The effect of electron irradiation on the properties of polyimide films of various grades

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Abstract. The physico-mechanical properties of PIAB polyimide film irradiated by high-energy electrons have been studied. Changes in the surfaces and chemical composition of PI under the influence of electron irradiation were studied. The effect of high-energy electrons on polyimides of various grades leads to significant changes in their deformation-strength characteristics and depends significantly on the structure and technology of material synthesis.

1. Introduction
In the period of rapid development of technology and the creation of various materials, the most relevant is their production with improved properties and parameters compared with existing ones [1]. Their modification is possible with the help of various influences. Because polymer materials have cheap mass production and unique properties, they are being introduced in all areas of human activity. The growing demand for the exploitation properties of materials poses the question of improving the properties of materials [2]. Recently, among polymer systems of various classes materials based on aromatic polyimides (PI) have caused close attention [3, 4]. They have a unique complex of extremely high parameters of thermal stability, excellent mechanical and electrical characteristics combined with high chemical and radiation resistance [5, 6]. The most important task, from a scientific and practical point of view, is the modification of these properties due to the irradiation with particle flows, thermal effects, mechanical loads, etc. An important property for the PI matrix is the ability to crystallize after melting and subsequent cooling [7]. In connection with this, it is important to obtain new fundamental results in the field of deformation, strength and optical properties of materials, determination of the safe deformation resource of products under the combined action of mechanical loads and operating temperatures, and assessment of the hazards of technological and operational defects [8, 9].

The effect of ionizing radiation on polymers leads to a change in their physico-chemical properties associated with simultaneous processes of structuring and destruction [10]. Accumulated experimental and theoretical results in this area are already used in science and technology. At the same time, the problem of creating a general theory of conformities and mechanisms of processes under the action of ionizing radiation and predicting their behavior remains unsolved [11, 12]. The article is devoted to the study of the physico-mechanical, optical properties and structure of a polyimide film subjected to electron irradiation.
2. Experimental
The object of the study is PI<sub>AB</sub> polyamide, 35 μm thick. The strain-strength characteristics (ε (σ)) of the polymers were studied on BM-0.05-1 type computerized rupture machine with a clamping extension rate of 36.09±0.05 mm·min<sup>-1</sup>, capture movement of 0.1 mm. The temperature of the samples was (20±2)°C, relative humidity of air was (45±5)%. The working length of the test sample is 50 mm, width 5 mm. PI<sub>AB</sub> polyamide film was irradiated on ELA-6 electron linear accelerator in air at 25°C with an energy of 2 MeV (beam current density was 0.5 μA/cm<sup>2</sup>, pulse duration was 5 μs, frequency was 200 Hz). The absorbed dose (D) was 50-250 kGy. The surface of PI<sub>AB</sub> polyamide was studied on the optical ((AFM) LeicaDM 6000 M) and atomic-force "Integra-Terma" microscopes. The IR spectra were taken at room temperature using the standard technique on Jasco IR-810 (Japan) spectrophotometer in the wave number interval of 400-4000 cm<sup>-1</sup>

3. Main results
The results of studies of the physico-mechanical properties of polyimide films of different grades are presented in table 1. The study of the physico-mechanical characteristics of irradiated samples showed that the dependences of the strength and relative elongation of PI<sub>AB</sub> film on the dose are linearly decreasing in nature, which is due to the prevailing destruction processes.

Table 1. The change in the physico-mechanical properties of polyimide films irradiated with electrons.

| The absorbed dose | PI<sub>AB</sub>, (kGy) | Apical PI [13], (MGy) |
|------------------|-----------------------|----------------------|
|                  | 0         | 100    | 250    | 0       | 1       | 3       | 10      |
| σ, (MPa)         | 51.7      | 47.6   | 39.62  | 145     | 162     | 125     | 124     |
| ε, (%)           | 36        | 33.5   | 28.4   | 72      | 77      | 62      | 61      |

For the Apical polyimide [13], both for σ and ε in the range of doses of 0–3 MGY there is a small maximum (~10 %) associated with partial cross-linking of the polymer. The difference in the dependences of the deformation-strength characteristics of PI<sub>AB</sub> and the Apical on the dose of irradiation is due to the difference in structures in synthesis technologies.

The study of the surfaces of unirradiated PI<sub>AB</sub> polyimide films (figure 1a) when the samples are examined for transmission on the optical microscope showed that the surfaces of the samples are homogeneous smooth and look matte-blue. The surfaces of PI<sub>AB</sub> polyimide samples irradiated with D=27 kGY dose (figure 1b) represent an absolutely inhomogeneous surface with different transmittance with dark and light spots of varying density ranging from one to several micrometers with clear boundaries of their localization regions. Individual areas with significant depressions are clearly visible on the surface. Electronic irradiation of polyimides enhances the processes of chemical erosion and gas formation. In this case, gel fractions and spherical molecular formations are formed that determine the mechano-thermal properties of the polymer.

AFM studies of the polyimide surface (figure 2) after treatment with accelerated electrons indicate changes in the film surface. For unirradiated PI<sub>AB</sub> polyimide, the surface of the initial material is not homogeneous, the shape of the particles is different (figure 2a). Electronic exposure of 100 kGY to PI<sub>AB</sub> polyimide leads to a change in the shape of the particles on the surface, to a more uniform increased surface roughness of the test sample (figure 2b).

For the Apical grade, the surface roughness after irradiation increases by more than 10 times in comparison with the surface of the initial polyimide film (before 2.6 nm, after 30 nm). The authors of [13] established that the electronic action leads to the destruction and removal of part of the polymer surface layer, and the polymer surface structure becomes fibrillar with the diameter of 2 μm.
Figure 1. Image of the surface of unirradiated (a) and irradiated (b) PIAB polyimide film. The image field is 44x33 μm.

Figure 2. The results of AFM tests of the polyimide surface: a – PIAB polyimide film with thickness of 35 microns, plot of 5x5; b – irradiated PIAB polyimide film (D=100 kGy).

IR spectra of the unirradiated and irradiated PIAB polyimide film and the Apical polyimide are shown in figure 3. The most informative lines lie in the ranges of 500-1700 cm\(^{-1}\) and 2500-3700 cm\(^{-1}\). In these spectra, the following changes were observed:

Figure 3. IR absorption spectra of polyimide films. a – unirradiated PIAB polyimide film; b – irradiated PIAB polyimide film (D=40 MGy); c – unirradiated (solid curve) and irradiated (D=300 MGy, dotted curve) polyimide film of the Apical brand produced by Kaneka (Japan) [13].
For PI_{AB} film, an increase in the intensity of the bands in the region of about 526.8 cm\(^{-1}\); 603.6 cm\(^{-1}\); 726 cm\(^{-1}\) and 835.8 cm\(^{-1}\) is observed, indicating an increase in the overtone benzene rings, valence oscillations of -C=O, aliphatic groups, substituted benzene rings, and vibrations of -C-C- groups.

For the Apical brand, a decrease in the intensity of the bands at 525 cm\(^{-1}\); 600 cm\(^{-1}\) and 850 cm\(^{-1}\) regions was recorded, which indicates the decyclization of imide fragments [13].

The electronic effect on PI_{AB} polyimide films leads to an increase in the intensity of the absorption bands of 1628.2; 1772.2; 2949.8; 3052.5 cm\(^{-1}\) in 2–6 times and a significant expansion of the bands, which is associated with the formation of hydrogen bonds, i.e. with the formation of cycles involving nitrogen and the formation of nitrogen oxides.

In the interval of 3000-3650 cm\(^{-1}\), an increase in the intensity is observed for both brands of polyimide: the range of 3050-3100 cm\(^{-1}\) is characteristic for -C-H vibrations of the aryl ring, in the 3400 cm\(^{-1}\) region there are stretching vibrations of -NH groups, 3500 cm\(^{-1}\) are the valence vibrations of -OH groups in unbound carboxyl groups. An increase in the intensity of these bands indicates the breaking of bonds between the aryl ring and the imide group with the reduction of the benzene ring, the destruction of imide cycles, and the oxidation of polyimide with the formation of carboxyl groups [13].

The data of [13] show that after irradiation, an increase in the amount of moisture sorbed by the polymer in the Apical polyimide is observed (an increase in the intensity of the absorption bands in the regions of 1620 and 3000-3650 cm\(^{-1}\)). The electron effect on polyimides of various grades leads to a change in the surface of the films and the chemical composition.

4. Conclusion
The effect of high-energy electrons on polyimides of various grades leads to significant changes in their deformation-strength characteristics and depends significantly on the structure and technology of material synthesis.

It has been established that the electron effect on polyimide of various grades leads to a change in the morphology of the layer on the surface of materials associated with chemical erosion, gas formation, gel fractions formation, etc.

The electron effect on polyimide of different grades leads to a change in the chemical composition (increased content of oxygen-containing groups, sorbed water, formation of cycles involving nitrogen and formation of nitrogen oxides, spherulolytic molecular formations, etc.).

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