Study of the influence of the electron irradiation dose on the deformation of mylar films taking into account the processes of destruction and crosslinking

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Abstract. Experimental studies of the dependence of the deformation ε on the dose of electron irradiation D taking into account the processes of destruction and crosslinking for films of the Mylar type have been carried out. It was obtained that the dependence of ε on D for the process of cross-linking is described by a linear and destruction by an exponential function.

1. Introduction
The study of the processes occurring in polymers under the influence of various factors makes it possible to predict their behavior in the fields of intense loads. The physico-mechanical properties of the material are determined by the number of defects contained in it and the probability of the occurrence of various reconstructions with their participation [1, 2]. One of the important directions of research in this case is the study of the change in the physico-mechanical characteristics of high molecular compounds under the action of high-energy particles, which cause significant transformations in the structure [2]. The mechanism of influence of high-energy particles on high-molecular compounds in the condensed state is characterized by the presence of physical and chemical stages. There is a spatial transformation of matter, the molecular weight of the macromolecule changes, and accumulation and disappearance of various types of chemical bonds, etc., which lead to a variety of properties of the polymer material [3, 4]. The most significant structural changes in the properties of polymers are due to irreversible processes of structuring and destruction. These processes are usually carried out simultaneously, and the predominance of one of them depends on the structure of the material, the nature of the substances present in the system and the irradiation conditions [5]. Structuring improves a number of properties of polymers. The transformation of a linear polymer into a spatial polymer is accompanied by a significant increase in the molecular weight, which leads to its insolubility in organic solvents, to an increase in the mechanical strength of the material, and so on. The destruction of the polymer material reduces its molecular weight. The mechanical strength and the softening temperature during degradation are reduced, since the forces of intermolecular bonds in the polymer are higher, the larger the size of the molecules. Therefore, for practice, it is of great importance to study methods of protecting polymers from degradation [6]. At present, there is a large number of theoretical and experimental studies describing the various stages of the radiation-physical
processes taking place in polymer materials, a significant amount of data on radiation-chemical transformations in these media under the action of ionizing radiation under various conditions has been accumulated. It becomes possible to solve not only the problems of predicting the behavior of structural polymers in the fields of ionizing radiation, but also the purposeful creation of materials with predetermined properties [7, 8].

2. Experimental

The object of the study is an industrial polyethylene terephthalate film manufactured in the USA (Maylar type) in the form of strips 5 mm wide, working length is 50 mm, 100 μm thick. Irradiation of the samples was carried out in air in special holders on an ELU-6 electron accelerator at 20 °C with an energy of 4 MeV, a current density of 0.5 μA/s, a pulse duration of 5 μs at a repetition rate of 200 Hz. Absorbed doses (D) were $0 - 3 \cdot 10^5$ kGy. Investigation of mechanical characteristics was carried out on a computerized tensile machine of the RMU-0.05-1 type with a clamping speed of 36.09 ± 0.05 mm/min. The movement of the grip associated with the meter was 0.1 mm. The tests were carried out in the form of uniaxial tension using a special reverser at a constant load and the temperature of 20 ± 2°C, relative humidity was (45 ± 5) %. Deformation was determined depending on the dose of irradiation. The obtained experimental data were transmitted directly to Excel tables. Their parameters were set by the user. All the experimental data obtained were mathematically processed (Mathematica 5 system).

3. Discussion of the results

Figure 1 (a, b) shows the experimental (points) dependences of the relative elongation ($\varepsilon$) on the dose of electron irradiation D at the temperatures of a) $T = 293$ K and b) $T = 473$ K. With an increase of D up to $10^4$ Gy at the temperatures of 293 and 473 K, the relative elongation first slowly increases and at $D \approx 10^6$ Gy $\varepsilon$ drops sharply to 0. It can be seen from the figure that up to $10^4$ Gy at the temperatures of 293 and 473 K, the crosslinking processes predominate for the Mylar film, and a further increase in the dose leads to destruction of the material (curves 1 and 2). With height of temperature of $\varepsilon$ grows. For an interval of doses of $0 - 2 \cdot 10^4$ Gy the specific elongation at $T = 473$ K is 1.93 times larger than at $T = 293$ K.

![Figure 1](image)

**Figure 1.** Dependence of the deformation on the dose of electron irradiation at different temperatures of Mylar type films
We have proposed a generalized model that simultaneously describes the processes of crosslinking and destruction for the whole range of doses from 0 to 10^6 Gy (before destruction).

The general formula for calculation is:

\[
\varepsilon = \varepsilon_1 + \varepsilon_2 ,
\]

\[
\varepsilon_1 = \varepsilon_0 \exp \left( -\frac{D}{D_0} \right) , \quad \varepsilon_2 = aD ,
\]

where \( \varepsilon_0 \) is the maximum value of material deformation before irradiation; \( a \) is a coefficient characterizing the crosslinking. Moreover, the crosslinking is taken into account as a linear, and the destruction as an exponential function (Figure 1a and b, curves 1 and 2). For the Mylar-type film, the crosslinking component is negligible and is \( \sim 5 \% \). Irradiation of polymers affects the crosslinking and degradation processes, forming chemically unsaturated bonds and gaseous products. This breaks the chemical bonds of C-C in the main and side chains of the macromolecule and the bonds of C-O, C-H, C-N, C-F, C-Cl, Si-C, and C-S. The investigated sample of the Mylar-type film has a complex heterogeneous structure of amorphous regions with a significant proportion of interfibrillar amorphous clusters separating adjacent microfibrils, along with intrafibrillar amorphous interlayers [9, 10]. When the material is irradiated, the absorbed energy causes simultaneous discontinuities of mainly C-C and C-H bonds. Crosslinking polymers are characterized by the recombination of a significant part of the broken C-C bonds and, as a result, the discontinuities of the C-H bonds predominate.

The impact of external loads on the polymer material creates a strain that propagates at a certain rate from the point of application of force from the clamps along the specimen. The weakened fragment of the film closest to the place of application of the load will be the point of discontinuity. The process of destruction consists of two stages: the first stage is the emergence and growth of primary cracks; in the second stage, cracks develop rapidly and germinate through the entire cross section of the sample, leading to its destruction [6]. In the polymer, the cause of the appearance of primary cracks is thermal fluctuations, which lead to a sharp increase in the kinetic energy of individual atoms, and consequently, the chemical bond breaks down in the polymer backbone. Increased temperature and applied stress increases the probability of rupture, especially those bonds that are overstressed [7]. For highly elastic polymers, along with the breakage of chemical bonds, slipping of one part of the sample from the other, accompanied by rupture of intermolecular bonds, takes place during destruction [1, 3].

We note that an increase in temperature to 473 K leads to an increase in strain by 90 \%, but the percentage of crosslinking processes decreases. This is confirmed by the curves of Figures 1a and b. At very high doses, fragments of the installation loosely coupled among themselves elements of the temperature aggravated by the action remain. This is due to the weak lateral branching of the PET polymer chain. At the same time, the number of passing molecules increases and the mechanism of their sweep from the cross-linked systems is violated. For destructive polymers, rapid recombination of broken ends of the chain is difficult, in them radicals are stabilized by the disproportionation reaction, forming two stable end groups, which fix the act of destruction. The competing processes of crosslinking and destruction are ultimately determined by the rate of recombination of the bond rupture.

It was established in [11 – 13] that irradiation in PET reduces the molecular weight by a factor of 3 compared to the unirradiated samples. From elemental analysis, it was also found that with increasing absorbed dose, the carbon content (n) decreases by 2.60 \% and hydrogen by 0.18 \%, but at the same time the oxygen content increases by 2.78 \%. All these data indicate the discontinuities of macromolecules and the predominance of the process of destruction. Studies have shown a reduction in the optical density of the film with an increase in the radiation dose, which also indicates
restructuring processes involving the displacement or misorientation of optical centers, the intensification of the destruction of polymer chains, and gas formation in the bulk of the polymer under the action of fast electrons.

4. Conclusions
1. Under the influence of temperature, irradiation and static loading on Mylar-type films, crosslinking and destruction processes are intensified.
2. Prior to doses of $10^4$ Gy at the temperatures of 293 and 473 K, the predominance of crosslinking processes is observed. A further increase in the irradiation dose to $10^6$ Gy increases the probability of rupture of chemical and intermolecular bonds associated with the slip of one part of the sample from the other, accompanied by a rupture, with a weak lateral branching of the PET polymer chain. At the same time, the mechanism of the development of molecules from cross-linked systems is violated.
3. As the temperature of the irradiated material increases, the deformation increases greatly, but the cross-linking process decreases, which is due to the instability of the fragments of the mounting loosely coupled elements, which are aggravated by the effect of temperature. Thermal fluctuations lead to a sharp increase in the kinetic energy of individual atoms, and as a result, the chemical bond breaks down in the polymer backbone.
4. A generalizing model of deformation dependence on the dose of electron irradiation is proposed, which takes into account competing processes of cross-linking and destruction. It is obtained that the process of cross-linking is described by a linear function, and the destruction process – by exponential one.

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