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Fig. 1

Figure 1: Fig. 1

## Abstract

## Full Text

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# ON THE THIXOTROPY OF POLYMERS IN THE VISCO-FLUID STATE

Deformation of condensed polymer systems that are in the visco-fluid state may be accompanied by a change in the state of their supramolecular structures. This phenomenon is observed upon transition through the yield point. It must be accompanied by thixotropy of the properties of the substance. However, for condensed polymer systems it is not known on what time scales the thixotropic changes occurring in them can be recorded. The transition through the yield point, accompanied by destruction of the structure of the substance, had previously been most widely studied using two-phase condensed systems as examples (^1, ^2). However, with respect to condensed polymer systems in the visco-fluid state, the phenomenon of thixotropy and hysteresis of mechanical properties had not been observed even in those cases where intense irreversible changes were noted (^3). Only Kepe (^4) pointed to the possible existence of thixotropy in polymers.

The purpose of the present work was to show the existence of thixotropy in polymers in the condensed state and the fact that reversible changes in their structure occur under conditions of transition through the yield point before entering the regime of steady flow; in the process of relaxation after the flow is stopped at constant deformation, and during rest, complete restoration of the polymer properties takes place.

Fig. 1. Deformation characteristics of polyisobutylene at +20° and −20°. Deformation rates, $\text{sec}^{-1}$:
1 $-8 \cdot 10^{-4}$; 2 $-1.3 \cdot 10^{-3}$; 3 $-4 \cdot 10^{-3}$; 4 $-1.3 \cdot 10^{-2}$; 5 $-1.6 \cdot 10^{-2}$; 6 $-4 \cdot 10^{-2}$; 7 $-8 \cdot 10^{-2}$; 8 $-0.4$; 9 $-0.8$; 10 $-1.2$

Polyisobutylene of grade P-20 was chosen as the object of study. Molecular weight by Staudinger $2 \cdot 10^4$; by Flory $1 \cdot 10^5$ (characteristic viscosity at 30°: in

Fig. 2

Figure 2: Fig. 2

benzene 0.375 and in cyclohexane 0.843). The experiments were carried out on a rotational elastoviscosimeter REV-1 (ˆ5). The instrument makes it possible to obtain the dependence of stresses $\tau$ on the duration of deformation; owing to the extremely high rigidity of the dynamometric device, this dependence is equivalent to the dependence of stresses on the relative deformation $\gamma$ at a constant deformation rate $\dot{\gamma}$. Typical graphs of the dependence $\tau(\gamma)$ are presented in Fig. 1. Dependences $\tau(\gamma)$ of two different types are observed: up to a certain deformation rate the dependence $\tau(\gamma)$ is monotonic, while at higher $\dot{\gamma}$ maxima appear on the curve $\tau(\gamma)$. Figure 2 shows the dependences of the extreme values of the stresses $\tau_m$ and of the stresses after reaching the

the regime of steady flow, $\tau_s$, on the rate of deformation. The rate of deformation has a substantial influence on the magnitude of the maximum. Moreover, the very existence of a maximum is found experimentally only above a certain rate of deformation, which depends on temperature. As is seen from Fig. 2, the experimental presence of a maximum on the curves $\tau(\gamma)$ is found only at such rates of deformation at which a considerable viscosity anomaly is already observed; i.e., the appearance of the maximum is not directly connected with deviation from the Newtonian flow regime, as was assumed for some disperse systems (6). It is possible that the curves $\tau(\gamma)$ also have a maximum at lower rates of deformation than shown in Fig. 2, but in any case its magnitude is extremely small and the deformation corresponding to it is very large. The dependence $\tau_s(\dot{\gamma})$ represents ordinary flow curves.

**Fig. 2.** Dependence of the maximum values of the stresses $\tau_m$ and of the stresses in the regime of steady flow $\tau_s$ on the rate of deformation $\dot{\gamma}$:
1—20°; 2—0°; 3—20°; 4—40°; 5—60°; 6—80°.

The temperature dependence of $\tau_s$ and $\tau_m$ characterizes the activation energy of the processes of viscous flow, $E_s$, and of transition across the yield-strength limit, $E_m$, at different constant $\dot{\gamma}$. Calculation of the values of $E_m$ and $E_s$ shows that, although $E_m$ and $E_s$ are quantities of the same order, nevertheless $E_m > E_s$. Thus, for example, at $\dot{\gamma} = 0.8$ sec$^{-1}$, $E_m = 9.16$ kcal/mol, and $E_s = 8.13$ kcal/mol.

The main experiments consisted in comparing the dependence $\tau(\gamma)$ obtained for specimens that had rested for a sufficiently long time after being loaded into the instrument with the same dependences obtained upon repeated deformation after various specified values of $\gamma$ or a specified rest time had been reached. This procedure is analogous to that previously used for studying the destruction of the structure of lubricants (2). By a polymer that has "rested for a sufficiently long time" is meant a specimen whose previous history ceases to affect its rheological characteristics. A change in the form of the dependence $\tau(\gamma)$ makes

Fig. 3

Figure 3: Fig. 3

it possible to judge the destruction and recovery of supramolecular structures. These investigations were carried out at one and the same rate of deformation.

The experimental results may be formulated as follows. If the flow was stopped before the stress maximum $\tau_m$ was reached, then upon repeated deformation the form of the deformation characteristic did not change. If the flow was stopped after passing through the maximum of the curve $\tau(\gamma)$, then upon repeated deformation a decrease in the value of $\tau_m$ was observed, the greater the larger the deformations at which the flow had been stopped. In this case, if the deformation was discontinued after the steady-flow regime had been reached, then upon repeated deformation no maximum on the curve was observed at all. In all the cases studied, the stresses in the regime of steady flow (determined—

···the value of the effective viscosity) remained unchanged and did not decrease no matter how long (up to several hours) the deformation continued. If the value of the structural strength of a "fresh" specimen is taken as 100%, then the change in this value upon repeated deformation after cessation of flow at different relative strains characterizes the degree of relative destruction of the structure. Indicative in this respect is the dependence of $(\tau_m' - \tau_s)/(\tau_m - \tau_s)$ on $\gamma$, shown in Fig. 3. Here $\tau_m$ and $\tau_m'$ are the stresses corresponding to the maximum of the curve for a "fresh" polymer and for a polymer preliminarily deformed to the value $\gamma$. In the same figure the dependence of $(\tau - \tau_s)/(\tau_m - \tau_s)$ on $\gamma$, obtained in experiments with a "fresh" specimen and showing the relative change in stresses after passing through the shear-strength limit, is plotted. As is evident from the data of Fig. 3, there is close agreement between the two constructed graphs. Destruction of the secondary structure of the polymer during its deformation begins and proceeds most intensively in the region of the maximum of the dependence $\tau(\gamma)$.

**Fig. 3.** Destruction of structure after passing through the shear-strength limit (1) and structural relaxation of stresses (2). $\dot{\gamma} = 8$ sec$^{-1}$; 20°

This justifies the view of the maximum of the curve $\tau(\gamma)$ as the shear-strength limit of the supramolecular structure of the polymer. The fall of stresses after passing through the maximum is due to the continuing destruction of the structure of the substance; therefore the change in stresses from $\tau_m$ to $\tau_s$ may be called structural relaxation of stresses.

Repeated deformation in the experiments described above was carried out practically immediately after cessation of flow. If the interval between successive deformation cycles is increased, i.e., the duration of the polymer "rest," then a gradual increase in the maximum on the curves $\tau(\gamma)$ is observed, indicating restoration of the structure. The limiting degree of restoration of the structure is reached after a sufficiently long "rest." It corresponds to the state of the initial

Fig. 4. Kinetics of structural recovery (1) and stress relaxation (2). $\dot{\gamma} = 8\ \text{sec}^{-1};\ 20^\circ$

Figure 4: Fig. 4. Kinetics of structural recovery (1) and stress relaxation (2). $\dot{\gamma} = 8\ \text{sec}^{-1};\ 20^\circ$

“fresh” polymer.

Figure 4 shows the kinetics of restoration of the structure of polyisobutylene after its maximum destruction, corresponding to the attainment of a regime of steady flow. Also shown there is the relative rate of decrease of stresses during relaxation proceeding in parallel with restoration of the structure. It is obvious that the rates of these processes are substantially different: if stress relaxation by 90% occurs in $\sim 7$ sec, then restoration of the structure by 90%, estimated from the shear-strength limit, takes more than 1 hour (at a temperature of 20° and a deformation rate before cessation of flow of $8\ \text{sec}^{-1}$). Therefore, from the practically complete completion of relaxation one cannot judge the completeness of restoration of the structure of polymers.

In all the experiments described above, irreversible changes in structure were not observed, even after repeated and prolonged deformations of the specimen, which, of course, does not exclude the possibility of mechanical destruction at higher rates of deformation. Precisely because, in viscometric studies of polymers, the region of steady flow was usually considered and, as a rule, transient regimes were not studied,

deformation, it had previously not been possible to observe thixotropy of the properties of polymers in the viscous-flow state.

Thus, in the present work it has been established that deformation of polyisobutylene may be accompanied by thixotropic destruction of its

**Fig. 4.** Kinetics of structural recovery (1) and stress relaxation (2). $\dot{\gamma} = 8\ \text{sec}^{-1};\ 20^\circ$

supramolecular structures, which occurs upon crossing the shear-strength limit. The rate of structural recovery is considerably lower than the rate of stress relaxation.

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## REFERENCES

1. G. V. Vinogradov, K. I. Klimov, DAN, **57**, 911 (1947); **58**, 1677 (1947).
2. G. W. Winogradow, W. P. Pawlow, Rheologica Acta, **1**, No. 4/6, 455 (1961).
3. R. S. Porter, J. F. Johnson, J. Polymer Sci., **50**, 379 (1961).
4. A. Kérés, Thèses, Univ. Strassbourg, 1958.
5. G. V. Vinogradov, I. M. Belkin et al., Zav. lab., **30**, No. 3 (1964).
6. A. A. Trapeznikov, DAN, **102**, 1177 (1955).

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