Changes in structure of PA6 during electron irradiation

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Abstract. The impact of electron irradiation on the structure of the PA6 polymer is researched in this article. The electron beam irradiation of samples from PA6 was carried out on an industrial pulse accelerator ILU-10 under different modes. Beam energy and radiation dose varied. The structural changes of PA6 were studied by scanning electron microscopy, X-ray phase analysis, IR Fourier spectroscopy, and the thermal characteristics of the polymer were studied by differential scanning calorimetry. It was revealed that after electron beam treatment, the melting temperature of the PA6 polymer decreases from 214 °C to 217 °C. It was found that electron beam treatment leads to a change in the surface morphology, that is, the surface becomes rough, the depth of the roughness and the structure of spherulites increase.

1. Introduction
In the last time quite intensively conducted research on the effect of ionizing radiation on the structure and properties of polymers [1-3]. At the same time, the mechanism of structural phase transformations in polymeric materials during electron beam processing has not been sufficiently studied. All the effects of irradiation affecting polymeric materials are difficult to predict. Despite the simple polymer structure, all changes occurring in the structure are quite complex. Since the destruction of chemical bonds requires the application of energy of several eV, it can be expected that the radiation of the incident electron beam, which is usually a few MeV, will inevitably lead to the destruction of the bonds of the polymer chain. Usually in polymers, either destruction or the formation of new transverse intermolecular bonds (crosslinking) occurs [4,5]. It is known that the formation of transverse intermolecular bonds in polyethylene improves its abrasion resistance, which is widely used in a number of industrial applications [6].

Therefore, studies related to the study of the properties of polymer-based materials subjected to electron beam irradiation are relevant. In connection with the foregoing, it seems to us necessary to study the laws of structural-phase transformations in the surface layers of the PA6 polymer during non-vacuum electron-beam treatment.

2. Materials and methods of research
Universal multifunctional semi-crystalline polymers of structural and cryotechnical purpose - polyamide PA6 were chosen as research materials. Billets of samples for research were cut from a polymer rod (rod diameter 30 mm) with a thickness of 3 mm.
Electron beam processing (EBP) of samples from polymeric materials was carried out on an industrial impulse accelerator ILU-10 in JSC "Park of Nuclear Technologies" (Kurchatov, Kazakhstan). Accelerators of the ILU type are quite specific linear high-frequency accelerators — it is single-resonator machines operating in the standing half-wave mode (unlike most linear accelerators) [7]. The composition of the accelerator includes: an accelerating system with an exhaust device, a vacuum system and an RF generator; switching power supply; control rack. The operating frequency of the ILU-10 accelerator is 118 MHz, the length of the accelerating gap of the accelerator is 26 cm. The main parameters of the ILU-10 accelerator are in table 1.

Table 1. The main parameters of the accelerator ILU-10.

| Parameters                        | Value |
|-----------------------------------|-------|
| Electron energy, MeV             | 2.5-5 |
| Average beam power, kW           | 50    |
| Average beam current, mA         | 15    |
| Power consumption, kW            | 150   |
| Accelerator weight, t            | 2.9   |

Samples are mounted on a table of an electron accelerator, which moves relative to the electron beam. Samples were irradiated by electrons with 2 MeV, 3 MeV, and 4 MeV energies. In this case, the radiation dose varied from 2 MGy to 9 MGy. The blanks moved longitudinally relative to the outlet. In this case, the cultivated area amounted to 1000×80 mm². EBP modes of polymeric materials are presented in table 2.

Table 2. EBP modes of PA6 polymers.

| № modes | Beam Energy, MeV | Beam current, mA | Exposure time, s | Number of runs | Irradiation dose, MGy |
|---------|------------------|------------------|------------------|----------------|-----------------------|
| 1       | 2                | 6,84             | 30               | 6              | 3                     |
| 2       | 3                | 6,84             | 30               | 6              | 3                     |
| 3       | 4                | 6,84             | 30               | 4              | 2                     |
| 4       | 4                | 6,84             | 30               | 6              | 3                     |
| 5       | 4                | 6,84             | 30               | 8              | 4                     |
| 6       | 4                | 6,84             | 30               | 10             | 5                     |
| 7       | 4                | 6,84             | 30               | 12             | 6                     |
| 8       | 4                | 6,84             | 30               | 14             | 7                     |
| 9       | 4                | 6,84             | 30               | 16             | 8                     |
| 10      | 4                | 6,84             | 30               | 18             | 9                     |

The morphology of the surface structure was studied using a JSM-6390LV scanning electron microscope equipped with an energy dispersive analysis attachment after irradiation of the samples. The phase composition and crystal structure of the samples were studied by X-ray phase analysis on an X’PertPro diffractometer using CuKα-radiation. The chemical composition and structure of the polymers were studied using an FTIR-801 Simex Fourier transform infrared spectrometer. The infrared spectrum was obtained as a result of 50 scans at a wavelength of 450-4700 cm⁻¹, a resolution of 1 cm⁻¹, t = 25 C˚. Samples were microtominated to a thickness of 200 μm sections from the surface of the sample. The thermal characteristics of the polymers were studied by differential scanning calorimetry (DSC). The measurements were carried out according to the requirements of GOST R 55134-2012 in the temperature range of 20-500 °C.
3. The results of research and their discussion

The surface morphology for all unirradiated and irradiated polymers is shown in Fig. 1. It can be seen that the surface of the samples has a uniform spherulite homogeneous structure before irradiation.

![Figure 1](image.png)

**Figure 1.** Scanning electron micrographs of polymers before (a) and after irradiation at a dose of 3 MGy, 4.5 MeV (b)

It is clearly seen in the irradiated films that the morphology improves significantly, that means the surface becomes rough, the unevenness and structure of the spherulites increase. The effect of electron radiation leads to a significant change in the surface morphology. Agglomeration regions, cracks and pores are observed on the surface after EBP. Spherulites are formed at the micro level which consisting of radially oriented fibrils. These changes clearly indicate the displacement of polymer molecules under the influence of radiation. Perhaps this is due to an increase in the volume surface due to the interaction of electrons with free radical groups of the polymer molecule and reduces the crystal intensity [8, 9]. These results correlate well with the results of X-ray diffraction on PA6 (Fig. 2). From the Figure, we can clearly see two strong diffraction peaks at $2\theta = 20.5^\circ$ and $24^\circ$ among all the samples, which are a distinctive feature of the $\alpha$-phase of PA6, designated as $\alpha_1$ and $\alpha_2$, respectively. Similar peaks from the same angle were reported by Sibilia [10] and Shailesh [11].
It can be seen from the X-ray diffraction pattern of the PA6 samples before and after EBP that the irradiation did not change the crystalline shape of the PA6 fibers, but the intensity of the same peak first decreased and then increased compared to the untreated polymer, which can be explained by a decrease in crystallinity. During the process, the radiation dose accelerated the crosslinking rate of free radicals and restrained pyrolysis and recombination, which led to a decrease in crystallinity.

The impact of irradiation on the general shape of DSC thermograms of PA6 samples is illustrated in Fig. 3. The melting peaks have shifted to a lower temperature, which may indicate that the crystalline region may become disturbed due to cross-linking between crystalline and amorphous regions. Typically, the width of the melting endotherms of DSC thermograms indicates a change in the crystallinity of the irradiated samples, which had the same tendency as the data of X-ray diffraction analysis.

**Figure 2.** Diffraction pattern of PA6 samples before and after EBP

1 - 3 MGy (2 MeV); 2 - 3 MGy (3 MeV); 3 - MGy (4 MeV); 4 - 3 MGy (4 MeV); 5 - 4 MGy (4 MeV); 6 - 5 MGy (4 MeV); 7 - 6 MGy (4 MeV); 8 - 7 MGy (4 MeV); 9 - 8 MGy (4 MeV); 10 - 9 MGy (4 MeV)
Figure 3. DSC thermogram of the initial and irradiated samples of PA6 polymer

Fig. 4 present the IR spectra of the PA6 polymer before and after irradiation. The characteristic peaks of the PA6 vibrational frequency are at the levels of 3579.4 (NH stretching), 2934.8 (CH₂ stretching), 1585.1 (C = O stretching, amide I), 1398.7 (NH bending vibration) and 776.28 cm⁻¹ (bending vibration NH). A peak at about 2860 cm⁻¹ may be associated with the doublet band of carbon dioxide absorption from atmospheric air during the measurement.

Figure 4. IR spectra of the initial and irradiated PA6 samples

Each peak position is fundamental to the molecular bond structure or functional group present in PA6. Thus, any change in the position of the peak in the spectrum directly relates to a change in the bond strength or bond angle. The weakening and strengthening of the bond shifts the wave number of the corresponding absorption peak to lower and higher values, respectively. The absence of a specific absorption band is associated with rupture or rupture in a particular binder structure. In addition, a change in the intensity of a particular peak in the spectrum correlates with the fraction of this functional group present in the material. PA6 has an amide (CONH-) group in the repeating unit, which leads to the formation of an H-bond between the C = O group in one chain and the N-H group of the other chain. The H bond is responsible for the formation of the crystal structure in PA6. The IR spectra of irradiated PA6 were identical to unirradiated. No new functional groups have been created. A possible reason may be that irradiation simply caused a bond break to form free radicals, and then rearrange to cause crosslinking [12].

4. Summary
Analyzing the experimental results obtained in the work, we can draw the following conclusions:

Thermal characteristics of polymer samples were determined by using the method of differential scanning calorimetry. To analyze the effect of radiation on the crystallization of polymers. It was revealed that the melting point of the PA6 polymer decreases from 214 °C to 217 °C after EBP. The most likely explanation is a decrease in chain mobility caused by strong interactions between the polymers that occur between oxygen ions and electron-deficient imide rings in PEI.

The result of IR spectroscopic research showed that the irradiated PA6 samples were identical to unirradiated samples. The formation of new functional groups was not detected, apparently due to the fact that irradiation simply caused a bond break to form free radicals, and then rearrange to cause crosslinking.

It was established that EBP leads to a change in the surface morphology, that means the surface becomes rough, the depth of the roughness and the structure of spherulites increase. Agglomeration regions, cracks and pores are observed on the surface after EBP. Spherulites are formed at the micro level which consisting of radially oriented fibrils. These changes clearly indicate the displacement of
polymer molecules under the influence of radiation.

Acknowledgments
The work was financially supported by the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan under the "Grant Financing of Scientific Research‖ program (project code - AR05134982).

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