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Abstract

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ON THE DEGRADATION OF POLYMER MOLECULES IN SOLUTION

(POLYISOBUTYLENE, POLYMETHYL METHACRYLATE)

DURING PASSAGE THROUGH THE PRESTATIONARY STAGE OF DEFORMATION

(Presented by Academician S. I. Vol' fkovich, 28 XI 1963)

The question of the mechanical destruction of polymer molecules has been discussed for a long time. This phenomenon was formerly called destruction, and is now called degradation. Frenkel [1] considered rupture of a polymer molecule in solution, but in a dilute one, where only purely hydrodynamic viscosity factors act. Many experimental works on solutions and melts have been devoted to polyisobutylene [2–4]. The results obtained were interpreted only from the standpoint of viscosity, including the stress maximum in [4].

The concepts we introduced [5] concerning destruction of structure in concentrated polymer solutions in the prestationary stage as a process of deformation of a "solid" body, including passage through the strength limit, are equivalent to deformation and destruction of a solid polymer in bulk; in general form they must be related both to reversible thixotropic destruction of structure, associated with the destruction of intermolecular bonds, and to irreversible destruction of molecules (degradation). The transition from a reversible deformation process to an irreversible one is determined by the deformation rate passing through a certain critical value $\dot{\varepsilon}_{kd}$.

In the present work we investigated a 5% solution of polyisobutylene (mol. wt. $\simeq 2.8 \cdot 10^6$) in nonpolar vaseline oil and a 3% solution of polymethyl methacrylate (Plexiglas) in acetone. The polyisobutylene was first dissolved in a volatile solvent (petroleum ether), then vaseline oil was introduced and the solvent was evaporated at $t \leq 150^\circ$ (solution No. 1); hexane also served as solvent (solution No. 3). The investigations were carried out in an elastorelaxometer (model 3) at $t = 20^\circ$. Cylinders with $R_1 = 2.8$ cm, $R_2 = 3.0$ cm, $L_1 = 8.0$ cm, $L_2 = 12$ cm were used; in one case the temperature was 30° and small assembled cylinders were used with $R_1 = 1.4$, $R_2 = 1.49$ cm, $L_1 = 5.02$, $L_2 = 5.3$ cm, of which

the inner cylinder had a conical bottom and top. A cone-disk working pair was also used (diameter 3-5 cm, cone angle 2-4°). The shear stress as a function of deformation was recorded on a loop oscillograph. The high-elastic (reversible) deformation ε_e was measured as a function of the imposed deformation ε.

Figure 1a shows the curves $P(\varepsilon)^*$ for $\dot{\varepsilon} = 55$; 110 and 220 s^{-1}, corresponding to the transition interval $\dot{\varepsilon}$. At $\dot{\varepsilon} = 55$ s^{-1} the curve $P(\varepsilon)$ has a maximum $P = P_r$ at $\varepsilon = \varepsilon_r = 20$, after which P smoothly decreases (exponentially) to $P = P_s$. At $\dot{\varepsilon} = 110$ s^{-1} the maximum P_r is noticeably shifted toward a larger $\varepsilon_r = 41$, and after it P decreases less steeply. At $\dot{\varepsilon} = 220$ s^{-1} the curve $P(\varepsilon)$ substantially changes its form. After a rapid rise there is only a slow growth of P in the form of a plateau $P = P_{pl}$, after which P again rises very steeply to a sharp maximum $P = P_r$, lying at $\varepsilon_r = 140$, and then falls very sharply. Figure 1b shows the curves $\varepsilon_e(\varepsilon)$ for the same $\dot{\varepsilon}$, from which it is seen that, with increasing $\dot{\varepsilon}$, $\varepsilon = \varepsilon_m$, at which $\varepsilon = \varepsilon_{e\,max}$ is reached, greatly increases, and the absolute values of $\varepsilon_{e\,max}$ increase noticeably. At $\dot{\varepsilon} = 220$ s^{-1}, after the maximum the drop is steeper.

Figure 1c shows the curves $\varepsilon_e(\tau_{rel})$, characterizing thixotropic destruction and restoration of structure at $\dot{\varepsilon} = 110$ s^{-1}, upon repeated deformation to the prescribed ε (indicated by the curves) after different times.

* Constructed from points taken from continuous oscillograms.

of rest τ_{rest}. The curves refer to ε smaller and larger than ε_m of the curve $\varepsilon_e(\varepsilon)$ shown in Fig. 1b. From the curves $\varepsilon_e(\tau_{rest})$ it follows that at $\tau_{rest} = 2$ min the value of ε_e is lowered, but at $\tau_{rest} = 15$-20 min the value of ε_e already differs little from the initial (or limiting) one, coinciding completely with it at $\tau_{rest} = 1$-3 h. Thixotropic destruction is more strongly expressed at $\varepsilon > \varepsilon_m = 120$. At the smallest $\varepsilon < 25 \ll \varepsilon_m$, the value of ε_e is not lowered at all under repeated deformations. In connection with such a complete restoration of the structure during rest, the repeated curves $\varepsilon_e(\varepsilon)$ and $P(\varepsilon)$ at the given $\dot{\varepsilon} = 110$ sec^{-1} are sufficiently reproducible*. At $\dot{\varepsilon} = 220$ sec^{-1} reproducibility disappears. Curve 1 in Fig. 1a at $\dot{\varepsilon} = 220$ sec^{-1} was recorded up to $\varepsilon \approx 300$. The 2nd and 5th curves recorded immediately after this, each after one hour of rest to larger ε, gave irreversibly decreasing values of P_r. Curve 5 up to $\varepsilon = 1420$ is shown as curve 2 at 220 sec^{-1} in Fig. 1a. From comparison with curve 1 it follows that the characteristic rise of "strengthening" on the curve $P(\varepsilon)$ has completely disappeared and the whole curve, including its initial part, has been greatly lowered. The data on $\varepsilon_e(\varepsilon)$ correspond to this as well. Repeated measurement of $\varepsilon_e(\varepsilon)$ (curve 2, Fig. 1b, 220 sec^{-1}), even after two days of rest of the solution that had been subjected to the first measurement of $\varepsilon_e(\varepsilon)$ up to $\varepsilon = 2200$ (curve 1, Fig. 1b, 220 sec^{-1}), shows a strong decrease in ε_e as a result of the irreversible destruction that occurred during the first measurements.

Fig. 1. 5% solution of polyisobutylene in Vaseline oil, $t = 20°$ (solution No. 1). a —curves $P(\varepsilon)$; b —curves $\varepsilon_e(\varepsilon)$; v —curves $\varepsilon_e(\tau_{rest})$ at $\dot{\varepsilon} = 110$ sec^{-1}

Thus, on passing from $\dot{\varepsilon} = 110$ sec^{-1} to $\dot{\varepsilon} = 220$ sec^{-1}, even a single deformation

Fig. 1

Figure 1: Fig. 1

Figure 2

Figure 2: Figure 2

and, in particular, repeated deformation to $\varepsilon > \varepsilon_m$ in elastic deformation and to $\varepsilon > \varepsilon_r$ in stress (the quantities ε_m and ε_r do not always coincide) leads to a sharp decrease in the quantities ε_e and P, which is explained by irreversible destruction of the structure, i.e., degradation of the molecules. It is especially important that irreversible lowering of P and ε_e appears clearly when passing through the limiting values of deformation ε_r and ε_m. For P this is clearly seen from Fig. 2a (solution No. 3, small cylinders, $\dot{\varepsilon} = 250$ sec^{-1}, $t = 30^\circ$). The oscillographic curves $P(\varepsilon)$ were recorded at points ε marked by arrows along the curve $\varepsilon_e(\varepsilon)$ in Fig. 2b. The second curve $P(\varepsilon)$, recorded up to $\varepsilon = 180$, coincides with the first up to $\varepsilon = 108$, which indicates the absence of structural destruction; this is shown by the solid line of the curve in Fig. 2a. On passing to larger ε (beyond the maximum), the curves $P(\varepsilon)$, recorded each time after a long rest of 1-2 h, become greatly stretched out and each has increasingly lowered P and maximum P_r. These values of P_r

* P reacts to repeated deformation more strongly than ε_e (5).

for the corresponding final ε, marked by arrows, are shown on the same curve $2a$ as a dashed line. In general, the curve shows the true values of P up to $\varepsilon \ll \varepsilon_r$ and the irreversibly reduced P_r at $\varepsilon > \varepsilon_r$.

Dependences close to this one, of P and ε_e on ε, are also observed for a solution of polymethyl methacrylate (Plexiglas) in acetone, investigated at $\dot{\varepsilon} = 1108$ sec^{-1} (Fig. 3). In Fig. 3, I, curve 1, consisting of solid and dashed parts, was obtained by visual reading of P by the "spot," with measurements of ε_e along the curve $\dot{\varepsilon}_e(\varepsilon)$ shown there for a fresh solution. The solid part of curve 1 reflects the true values of P, while the points on the dashed part show the highest P, i.e., P_r, at each deformation up to $\varepsilon > \varepsilon_r$ (analogous to the dashed part of the curve in Fig. 2a). The oscillographically recorded dependence $P(\varepsilon)$ at the point $\varepsilon = 2250$ is shown as curve 2 in Fig. 3I. The points marked by black triangles were obtained by reading from the "spot" during the reverse change of ε (decrease) from $\varepsilon = 2250$; they lie at the same level, indicating the preserved strong destruction of the structure that occurred with increasing ε. The height of this line coincides with the maximum of the oscillographic curve (the visual reading is less precise). In Fig. 3II the curves $\varepsilon_e(\varepsilon)$ show the decrease of ε_e during direct and reverse changes of ε. The first transition through $\varepsilon_m = 110$-130

Fig. 2. 5% solution of polyisobutylene in vaseline oil. $t = 30^\circ$ (solution No. 3). a—curve $P(\varepsilon)$; b—curve $\varepsilon_e(\varepsilon)$

Figure 3

Figure 3: Figure 3

(up to $\varepsilon = 200$) gives a strong decrease of ε_e, which is seen from the subsequent curves $(2, 3, 4)$ of direct and reverse changes of ε, up to the same $\varepsilon = 200$. Increasing the prescribed ε to 2250 in the 4th direct run again lowers ε_e, as is seen from the 5th curve of the direct run. Each increase of ε in the interval $\varepsilon > \varepsilon_m$ and $> \varepsilon_r$ intensifies degradation as a result of the fact that at large ε many chains of the network reach an extremely extended and extremely stressed state.

Conclusions. 1. Degradation occurs: a) when $\dot{\varepsilon}$ passes through the critical deformation rate $\dot{\varepsilon}_{kd}$; b) when, at each $\dot{\varepsilon} > \dot{\varepsilon}_{kd}$, ε passes through ε_r or ε_m, which are critical rupture strains corresponding to the maximum stresses of the network structure and its maximum elastic deformations. This means that the moment at which degradation begins in a concentrated solution is equivalent to the attainment of the rupture strain and strength of the polymer in bulk and is characterized by the deformation-strength properties of the solution, not by its viscosity. For the mechanism of degradation of the solution, the decisive factor is the passage of the structural network through the initial prestationary part. The determining factor in these processes is the relation: the deformation rate must be greater than the relaxation (disentanglement) rate of chains in the network structure.

2. To a small degree, degradation also occurs at $\dot{\varepsilon} < \dot{\varepsilon}_{kd}$, characteristic of the system as a whole, and also at $\varepsilon < \varepsilon_r$ and $\varepsilon < \varepsilon_m$ (at the corresponding $\dot{\varepsilon}$), which is explained by the attainment of the critical deformation ε_{ki} in some parts of the chain that are in a particularly stressed state. 3. At $\dot{\varepsilon} < \dot{\varepsilon}_{kd}$ the structure of the solution is also destroyed and charac-

is characterized by the curves $P(\varepsilon)$ and $\varepsilon_e(\varepsilon)$, which have maxima. However, these destructions are for the most part reversible, thixotropic, and are explained by the destruction of intermolecular bonds and by the displacement of chains from their most probable positions, which determine the entropy maximum and the energy minimum. 4. The use in the elastorelaxometer of cone–disk working bodies (c–d) showed that in a 5% solution of polyisobutylene the values $\varepsilon_{e\,\max} = 60$-$80$ and $\varepsilon_m = 140$ relative units at $\dot{\varepsilon} = 150$-250 sec^{-1} coincide with those obtained in the cylinder–cylinder gap (c–c), whereas P in the interval $\varepsilon < \varepsilon_r$ is somewhat higher, and the values of ε_r somewhat lower. The difference is explained by weakening of the stressed state in c–c as a result of slight squeezing of the solution out of the c–c gap under the influence of normal stresses acting

Fig. 3. 3% solution of polymethyl methacrylate in acetone, $t = 20°$.
I–$P(\varepsilon)$ and $\varepsilon_e(\varepsilon)$; II–$\varepsilon_e(\varepsilon)$ under repeated deformation.
a–1st forward run, b–1st reverse run; v–2nd forward run; g–2nd reverse run; d–3rd forward run; e–4th forward run; zh–5th forward run

upward along the cylinder axis. It was noted that in the case c–d, during passage through $\varepsilon = \varepsilon_m$ at high $\dot{\varepsilon}$, the degradation of molecules causes rupture of the structure as a whole and squeezing of pieces of the solution out of the gap to the outside, despite the action of normal stresses directed toward the axis of rotation. The values of $\varepsilon_{e\,\max}$ at similar $\dot{\varepsilon}$ in a 5% solution of polyisobutylene in vaseline oil (60–80 relative units) are considerably greater than in 5–20% solutions in orthoxylene, 8–9 relative units ([5]), which is associated with the nature of the solvent.

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