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Abstract

Full Text

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ON SOME FEATURES OF THE RADIATION DESTRUCTION OF POLYMERS

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The destruction (depolymerization) of polymers caused by the action of high-energy radiation is accompanied by the formation of gases which, being in a state of high supersaturation, create large internal stresses in the material, thereby accelerating its destruction.

It is difficult to establish a direct connection between the radiation resistance of polymers and the quantities of gases released from them upon irradiation ([1]); however, this is not the result of a weak influence of gas formation on their destruction, but is caused by the complex character of the radiolysis processes leading to the appearance of gaseous destruction products. A number of features of this process are revealed under the simultaneous influence on polymers of radiation and elevated temperature, as a result of which in the present work gas formation and its influence on the destruction of polytetrafluoroethylene (PTFE), polymethyl methacrylate (PMMA), and polyethylene (PE) were investigated during their irradiation at various temperatures with a beam of fast electrons.

Heating of the specimens was carried out by electric current in a special cuvette in which irradiation was also performed. The temperature was measured with a thermocouple, the junction of which was introduced directly into the body of the specimen. The dose rate of the beam, obtained on an accelerator operating at a voltage of 600-900 kV, was $E \sim 2 \cdot 10^{17}$—$4 \cdot 10^{19}$ eV/cm$^3 \cdot$ s.

Fig. 1. Gas formation in polymers upon irradiation as a function of temperature. **1** and **1a** –polymethyl methacrylate, plasticized with 6% dibutyl phthalate (**1**), unplasticized (**1a**). Dose $E_0 = 4.3 \cdot 10^{21}$ eV/cm^3, dose rate $E = 14.4 \cdot 10^{18}$ eV/cm$^3 \cdot$ s, $\tau = 5$ min. **2** –Polytetrafluoroethylene; $E_0 = 12.7 \cdot 10^{21}$ eV/cm^3, $E = 42 \cdot 10^{18}$ eV/cm$^3 \cdot$ s, $\tau = 5$ min.

The thickness of the specimens (2-3 mm) in all cases exceeded the thickness penetrated by the electrons. The quantity of gaseous products formed was determined in PTFE from the loss in weight of the specimens (Δm), and in PMMA from the volume (Q) of gases released upon dissolving the specimens in dichloroethane.

As is seen from Fig. 1, the process of gas formation under the combined action of irradiation and elevated temperature in the polymers studied proceeds in a very distinctive manner. For example, in PTFE the intensity of gas formation over a wide temperature interval is negligible, amounting to hundredths of a percent, and even at 250° Δm does not exceed 0.5%. However, in the region close to the melting temperature, near the point of transition of PTFE into the viscous-flow state ($\sim$ 330—350°), gas formation increases sharply, so that at the same dose the irradiated specimen loses about half its weight in 5 min. With a somewhat longer duration of irradiation, the specimen is completely converted into gaseous products.

An analogous dependence of the rate of degradation on temperature at a constant dose is also observed upon irradiation of PMMA. It follows from Fig. 1 that the amount of gases, extremely insignificant up to 100-110°, increases in the region of strong softening of the polymer just as sharply as in the case of PTPÉ. The gas bubbles, being unable to escape from the specimens, swell them and turn them into a sponge whose volume is 5-10 times greater than the volume of the initial specimen. For unplasticized PMMA (the preceding specimen contained 6% dibutyl phthalate), the indicated transition, as might have been expected, lies in the region of higher temperatures (150-170°) (dashed curve *1a* in Fig. 1).

Finally, the same effect of a sharp acceleration of the degradation process was also found for PE at 110-120°. It is important to note here that an increase in the intensity of radiolysis affected the mechanical strength of the specimens much less than irradiation at temperatures below the temperature of this transition.

The general character of the phenomenon of a sharp enhancement of radiation degradation of polymers in the narrow temperature range of melting (softening) of the material apparently indicates the reversibility of the radiolysis reactions that give rise to gaseous products. Dissolving in the polymer, the gases form highly supersaturated solutions; however, subsequently, owing to the low rate of their liberation by diffusion (⌢2), further gas formation is rapidly inhibited by the increase in the concentration of the solution, or, equivalently, of the pressure. With the transition of the polymer into a viscous liquid, the strong increase in the rate of diffusion of the gases reduces the supersaturation, owing to a sharp facilitation of the formation of nuclei of a new gas phase and of their growth.

The rapid removal of degradation products from the reaction sphere shifts to the left the equilibrium of the reversible process: degradation   recombination of free radicals and, thus, sharply increases the rate of radiolysis processes. As a result, one and the same irradiation dose can cause degradation of entirely

Figure 3

Figure 2: Figure 3

different intensity in two temperature regions: below and above the region of the sharp break in the gas-formation–temperature curves. Since the increased mobility of macromolecules in the region after the break in the curve ensures complete relaxation of the stresses arising in the material, larger amounts of gases evolved affect the mechanical properties of polymers to a lesser degree than small volumes of them formed at temperatures below this transition.

This indicates the role that internal stresses caused by gas formation may play in the destruction of polymers, even if the gases have not separated from the supersaturated solution as a new phase. This also apparently makes it possible to explain the reason why there is no correspondence between the resistance of polymers and the amount of gases evolved from them upon irradiation. There is no basis for associating the indicated effect of a sharp increase in the intensity of degradation and gas formation with thermal activation of radiolysis reactions, since in that case the influence of raising the temperature should have increased monotonically. Meanwhile, the change in the rate of the process occurs by a jump, in a narrow temperature interval.

The dependence of gas-formation processes during irradiation on the state of the polymer is also manifested in the violation of the rule of equivalence of the action of equal doses, irrespective of dose rate, which is valid in a number of cases for radiation degradation. This is seen from Fig. 2, which presents for PMMA the dependence of the amount of gases evolved from the specimens on the dose rate (E). The reason for the appearance of the sharp bend in this curve is that, at the values of E used by us, irradiation greatly raises the temperature of the specimens and, at sufficiently large E, transfers them into the state of a viscous liquid. This occurs within a narrow zone in which the ionizing action of the radiation and the release of heat are greatest—in accordance with the shape of the distribution curves of the absorbed energy of slowed electrons over the thickness of the specimen, hav—

Fig. 3. *a*—formation of cracks in polymethyl methacrylate, $E_0 = 0.17 \cdot 10^{21}$ eV/cm^3, $E = 8.5 \cdot 10^{18}$ eV/cm$^3 \cdot$ sec, $\tau = 20$ sec; *b*—pattern of crack development in polymethyl methacrylate and of the formation of gas bubbles from them, $E_0 = 0.65 \cdot 10^{21}$ eV/cm^3, $E = 32.4 \cdot 10^{18}$ eV/cm$^3 \cdot$ sec, $\tau = 20$ sec. (150×)

···having a sharply pronounced maximum in this zone[1] (for PMMA, for example, at an electron velocity corresponding to a voltage of 900 kV, this zone lies at a depth of about 1.65 mm). Therefore, in the range of values

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[1] J. G. Trump, R. J. van de Graaff, *J. Appl. Phys.*, **19**, No. 7, 566 (1948).

Fig. 2

Figure 3: Fig. 2

$$E \sim 30\text{–}35 \cdot 10^{18}\ \text{eV/cm}^3 \cdot \text{s},$$

in which the temperature of the specimens rises to

$$t \simeq 110\text{–}130^\circ,$$

gas evolution increases sharply. It is interesting to note here that if, from the values of the specimen temperature indicated near each experimental point of the curve $Q = \varphi(E)$ (Fig. 2), one constructs the curve $Q = f(t)$, then its position practically coincides with the position of curve 1 in Fig. 1, which characterizes the analogous dependence $Q = \psi(t)$. This shows that a definite relation exists between the quantities Q and t, although in a number of cases the results of irradiation may differ depending on whether the given specimen temperature was reached by preliminary heating in a furnace (the experimental conditions of Fig. 1) or as a result of the irradiation process itself (the experimental conditions of Fig. 2).

Fig. 2. Dependence between gas evolution in polymethyl methacrylate and dose rate at a constant dose $E_0 = 4.8 \cdot 10^{21}$ eV/cm^3 = const. E varied in the interval from 0.67 to $40 \cdot 10^{18}$ eV/cm$^3 \cdot$ s.

The reversible character of the destruction process also makes it possible to explain the formation, under electron irradiation, of tree-like cracks, studied in detail in polymer glasses[2]. We also observed this phenomenon in PE. The results obtained show that, in contrast to the adsorption mechanism proposed in[3], the formation of these cracks (Fig. 3a) should be regarded as a phenomenon caused by gas evolution, and the cracks themselves as channels through which the gases move. Without dwelling in detail on these results, we present microphotographs (Fig. 3b) indicating a genetic connection between these cracks and gas bubbles. They show how a thin crack, formed in the region of weak influence of the electron beam displaced relative to the PMMA specimen (to the right of the line $\times - - - - \times$), where the beam acted on it with the full dose, sharply widened into a cavity filled with gas. Depending on the conditions of gas evolution at individual points of the specimen, determined by the distribution of the radiation energy absorbed by them over area and thickness, cracks may: 1) expand intensively and turn into channels constituting a system of not fully developed bubbles, which, because of the high viscosity of the medium, slowly merge with one another, or 2) without expanding especially strongly, grow into separate isolated, fully formed bubbles (Fig. 3b).

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[2] B. L. Tsetlin, N. G. Zaitseva, V. A. Kargin, DAN, **113**, No. 2 (1957).

[3] B. L. Tsetlin, N. G. Zaitseva, V. A. Kargin, DAN, **113**, No. 2 (1957).

Thus, arising as a result of the stressed state of the material caused by the evolution of gases, after their formation cracks lead to a decrease in the supersaturation of the solutions and to the liberation in them of the excess gases being formed.

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