RELAXATION PROCESSES IN POLYMER FLUIDS

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An experimental study was made of the conditions under which the same relaxation processes will occur after different modes of uniform tension.

In this study, on the basis of experimental data, are established the conditons under which the processes of stress and strain relaxation (retardation) will be the same after different modes of tension.

Relaxation was studied on a typical high-molecular fluid, namely a melt of grade P-20 polyisobutylene,* under isothermal conditions at 22°C. At this temperature the maximum Newtonian viscosity of the specimen reached $\eta = 1.3 \cdot 10^6$ Pa•sec. The high-elasticity equilibrium modulus was $G_e \approx 4.4 \cdot 10^3$ Pa and the activation energy of viscous flow was E = 57.3 kJ/mole. The values of η and G_e had been determined under tension as well as under shear [1].

The experiments were performed in tensile testing machines under constant deformation rate $\varkappa$ [2, 3] and under constant force F [3, 4]. The cylindrical specimens d ≈ 0.5 cm in diameter had been prepared as before [2-4].

One end of a specimen was fastened to the dynamometer, while the other end was pulled according to specifications with regard to deformation rate or force. Both test stands were equipped for stress relaxation and for retardation. For the former the moving end of a specimen was almost instantaneously stopped (with the length l recorded), whereupon the decrease of stress σ during time t was measured at the stationary end. For retardation the stress was dumped almost instantaneously (a specimen stretched to length l was cut with scissors), whereupon the length l_r of the subsequently contracting specimen was measured ($l_r(0) = l$).

In this way, during any given process at any instant of time t could be measured stress σ, length l of the stretched specimen, and length l_r of the contracting specimen, then could be calculated the elastic strain $\alpha = l/l_r(\infty)$ and the rate of irreversible strain $e_p = \varkappa - (d/dt) \ln \alpha = d/dt \ln \varepsilon/\alpha$.

The thus experimentally determined relations are shown in Figs. 1-3. It appears at first that the retardation process is determined only by the magnitude of α (this hypothesis has been tested before indirectly [5]). The retardation curves $l_r(t)/l$ in Fig. 1 corresponding to the same elastic strain $\alpha = 2.2$ ($l/l_r = 1$ at $t = 0$ and $l/l_r = \alpha$ at $t \to \infty$) differ from one another (which contradicts the conclusion in study [5]). The retardation process was preceded by elongation to a given α at various deformation rates $\varkappa$. As to the $\sigma(t)$ curves obtained in process of stress relaxation (after elongation at various rates $\varkappa$), their indeterminacy at a fixed α is quite evident [2].

For a determination of other parameters which, in addition to α, govern the relaxation process, let us examine the $\sigma(\alpha)$ shown in Fig. 2 for various modes of tension and stress relaxation. Arrows with corresponding numerals indicate intersection points of $\sigma(\alpha)$ curves. At these points are also equal the rates e_p of irreversible strain. Therefore,

$$\sigma = \sigma(\alpha, e_p). \tag{1}$$

Under active tension we have also

$$\sigma = \sigma_*(\alpha, \varkappa). \tag{2}$$

*This grade of polyisobutylene was somewhat different than the grade used in [2-4].

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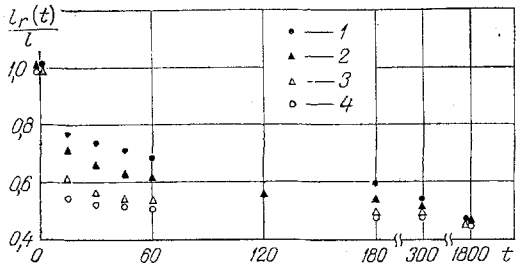

Fig. 1. Relative length $l_r(t)/l$ as function of time t (sec) in retardation process (points 1-4) preceded by elongation to $\alpha = 2.2$ at $\varkappa = 3.76 \cdot 10^{-3}$ sec^{-1}, $9.3 \cdot 10^{-3}$ sec^{-1}, $3.25 \cdot 10^{-2}$ sec^{-1}, 10^{-1} sec^{-1}.

All these conclusions are based on experimental data in studies [2-4] and this study (Table 1).*

We note that

$$\sigma = 3\eta e_p \tag{3}$$

as $\alpha \to 1$ (linear range of deformation), which has been established in an earlier study [1].

The existence of functional relation (1) suggests that relaxation proceeds in time along the same curve after different modes of uniform tension (and even after preliminary partial relaxation), if the built up elastic strain α and the rate of irreversible deformaion e_p are the same at the instant relaxation begins. According to expressions (1) and (2), parameters α and e_p can be replaced, for instance, with parameters σ and α or, in the case of active tension, α and $\varkappa$. All this is illustrated in Fig. 3 and in Table 1. The data on stress relaxation are shown in Fig. 3a and the data on retardation are shown in Fig. 3b. It must be emphasized that, when the relaxation processes concur in time and the initial conditions (α, e_p) are the same, the retardation will automatically concur in time as well. It is also interesting to note that, with the initial stress σ fixed, the stress relaxation proceeds slower as the initial elastic strain α becomes larger.

Let us also examine the temperature dependence of the relaxation processes. Stress relaxation and retardation occurring with fixed initial σ and α will proceed according to the principle of thermal invariance [6] with deformation

$$t_k = t\frac{\theta_k}{\theta}$$

of the time axis. Here t_k and θ_k are, respectively, process time and relaxation time at a varying temperature T_k; t and θ are those at a fixed temperature T. In this study the temperature was T = 295°K.

The ratio of relaxation times is [6]

$$\frac{\theta_k}{\theta} = \exp\left[\frac{E}{R}\left(\frac{1}{T_k} - \frac{1}{T}\right)\right].$$

In order to examine how e_p varies with varying temperature, we determine the effect of a temperature change on the $\sigma(\alpha)$ curves (Fig. 2). These curves for tension with F = const and for relaxation with fixed (σ, α) points do not change as T changes. Under tension with $\varkappa$ = const these $\sigma(\alpha)$ curves remain the same, if a change of the temperature results in a change of the deformation rate $\varkappa_k$ according to the relation

$$\varkappa_k = \varkappa\frac{\theta}{\theta_k}.$$

At points of intersection of $\sigma(\alpha)$ curves the rate of irreversible deformation changes according to the relation

$$e_{p,k} = e_p\frac{\theta}{\theta_k}.$$

*The data in Table 1 do not include those for point IV, because of the difficulty of measuring d ln α/dt at the first instant of stress relaxation.

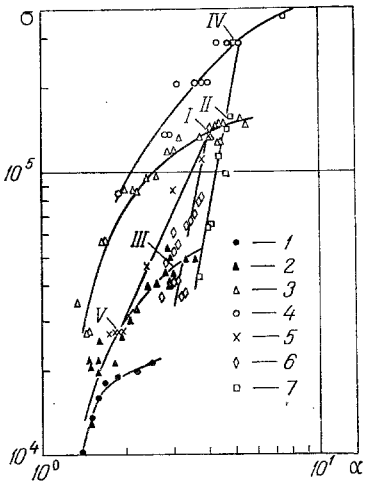

Fig. 2. Dependence of stress σ (Pa) on elastic strain α: 1-4) tension at constant deformation rate $\varkappa = 3.76 \cdot 10^{-3}$ sec^{-1}, $9.3 \cdot 10^{-3}$ sec^{-1}, $3.25 \cdot 10^{-2}$ sec^{-1}, 10^{-1} sec^{-1}, 5) tension with constant force F ($\sigma_0 = 6.3 \cdot 10^3$ Pa); 6, 7) relaxation data (relaxation preceded by tension with $\varkappa = 3.25 \cdot 10^{-2}$ and 10^{-1} sec^{-1}, respectively.

TABLE 1. Quantities Characterizing State of Strain at Intersection Points of Curves in Fig. 2

Point No.	σ, Pa	α	$\frac{d\ln\alpha}{dt}$, sec^{-1}	χ, sec^{-1}	e_p, sec^{-1}
I	$1{,}35 \cdot 10^5$	4,0	$1{,}82 \cdot 10^{-2}$	$3{,}25 \cdot 10^{-2}$	$1{,}43 \cdot 10^{-2}$
	$1{,}35 \cdot 10^5$	4,0	$1{,}75 \cdot 10^{-2}$	$3{,}07 \cdot 10^{-2}$	$1{,}32 \cdot 10^{-2}$
II	$1{,}5 \cdot 10^5$	4,8	$1{,}61 \cdot 10^{-2}$	$3{,}25 \cdot 10^{-2}$	$1{,}64 \cdot 10^{-2}$
	$1{,}5 \cdot 10^5$	4,8	$-1{,}63 \cdot 10^{-2}$	0	$1{,}63 \cdot 10^{-2}$
III	$4{,}5 \cdot 10^4$	3,0	$3 \cdot 10^{-3}$	$9{,}3 \cdot 10^{-3}$	$6{,}3 \cdot 10^{-3}$
	$4{,}5 \cdot 10^4$	3,0	$-6{,}29 \cdot 10^{-3}$	0	$6{,}29 \cdot 10^{-3}$
V	$2{,}65 \cdot 10^4$	1,87	$4{,}68 \cdot 10^{-3}$	$9{,}3 \cdot 10^{-3}$	$4{,}62 \cdot 10^{-3}$
	$2{,}65 \cdot 10^4$	1,87	$4{,}29 \cdot 10^{-3}$	$8{,}88 \cdot 10^{-3}$	$4{,}59 \cdot 10^{-3}$

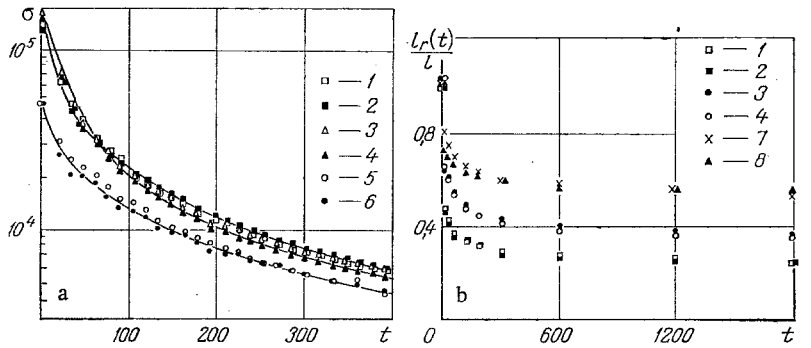

Fig. 3. Relaxation curves of stress σ (Pa) as function of time t (sec) during relaxation (a) and of relative length l_r/l as function of time t (sec) during retardation (b): 1-8) relaxation processes occurring after tension at constant deformation rate, at constant force, or after preliminary stress relaxation; arrows with corresponding numerals as in Fig. 2: (σ, α) points from which these processes are run, points 1, 2 (I), 3,4 (II), 5,6 (III), 7,8 (V).

NOTATION

σ, stress; l, l_0, lengths of stretched specimen at time t and at time t = 0, respectively; l_r, length of a contracting specimen of elastic fluid after tension force has been removed; $l_r(\infty)$, length l_r at $t \to \infty$; d, diameter of a cylindrical specimen; α, elastic strain; $\varkappa$, deformation rate; F, tension force; $\sigma_0 = F/S_0$; S_0, cross-sectional area of a specimen at time t = 0; e_p, rate of irreversible deformation; η, maximum Newtonian viscosity; G_e, high-elasticity equilibrium modulus; $\theta = \eta/G_e$, relaxation time; E, activation energy of viscous flow; R, universal gas constant; T, some fixed temperature; T_k, some variable temperature; θ_k, $\varkappa_k$, t_k, relaxation time, deformation rate, and time at temperature T_k; and ε, full strain.

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TRANSIENT PROCESSES IN SHEAR FLOWS OF VISCOELASTIC FLUIDS.

I. PROPAGATION OF A SHEAR WAVE

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A theoretical investigation is made of the initial stage of a transient process in the shear flow of a viscoelastic fluid having a relaxation-time spectrum.

A number of solutions are presently known for problems of transient shear flows of viscous and viscoelastic fluids. For example, flows of viscoelastic Maxwell and Oldroyd liquids having one relaxation time in a plane gap between parallel plates and a half-space with a plate set into motion impulsively were investigated in [1-6]. The nonsteady rotation of an infinite cylinder in a viscous fluid was analyzed in [7-9]. The development of fluid flow with relaxation and aftereffect of the Oldroyd type with an impulsively twisted cylinder is investigated in [10]. In [11] this same model was used to analyze freely damped oscillations of a cylinder by the method of a torsion pendulum. The results of such calculations are used to analyze nonsteady measurements in viscosimeters [12].

Because of the complexity of the molecular structure of polymer materials, their rheological behavior cannot be described by models of viscoelastic behavior with one relaxation time. For such media the character of the transient modes of deformation is determined to a considerable extent by the presence of a discrete relaxation spectrum. In this case a complete investigation of the dynamics of transient modes of deformation requires the distinguishing of the characteristic stages of flow, as well as their detailed qualitative and quantitative analysis, which are absent in [1-12].

As the rheological equation of state of the fluid we use Maxwell's generalized model with a relaxation-time spectrum reflecting the relaxation properties of polymers:

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