaxation times. The simplest continuous distribution is the box distribution. Let us study the case

$$R(\theta) = 0, \quad \theta \in \text{ext} \langle \theta_{\min}, \theta_{\max} \rangle, \quad (7a)$$

$$R(\theta) = R_0, \quad \theta \in \langle \theta_{\min}, \theta_{\max} \rangle, \quad (7b)$$

where θ_{\min} , θ_{\max} are minimum and maximum relaxation times of the model $0 \leq \theta_{\min} < \theta_{\max} < \infty$. In such case, the instantaneous viscosity in time t is given by

$$\eta(t) = \eta_0 - A[1 - BE(t)], \quad (8)$$

where

$$E(t) \equiv \int_{\theta_{\min}}^{\theta_{\max}} e^{-t/\theta} d\theta. \quad (9)$$

The curves $\eta(t)$ according to Eq. (8) have the analogous form as for the case of distribution of relaxation times given by the Dirac's δ -function, but in general they are steeper *i.e.* they approach the limiting value η_∞ in a shorter time interval. For simplification we will assume further on that θ_{\min} is so small that it can be substituted in the calculation by the zero value. Then it holds

$$E(t) = \int_0^{\theta_{\max}} e^{-t/\theta} d\theta, \quad (10)$$

$$E(0) = \theta_{\max}, \quad E(\infty) = 0.$$

From Eq. (8) the constants A , B ; $A = \eta_0 - \eta_\infty$, $B = 1/\theta_{\max}$ are determined. Then it holds

$$\frac{\eta_0 - \eta}{\eta_0 - \eta_\infty} = 1 - \frac{E(t)}{\theta_{\max}}. \quad (11)$$

On the left hand side of Eq. (11) is the function which can be easily determined experimentally, on the right hand side is, additionally to numerical constants, only the looked for parameter θ_{\max} . Therefore it is necessary to find a suitable approximation of the function $E(t)$ so that Eq. (11) can be practically solved for concrete times. By introducing the new variable $x \equiv -t/\theta$ into Eq. (10) the relation is obtained

$$E(t) = \int_{-\infty}^{-t/\theta_{\max}} \frac{t e^x}{x^2} dx, \quad (12)$$

$$\frac{E(t)}{t} = \left[-\frac{e^x}{x} \right]_{-x}^{-t/\theta_{\max}} + \int_{-\infty}^{-t/\theta_{\max}} \frac{e^x}{x} dx. \quad (13)$$

The second term in Eq. (13) is the integrally exponential function E_i . Since $-t/\theta_{\max} < 0$, the integral exists and equals to

$$E_i = C + \ln \left| \frac{-t}{\theta_{\max}} \right| + \frac{-t/\theta_{\max}}{1 \cdot 1!} + \frac{(-t/\theta_{\max})^2}{2 \cdot 2!} + \dots \quad (14)$$

For small t , expansion of the first term in Eq. (14) can be made and the first terms of the expansion can be used up to the second power of $1/\theta_{\max}$. After arrangement an approximate equation for θ_{\max} is obtained

$$\frac{\eta_0 - \eta}{\eta_0 - \eta_\infty} = - \frac{t}{\theta_{\max}} (-1 + C + \ln t) + t \frac{\ln \theta_{\max}}{\theta_{\max}} + \frac{3}{4} \frac{t^2}{\theta_{\max}^2} + \dots \quad (15)$$

If two different small times t and the corresponding values are substituted into Eq. (15), two equations are obtained in which only the unknown quantity θ_{\max} appears. If these both equations are divided by the corresponding value of t , their difference is a simple quadratic equation for determination of θ_{\max} .

EXPERIMENTAL

To verify that the proposed method is applicable, three samples of block copolymers propylene oxide-ethylene oxide were used of the type Slovanik (Chemical Works W. Pick, Nováky). The content of ethylene oxide was in the sample denoted by the number 330-30%, in 340-40% and in 350-60%. The molecular weight of all three samples was 950. Densities of individual samples for No 330, 340 and 350 were 1.0454, 1.0726 and 1.0697 and the pH values were 11.06, 10.33 and 9.67.

For measurements of viscosity the Weissenberg's rheogoniometer of the type R 18 (Sangamo Controls Ltd., London) was applied, density was determined pycnometrically, pH by the pH meter M 26 (Radiometer Ltd., Copenhagen) with the calomel and glass electrodes. All measurements were made at the temperature $20 \pm 0.2^\circ\text{C}$.

RESULTS AND DISCUSSION

Rheograms of individual samples of block copolymers of propylene oxide-ethylene oxide denoted by No 330, 340 and 350 formed by characteristic hysteresis loops are given in Fig. 1. With increasing content of ethyleneoxide the position of the loop on the plot $\tau-D$ is changing so that for reaching the same value of shear stress taken in corresponding parts of loops a greater shear velocity is needed. The differences in shear velocities are about one order of magnitude.

At first the model with the Dirac's distribution of relaxation times has been applied. The value of β has been chosen so that the limiting values of η_∞ for the model compound would be the same as for the actual compound under the assumption that this

limiting value is practically reached for both compounds in about the same time. Table I gives the limiting viscosities and the corresponding values of β for individual samples. As is obvious from this Table, the asymptotic viscosity values corresponding to the same sample are greater for smaller D for limiting values of the velocity gradient, which is in agreement with the theoretically expected values. The graphical plot of Eq. (5) for individual experiments with their constants given in Table I are plotted in Fig. 2. In agreement with the statement already made in the theoretical part of this study, all experimental viscosities for finite times are smaller than would correspond to the liquid with the discrete distribution of relaxation times. The differences between the theoretical and actual values are considerable which is especially true for short times. Therefore we consider this model to be unsatisfactory and it can be used only for a rough estimate of a certain curve which is from the upper end limiting the actual values. Mathematically speaking the result can be formulated

$$\prod_{t \in (0, \infty)} [\eta_D(t) > \eta(t) > \eta_\infty], \quad (16)$$

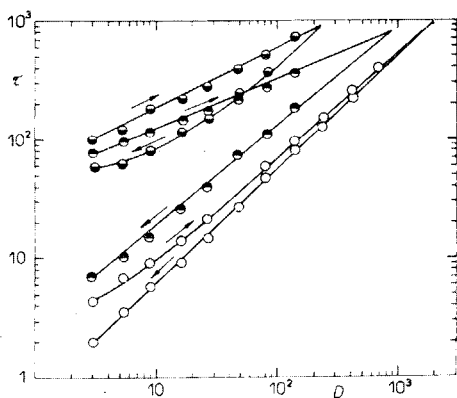


FIG. 1

Rheograms of Block Copolymers of Propylene Oxide and Ethylene Oxide

Sample: 330 ○, 340 ●, 350 ◐.

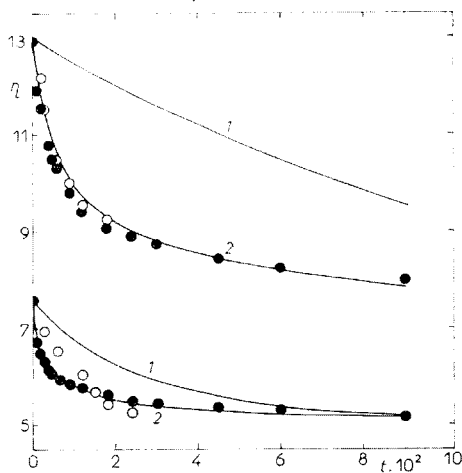


FIG. 2

Viscosity in Dependence on Time for Two Velocities of Deformation for the Sample No 330

Curves: 1 Dirac's distribution of relaxation times, 2 theoretical curve approximating the given dependence; Points: ● experimental, ○ calculated for the compound with the box distribution of relaxation times for $\Theta_{\min} = 0$.

where $\eta_D(t)$ is the calculated value of η for the compound with the discrete distribution of relaxation times according to Eq. (6).

For the formal analytical expression of the experimentally found time dependences we have assumed that during the shear such change in the internal structure takes place that we can speak of a certain relaxation time but even this value must be considered variable. For this purpose was for all the measurements calculated the corresponding value of β from Eq. (6). The calculated $\beta = \beta(t)$ in the logarithmic plot gives in the whole range of considered times a linear dependence $\log \beta = k \log t + q$. By taking the corresponding constants k and q , the analytical expression of the function $\beta = \beta(t)$ has been obtained nearly for the whole range of times considered; these constants are also given in Table I. By combining the data from Table I with Eq. (9) for individual samples of block copolymers propylene oxide-ethylene oxide, the time dependence of viscosities is obtained

$$\eta = a + b e^{-\gamma t^z}, \quad (17)$$

with the following values of γ and z

Sample	330	330	340	340	350	350
D, s^{-1}	16.2	437.4	9.0	81.0	9.0	145.8
γ	0.54	0.98	0.36	1.48	0.45	0.66
z	0.37	0.45	0.36	0.27	0.45	0.66

In Fig. 2 (curve denoted by No 2) is given the time dependence of viscosities of a single block copolymer propylene oxide-ethylene oxide denoted by No 330 according to Eq. (17). The agreement of the experimentally determined curve with the Eq. (17) is very good.

Finally, the most important part of this study — the application of the proposed theoretical method for calculation of θ_{\max} is considered. According to the assumption made already in the theoretical part of this study, let $\theta_{\min} = 0$ and for calculation Eq. (15) is applied. But for this equation only short times can be applied which we have chosen as 1/12 and 1/24 part of min. The values $\eta(1/12)$ and $\eta(1/24)$ have been determined by extrapolation of experimental values. The resulting relaxation times are given in Table I. They are almost independent of D which is in full agreement with theory because certain theoretical quantities are concerned. For verification, the calculated values θ_{\max} were again substituted into Eq. (15) from which the time dependence of viscosity for several values of t was calculated (these points are in Fig. 2 represented by O). Though we have used for calculation of θ_{\max} very short times it is obvious

TABLE I
Rheological Properties of Block Copolymers of Propylene Oxide and Ethylene Oxide Measured Two Different Shear Velocities

Sample No	D s^{-1}	η_0 Nsm^{-2}	η_∞ Nsm^{-2}	β s^{-1}	k	q	θ_{max} s
330	16.2	12.96	6.64	0.056	-0.63	-0.252	5.4
330	437.4	7.59	5.05	0.200	-0.55	-0.010	5.4
340	9.0	191.11	17.00	0.040	-0.64	0.000	6.0
340	81.0	57.41	9.20	0.094	-0.73	+0.170	5.7
350	9.0	37.80	16.50	0.053	-0.44	+1.650	6.2
350	145.8	36.40	26.10	0.240	-0.55	-	6.3

that the agreement with the experimental results is very good for longer times (up to 2 min) as well. Therefore the model of box distribution is much more satisfactory than the model with discrete distribution of relaxation times and the proposed method can be used without doubt for estimation of θ_{max} . The actual distribution of relaxation times will than have a general form $R(\theta)$, $\theta \in (\theta_1, \theta_2)$ while $0 \leq \theta_1 < \theta_2 \leq \theta_{max}$. For thixotropic materials the value of θ_1 and θ_2 will be independent of the velocity gradient.

LIST OF SYMBOLS

A	constant determined by Eq. (8)
a	constant determined by Eq. (17)
B	constant determined by Eq. (8)
b	constant determined by Eq. (17)
C	Euler's constant (= 0.577)
D	shear velocity (s^{-1})
D_{ij}	components of the tensor of velocity deformation
E	function defined by Eq. (9)
E_i	integral exponential function
I_2, I_3	second and third invariant of tensor of velocity deformation
k	slope
q	intercept on the ordinate axis
$R = R(\theta)$	distribution function of relaxation times
u_i	velocity component (ms^{-1})
t	time (s)
$x \equiv -t/\theta$	
β	parameter defined by Eq. (6)
δ	Dirac's δ function
η	apparent viscosity ($N s m^{-2}$)
$\eta_0 = \eta(t = 0)$	($N s m^{-2}$)

$$\eta_{\infty} = \lim_{t \rightarrow \infty} \eta(t) \quad (\text{N s m}^{-2})$$

θ_{\max} maximum relaxation time (s)

θ_{\min} minimum relaxation time (s)

θ_1, θ_2 actual minimum or maximum relaxation time (s) for a compound with a general distribution of relaxation times (s)

θ_0 relaxation time of model compound (s)

τ shear stress (Nm^{-2})

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