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## Abstract

## Full Text

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# STUDY OF THE MECHANISM OF POLYMER FRACTURE BY THE E.P.R. METHOD

The study of the temperature-time regularity of the change in the strength of polymers made it possible to formulate the concept of a fluctuation mechanism of fracture ($^1$-$^3$). According to this theory, the strength of polymers is determined by the rate of rupture of chemical bonds in chain macromolecules. Such ruptures should produce, and allow the accumulation of, free radicals. To detect radicals and to study the kinetics of their formation, it is expedient to use the e.p.r. method. As is known, this method has been successfully applied in a number of works ($^4$-$^{11}$) to the study of macroradicals formed in the products of crushing of solid polymers. The appearance of radicals in ebonite during compression testing of specimens has also been recorded ($^{12}$).

The present work was undertaken in order to trace the appearance of macroradicals in the process of polymer fracture under the action of uniaxial tensile stresses. After a number of exploratory experiments it was established that, by the e.p.r. method, one can detect the rupture of chemical bonds in stressed highly oriented fibers of polycaprolactam (capron). The experiments were carried out at room temperature under atmospheric conditions on capron specimens both containing and not containing the stabilizer di-$\beta$-naphthyl-$p$-phenylenediamine (DNPDA). Stretching of specimens in the form of a bundle of $15 \cdot 10^4$ fibers with a total cross section of 4 mm$^2$ was performed directly in the resonator of a laboratory e.p.r. spectrometer ($^7$) of the 3-centimeter range with high-frequency modulation of the magnetic field.

**Fig. 1.** E.p.r. spectrum of free radicals: *a*—in fibers without DNPDA at $L \perp H$; *b*—the same at $L \parallel H$; *c*—in fibers with DNPDA

When fibers not containing stabilizer were stretched, the appearance of radicals was registered; their spectrum is shown in Fig. 1*a*. The e.p.r. spectrum is a doublet of triplets. The doublet splitting reaches a maximum when the fibers $L$

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

are arranged parallel to the field $H$ (Fig. 1*b*). A similar spectrum was observed in $\gamma$-irradiated oriented polyamides ($^{13}$-$^{15}$) and belongs, as was shown in ($^{15}$), to the radical

$$-\mathrm{NH}-\dot{\mathrm{C}}\mathrm{H}-\mathrm{CH}_2-.$$

This radical is not primary, since in capron fractured at low temperature (77°K) another spectrum was observed ($^{4}$, $^{6}$). It may be assumed that the primary event in mechanical destruction is rupture of the chain at the bond

$$-\mathrm{CH}_2-\mathrm{NH}-\mathrm{CO}-,$$

and the active radicals formed in this process abstract hydrogen atoms from neighboring chains, which ultimately leads to the appearance of more stable radicals of the type

$$-\mathrm{NH}-\dot{\mathrm{C}}\mathrm{H}-\mathrm{CH}_2-.$$

When fibers stabilized with 0.5% DNFPDA were loaded, another EPR spectrum was recorded, with a poorly resolved hyperfine structure (Fig. 1b). This spectrum arises against the background of the singlet line present in the original specimen and apparently belongs to the inhibitor radical. Such a radical appears as a result of the interaction of DNFPDA molecules with the primary radicals formed when the chains break.

**Kinetics of radical accumulation under load.** In stabilized and unstabilized capron fibers, the formation and accumulation of free radicals under the action of a constant load were traced. The results of these experiments are shown in Fig. 2.

**Fig. 2.** Kinetics of radical accumulation at different stresses: *a*—fibers without stabilizer; *b*—fibers with DNFPDA.
1—$\sigma$ = 60 kg/mm$^2$; 2—$\sigma$ = 66; 3—$\sigma$ = 70; 4—$\sigma$ = 51; 5—$\sigma$ = 56.4; 6—$\sigma$ = 65 kg/mm$^2$; 7—$\Delta l$ at $\sigma$ = 65 kg/mm$^2$

**Fig. 3.** Increase in the EPR signal with increasing load

In both types of fibers the magnitude of the EPR signal (and consequently the number of radicals) increases with time and rises sharply with the value of the tensile stress. However, a certain difference in the kinetics is also observed. In unstabilized fibers, at comparatively small stresses (60-66 kg/mm$^2$), the number of registered radicals, after reaching a maximum value, begins gradually to fall.

Fig. 4. Dependence of the concentration (a) and the rate of formation of radicals (b) on stress

Figure 3: Fig. 4. Dependence of the concentration (a) and the rate of formation of radicals (b) on stress

At higher stresses (70 kg/mm$^2$), the increase in the number of radicals continues up to rupture of the specimen.

In fibers with DNFPDA, the number of free radicals increases monotonically, without showing a decrease in concentration. This difference in the kinetics is associated with the difference in the rates of disappearance of the radicals. Experiment shows that at room temperature in stressed fibers two processes proceed simultaneously: the formation of radicals and their recombination. When the load is removed, the radicals gradually disappear. The rate of disappearance of the radicals $-\mathrm{NH}-\dot{\mathrm{C}}\mathrm{H}-\mathrm{CH}_2-$is approximately 50 times greater than that of the inhibitor radicals. Therefore fibers with DNFPDA are a more convenient object for kinetic studies, since the recombination process does not introduce strong distortions into the kinetics of radical accumulation.

The number of radicals formed in capron with DNFPDA increases under constant load according to the curves shown in Fig. 2b. It should be noted that the radical-accumulation curves are very similar to creep curves. For comparison, a creep curve for $\sigma = 65$ kg/mm$^2$ is plotted in the same figure. In general features the accumulation curves repeat the creep curves. The radical-accumulation curve can likewise be divided into three regions: a region with a nonstationary, decreasing rate (initial); a region with a constant rate; and a pre-rupture region, with an increasing rate of destruction. This similarity of the curves shows that the rate not only of steady-state [16], but also of nonstationary creep, is connected with the process of destruction of chemical bonds.

The maximum concentrations of radicals by the moment of rupture of the specimen, according to the estimates made, reached a value of $\simeq 10^{17}$ cm$^{-3}$. This corresponds to a single rupture of approximately $2 \cdot 10^{-3}$ of the polymer chains in the entire volume of the specimen. Since the process of destruction proceeds predominantly in overstressed regions, the local concentrations of radicals, naturally, considerably exceed the average value.

**Dependence of the concentration of free radicals on stress.** The change in radical concentration as a function of the magnitude of the tensile stress was measured under two loading regimes: stepwise and smooth.

Figure 3 gives the curves of the change in the intensity of the EPR signal under stepwise increase of the load for different capron specimens. The time between load steps was equal to the period of recording the spectrum, 2 min. The data presented indicate a sharp dependence of the concentration on the load.

**Fig. 4.** Dependence of the concentration (*a*) and the rate of formation of

radicals ($b$) on stress.

In Fig. 4a the curve of continuous recording of the amplitude of the EPR signal during smooth loading at a constant rate ($\dot{\sigma} = \text{const}$) is shown. Differentiation of this curve gives an idea of the change in the rate of radical formation:

$$dn/dt = \dot{\sigma}\, dn/d\sigma \sim dU/d\sigma,$$

since $\sigma = \dot{\sigma}t$. The results of such processing are presented graphically in semilogarithmic coordinates (Fig. 4b). As is seen, the dependence $\lg dU/dt = f(\sigma)$ is close to linear. Thus, the rate of radical formation measured by the EPR method, and consequently also the rate of bond rupture, depend exponentially on the magnitude of the applied stress. This result agrees qualitatively with data on the time dependence of strength, according to which the lifetime of the specimen tested changes exponentially with stress ($\tau = A \exp -\alpha\sigma$). The observation of free radicals in a stressed polymer and the exponential character of the dependence of the rate of their formation may be regarded as experimental confirmation of the concept of the fluctuation mechanism of polymer fracture. The results obtained also show that application of the EPR method makes it possible to obtain important information on the mechanism of destruction and deformation of polymers.

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