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## Abstract

## Full Text

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# THE EFFECT OF IONIZING GAMMA RADIATION ON THE STRUCTURAL-MECHANICAL PROPERTIES OF STARCH GELS

*(Presented by Academician P. A. Rehbinder, 18 III 1960)*

Ionizing gamma radiation causes destruction of the polymer molecules of starch ([1,2]), which should lead to a change in the structural-mechanical properties of gels prepared from irradiated starches. In the present work we investigated the change in the plastic strength of starch gels as a function of the dose of ionizing radiation. The studies were carried out with potato starch having an equilibrium moisture content of 16.6%.

Starch in sealed glass ampoules was irradiated at room temperature with various doses of $Co^{60}$ gamma radiation from $1 \cdot 10^6$ to $18.2 \cdot 10^6$ r at a dose rate of $2 \cdot 10^3$ r/min. From the irradiated and control starch, gels containing 12.0% dry starch were prepared under strictly identical conditions, and the limiting shear stress $P_m$ was measured by the method of the conical plastometer ([3]).

**Fig. 1.** Change in the limiting shear stress $P_m$ with time $\tau$. The numbers at the curves are the dose in millions of roentgens.

The character of the change in the plastic strength of starch gels irradiated with different doses as a function of time is shown in Fig. 1. The change in the limiting shear stress of a fully formed gel as a function of the radiation dose is shown in Fig. 2.

The action of ionizing gamma radiation initially causes an increase in the plastic strength of the system, and then, with increasing radiation dose, a decrease in the limiting shear stress is observed. At a dose of $7.1 \cdot 10^6$ r the limiting stress is close to zero ($P_m = 3$ g/cm$^2$), and at a dose of $18.2 \cdot 10^6$ r the gel has a semiliquid consistency and measurement of $P_m$ with the aid of the conical plastometer becomes practically impossible.

The character of the increase in plastic strength with time differs (Fig. 1) for gels prepared from starches irradiated with doses of $4 \cdot 10^6$ and $7.1 \cdot 10^6$ r and for gels obtained from starches irradiated with smaller doses. This indicates a substantial change in the mechanism of formation of the structural network of the gel with increasing absorbed dose and is connected with depolymerization of the polymer molecules of starch under the action of radiation.

Since in starch gels the formation of the structural network is due to hydrogen bonds arising between the hydroxyls of the glucopyranose rings of the polymer molecules of starch ([2]), it may be assumed that the extremal character of the curve $P_m = f(D)$ (Fig. 2) is associated with a change–

···in the number of hydroxyl groups capable of forming hydrogen bonds under the action of gamma radiation.

In native, unirradiated starch, some of the hydroxyls are screened and do not participate in the formation of the structural network of the gel. Depolymerization under the action of radiation should promote the opening up, the liberation, of screened hydroxyls, which will lead to an increase in the plastic strength of the system. The subsequent decrease in $P_m$ with increasing radiation dose is undoubtedly associated with a decrease in the total number of hydroxyls, caused by their cleavage with the formation of gaseous products ([1]). As was shown by V. F. Oreshko and K. A. Korotchenko ([1]), when the polymer molecule of starch is split at the bonds of the main valences 1—4 and 1—6 under the action of radiation, $n$ molecules are formed

$$n = \frac{\overline{M}_0}{\varepsilon_d N_0} D. \tag{1}$$

**Fig. 2. Dependence of the limiting shear stress on dose**

If each splitting leads to the opening up of screened hydroxyls, then additional hydrogen bonds are formed in the gel $[\mathrm{H}\,...]_1$

$$[\mathrm{H}\,...]_1 = \frac{\chi}{2} \frac{\overline{M}_0}{N_0 \varepsilon_d} D, \tag{2}$$

where $\overline{M}_0$ is the number-average molecular weight of unirradiated starch, $N_0$ is Avogadro' s number, $\varepsilon_d$ is the energy required to break one bond in a starch molecule, and $D$ is the radiation dose. The cleavage of hydroxyls, occurring simultaneously with depolymerization ([1]), obeys the equation:

$$[\mathrm{OH}]_{11} = k n_0 D + \frac{\rho}{2} \frac{\chi \overline{M}_0}{N_0 \varepsilon_d} D^2. \tag{3}$$

Neglecting the first term in equation (3), we obtain an expression for the total number of hydrogen bonds in the starch gel:

$$[\mathrm{H}\,...] = [\mathrm{H}\,...]_0 + \frac{\chi \overline{M}_0}{2N_0\varepsilon_d}\,D - \frac{\chi\rho\overline{M}_0}{4N_0\varepsilon_d}\,D^2. \tag{4}$$

Assuming that $P_m \sim [\mathrm{H}\,...]$, we obtain*

$$P_m = k[\mathrm{H}\,...] = P_m^0 + \frac{k\chi}{2}\frac{\overline{M}_0 D}{N_0\varepsilon_d} - \frac{k\chi}{4}\frac{\rho\overline{M}_0}{N_0\varepsilon_d}\,D^2, \tag{5}$$

where $\chi$ is the number of screened hydroxyls opened up at each rupture of a molecule; $k$ and $\rho$ are coefficients; and $P_m^0$ and $P_m$ are the limiting shear stresses of gels made from unirradiated and irradiated starches, respectively.

The dependence

$$\frac{P_m - P_m^0}{D} = \frac{k\chi\overline{M}_0}{2N_0\varepsilon_d} - \frac{k\chi\rho\overline{M}_0}{4N_0\varepsilon_d}\,D, \tag{6}$$

* According to Zuev ([5]), $P_m \sim n^{2/3}$, where $n$ is the number of contacts in 1 cm$^3$ of gel; however, in the case of starch the experimental data reveal the existence of direct proportionality between these quantities.

constructed from the experimental data, is expressed by a straight line within the range from $1 \cdot 10^6$ to $4 \cdot 10^6$ r (Fig. 2), which confirms the correctness of the initial assumptions used in deriving equation (5).

It follows from the experimental data that

$$\frac{kx}{2}\frac{\overline{M}_0}{N_0\varepsilon_d} = 15.1 \cdot 10^6 \frac{\mathrm{r}}{\mathrm{cm}^2 \cdot \mathrm{r}}; \qquad \frac{kx\rho\,\overline{M}_0}{4N_0\varepsilon_d} = 4.1\,\frac{\mathrm{g}}{\mathrm{cm}^2},$$

whence $\rho = 0.54 \cdot 10^{-6}$ r$^{-1}$.

It also follows from an analysis of equation (5) that the maximum of the curve $P_m = f(D)$ is located at $\frac{1}{\rho} = 1.85 \cdot 10^6$ r, and $kx = 20.8$, taking, according to the measurements of V. F. Oreshko and K. A. Korotchenko, for this starch $\overline{M}_0 = 462\,000$, $\varepsilon_d = 26$ eV ([1]).

In Fig. 2 the solid line shows the theoretical curve obtained from equation (5), and the circles are the experimental points.

Thus, in the region of integral doses $< 4 \cdot 10^6$ r, the change in the plastic strength of gels of irradiated starches is due to a change in the number of hydroxyls capable of forming hydrogen bonds. The depolymerizing action of ionizing gamma radiation leads to the uncovering of shielded hydroxyls and to strengthening of the gel network, whereas the destructive action, causing cleavage of functional groups and reducing the total number of hydroxyls, leads

to a decrease in the number of hydrogen bonds and to a lowering of the strength of the system.

Apparently, the terminal groups of the chains of starch macromolecules (for example, aldehyde groups) can also participate in the formation of the structural network, but in ordinary unirradiated starch their role is very small, and the strength of the gel is determined by hydrogen bonds arising between the hydroxyls of glucopyranose rings. As a result of the depolymerizing action of radiation, the number of terminal groups increases greatly, while the size of the molecules decreases. In Fig. 2 a curve is given for the decrease of the average molecular weight with increasing dose, obtained by V. F. Oreshko and K. A. Korotchenko ([1]). At $4\text{-}5 \cdot 10^6$ r the number-average molecular weight decreases by a factor of 10. The destructured molecules acquire greater mobility and can take part in the formation of the structural network of the gel by interaction of terminal groups, which should lead to some increase in plastic strength and to a change in the character of formation of the gel structure with time, as is observed in our experiments.

In the dose region where the structural network is formed by hydrogen bridges (from 0 to $\simeq 4 \cdot 10^6$ r), the plastic strength of the gel increases rapidly, reaching the limiting value $P_m$. Already at $4 \cdot 10^6$ r and above (Fig. 1), another mechanism has a significant effect—the formation of a structural network by interaction of terminal groups of macromolecules; the plastic strength increases slowly and, apparently, does not reach a limiting value. With time, the gel network is gradually strengthened as a result of the displacement and deformation of molecules which, although destructured, are still fairly large. Further depolymerization under the action of ionizing radiation ($18.2 \cdot 10^6$ r) leads to such a large decrease in molecular size that the latter lose the ability to form gels.

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## CITED LITERATURE

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