DOI 10.31489/2020Ph1/35-41

UDC 621.791

Zh.B. Sagdoldina[1], B.K. Rakhadilov[1], K. Akatan[1], P. Kowalewski[2], D.Zh. Karabekova[3]

[1]S. Amanzholov East Kazakhstan State University, Ust-Kamenogorsk, Kazakhstan;
[2]Wroclaw University of Science and Technology, Poland
[3]Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: sagdoldina@mail.ru)

The impact of non-vacuum electron beam treatment on the structure and properties of ultra-high molecular weight polyethylene

The results of work on the impact of electron beam treatment on the structure, mechanical properties, microhardness, and thermal stability of ultra-high molecular polyethylene (PE-UHMW) are presented in this work. Electron beam processing was carried out on an industrial impulse accelerator ILU-10. The samples were irradiated with electrons with energies of 2.5 MeV, 3.5 MeV and 4.5 MeV, and the radiation dose varied from 2MGy to 9 MGy. It was determined by the method of differential scanning calorimetry that the melting temperature of the PE-UHMW polymer practically does not change for all samples, regardless of the radiation dose. After electron beam treatment, the morphology of the surfaces of the PE-UHMW polymer is significantly improved, spherulites are formed at the micro level, which indicate the displacement of polymer molecules under the influence of irradiation. It was revealed that during electron beam treatment oxidation occurs as a result of chemical reactions of the polyethylene chain with oxygen O_2. Significant changes in the mechanical properties of the PE-UHMW polymer were not observed after electron beam treatment. However, a significant decrease in the elongation from 300 % to 10 % as a result of radiation aging was observed after electron beam treatment.The hardness of the PE-UHMW polymer varies slightly in the studied mode of electron beam processing.

Keywords: electron beam treatment, ultra-high molecular weight polyethylene, structure, mechanical property, oxidation.

Introduction

The article deals with quite intensively conducted research on the impact of electron beam processing on the structure and properties of polymers. At the same time, the mechanism of structural-phase transformations in polymeric materials during non-vacuum electron-beam processing in industrial pulse accelerators has not been sufficiently studied. All impacts of irradiation affecting polymeric materials are difficult to predict. Despite the simple polymer structure, all changes occurring in the structure are quite complex. 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 features of the formation of the structure and properties of ultra-high molecular polyethylene during electron-beam non-vacuum electron-beam processing.

Materials and methods of research

In accordance with the tasks, ultra-high molecular weight polyethylene(PE-UHMW)was chosen as the object of study. Samples 3 mm thick were cut from a polymer rod (rod diameter 30 mm). Electron beam processing (EBP) was carried out on an ILU-10 industrial pulse accelerator at JSC «Nuclear Technology Park»

(Kurchatov). Accelerators of the ILU type are quite specific linear high-frequency accelerators — these are single-resonator machines operating in the standing half-wave mode (unlike most linear accelerators). The composition of the accelerator includes: an accelerating system with an exhaust device, a vacuum system and a high-frequency generator; switching power supply; control rack. The operating frequencies of the ILU-10 accelerator are 118 MHz, the length of the accelerating gap of the ILU-10 accelerator is 26 cm. The main parameters of the ILU-10 accelerator are presented in Table 1.

Table 1

The main parameters of the ILU-10 accelerator

Parameters	Meanings
Electronenergy, MeV	2.5–5.0
Averagebeampower, kW	50
Averagebeamcurrent, mA	15
Powerconsumption, kW	150
Acceleratorweight, t	2.9

Samples are mounted on a table of an electron accelerator, which moves relative to the electron beam. Samples were irradiated with electrons with energies of 2.5 MeV, 3.5 MeV and 4.5 MeV. In this case, the radiation dose varied from 2MGy to 9 MGy. The blanks moved longitudinally relative to the outlet. In this case, the cultivated area amounted to 1000×80 mm^2. EBT modes of polymeric materials are presented in Table 2.

Table 2

EBT modes of polymeric samples PE-UHMW on ILU-10 accelerator

Mode number	Electron energy, MeV	Beam current, mA	Exposure time, s	Number of runs	Radiation dose, MGy
1	2.5	6.84	30	6	3
2	3.5	6.84	30	6	3
3	4.5	6.84	30	4	2
4	4.5	6.84	30	6	3
5	4.5	6.84	30	8	4
6	4.5	6.84	30	10	5
7	4.5	6.84	30	12	6
8	4.5	6.84	30	14	7
9	4.5	6.84	30	16	8
10	4.5	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 infrared spectrometer with transformation of Fourier FTIR-801 Simex. The infrared spectrum was obtained as a result of 50 scans at a wavelength of 450–4700 cm^{-1}, resolution 1 cm^{-1}, t = 25 ºC. 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 20–500 ºC. The antifriction properties of polymers were studied using a THT-S-AX0000 tribometer based on the results of the friction coefficient and areas of wear tracks. The measurement of the area of the wear track after testing for wear resistance and surface morphology was studied using a non-contact MICROMEASURE 3Dstation ZD profilometer. To measure the hardness of a sample according to the Rockwell method in accordance with GOST 4670–91 on a TK-2M hardness tester in accordance with GOST 4670–91.

Mechanical experiments of polymer samples at room temperature was carried out on a universal testing apparatus WDW-5E, in accordance with the requirements of GOST 11262–80 for polymers PE-UHMW and after electron irradiation. The experiment consisted of uniaxial static tension of flat specimens before rup-

ture, with the measurement of the conditional yield strength — $\sigma_{0.2}$, tensile strength — σ_B, and elongation to break — δ. The conditional tensile strength σ_B (temporary resistance) was calculated by the formula:

$$\sigma_B = \frac{P_{max}}{F_0}, \quad (1)$$

where P_{max} — maximum load on the primary tensile diagram.

Offset yield strength $\sigma_{0,2}$was calculated by the formula:

$$\sigma_{0.2} = \frac{P_{0.2}}{F_0}, \quad (2)$$

where $P_{0.2}$ — a load corresponding to a residual elongation of 0.2 % of the initial working length of the sample.

Total extension after rupture was calculated by the formula:

$$\delta = \frac{l_к - l_0}{l_0} \cdot 100\ \%. \quad (3)$$

At least 3 samples for each mode were tested under determining the tensile strength, yield strength and elongation of polymers and mechanical characteristics were determined from averaged data. Tensile strength measurement errors and yield strength did not exceed 7 %.

Results and its discussion

One way to increase the mechanical and tribological properties of polymers is their irradiation with charged particle beams. When irradiated by beams of charged particles in polymers, intermediate formations with high reactivity arise — free radicals, ions, excited molecules. They are sources of further chemical transformations, leading to changes in the chemical structure, and hence the properties of polymers [1].

The hardness of the polymer samples was measured on a TK-2M instrument in accordance with GOST 4670–91 according to the Rockwell method. Figure 1 shows the result of measuring the hardness of polymers before and after EBT. The research of PE-UHMW polymers irradiated at doses higher than 4MGy (beam energy 4.5 MeV) was not possible as a result of radiation aging of the polymers.

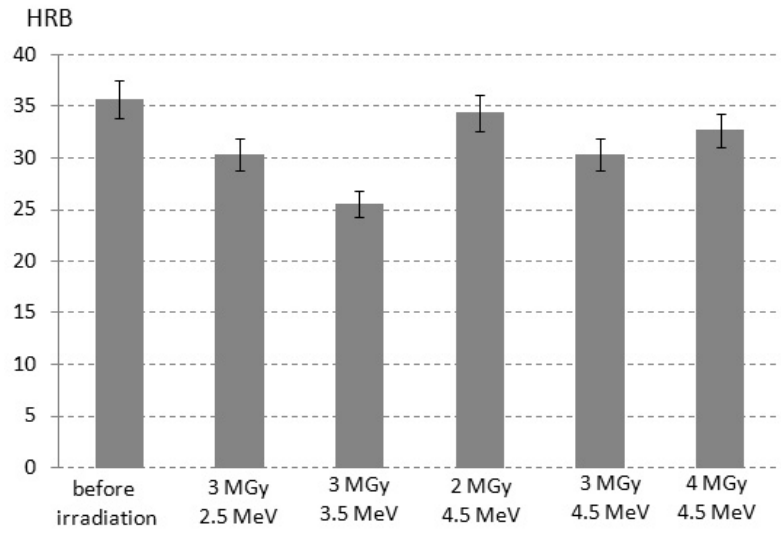


Figure 1. The hardness of PE-UHMW polymer before and after EBT

It was found that the hardness of PE-UHMW changes relatively slightly in the studied EBT mode on the analysis base of obtained results. The hardness of the PE-UHMW polymer varies slightly compared to the initial sample in all studied irradiation modes at energies of 2.5 MeV, 3.5 MeV, 4.5 MeV and an irradiation dose of 2 MGy to 4 MGy.

The dynamic crystallization of polymers is of great interest, because most technological processes occur under these conditions from a technological point of view. The samples were subjected to differential scanning calorimetry (DSC) analysis to evaluate the possible effect of EBT on the crystallization properties of the

polymer matrix. The thermal characteristics of PE-UHMW are determined by DSC. The measurements were carried out in accordance with the requirements of GOST R 55134–2012 and described in the operating instructions for the «LabsysEvo» instrument (Setaram, France) in the temperature range of 20–500 ºC. Samples weighing approximately 10 mg were weighed and sealed in aluminum sample dishes. The polymers during heating and cooling were melted at 500 ºC and kept at this temperature for 5 min and it was before scanning. Then they were cooled from 500 ºC to 20 ºC at a speed of 10 ºC/min in a stream of nitrogen, and then heated from 20 ºC to 500 ºC at a speed of 10 ºC/min.

The results of changes in the melting temperature and an estimate of the data for PE-UHMW are shown in Figure 2. The data of the melting temperature show that the radiation dose has almost no effect on the melting temperature of PE-UHMW. This means that the effect of crosslinking is not significant with respect to the crystal structure (lamella thickness) and is almost the same for all samples regardless of the radiation dose, which is demonstrated by a uniform polymer melting temperature.

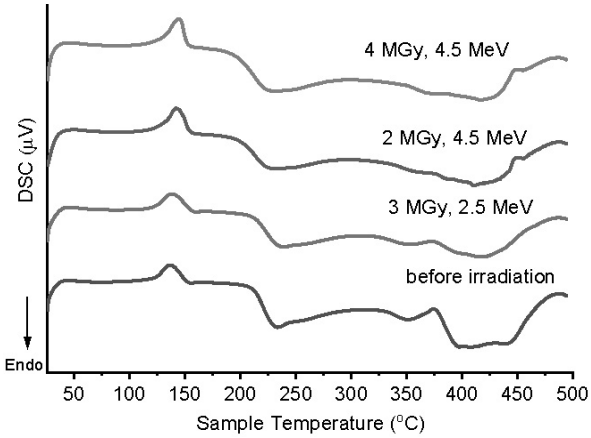


Figure 2. DSC thermogram of PE-UHMW polymer before and after EBT

Figures 3 and 4 presents infrared spectra of unirradiated and irradiated PE-UHMW polymer samples. The IR spectrum was recorded in transmission mode with a resolution of 0.1 cm^{-1}. In order to detect the occurrence of crosslinking, a spectral region between 4000 cm^{-1} and 600 cm^{-1} was analyzed, especially in the region of double vinyl bonds (stretching =C=C= for a vinylidene group of about 1647 cm^{-1}) and the region of trans-vinylylene groups (about 965 cm^{-1}). Peak at 718 cm^{-1}, combined band associated with vibration of oscillation in the plane $=CH_2$ [2].

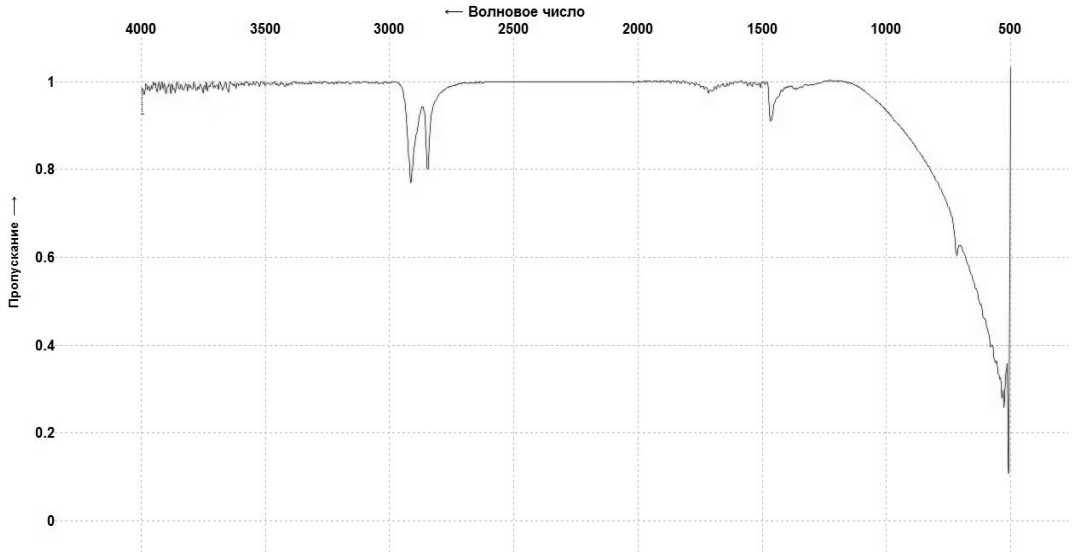


Figure 3. IR spectra of an unirradiated PE-UHMW sample

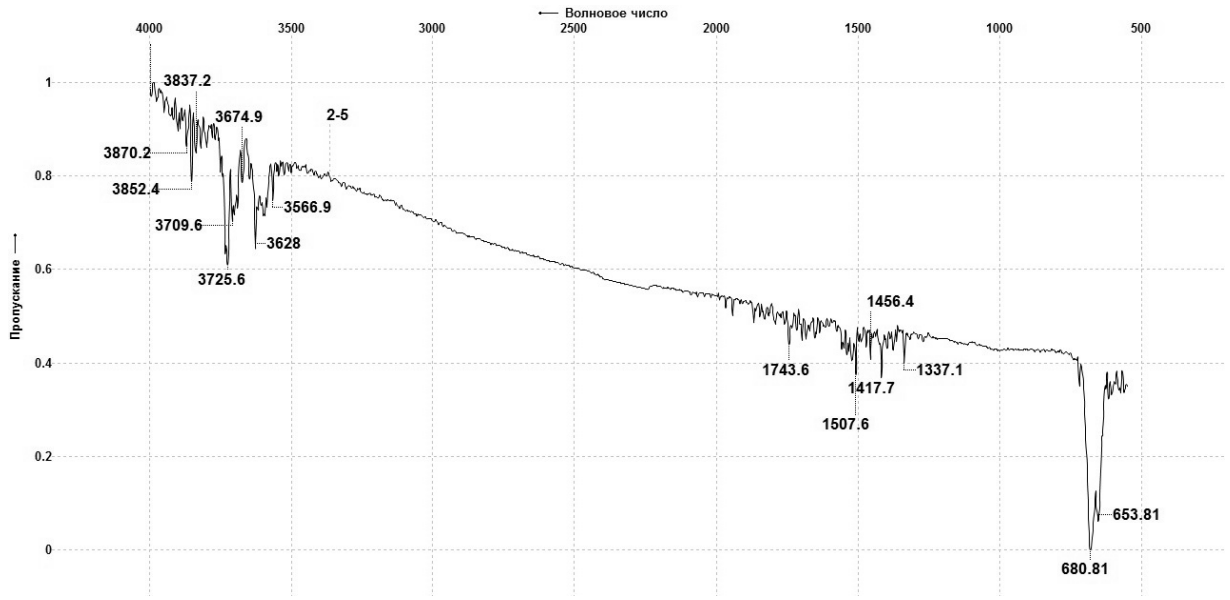
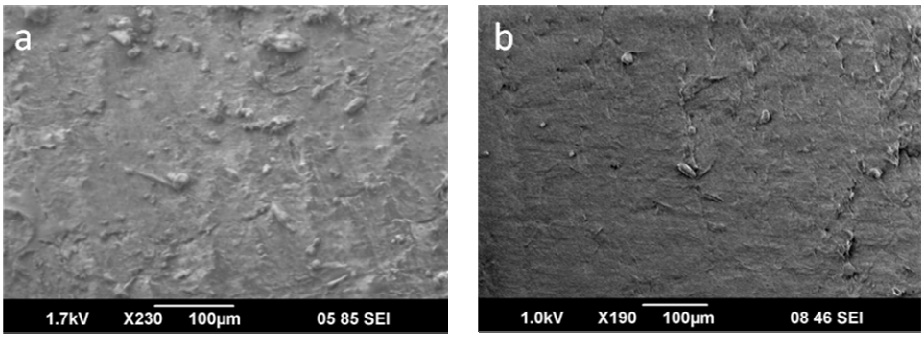


Figure 4. IR spectra of an irradiated PE-UHMW sample at a dose of 4MGy and an energy of 4.5 MeV

The bands at 718 cm^{-1} (swing plane $=CH_2$) and 1460 cm^{-1} (scissor vibration $=CH_2$), which represent $–CH_2–$ in PE-UHMW, have no obvious changes, illustrating that the basic structure of PE-UHMW has not undergone any changes in the process of irradiation. The absorption band of trans-vinylene appears at 965 cm^{-1} in the spectra of irradiated PE-UHMW, and its intensity increases with increasing dose. The peak appears and becomes wider after increasing the dose of radiation in the region of carbonyl groups (1732 cm^{-1}), which refers to irradiated PE-UHMW. In the spectrum of the irradiated sample, the absorption of carbonyl groups (C=O, 1742 cm^{-1}) becomes wider after irradiation. They show that the oxidation reaction of PE-UHMW with oxygen O_2 occurred during and after irradiation. The formation of typical products, such as isolated hydroperoxides (3707 cm^{-1}), hydroxides bound to H_2, including hydroperoxide (3626 cm^{-1}), and lactones (1860 cm^{-1}), was included during the oxidation of polyethylene samples. Thus, such results are convincing evidence that the oxidation of PE-UHMW occurred as a result of chemical reactions of the polyethylene chain with oxygen O_2 [3].

The morphology of the PE-UHMW surfaces before and after EBT is presented in Figure 5. It can be seen that the morphology is significantly improved. Spherulites are formed, consisting of radially oriented fibrils at the micro level. These changes clearly indicate the displacement of polymer molecules under the influence of radiation. This possibly, is associated with 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 [4, 5].



a — before irradiation; *b* — after irradiation (dose — 4MGy; energy — 4.5 MeV)

Figure 5. Scanning electron micrographs of the PE-UHMW polymer

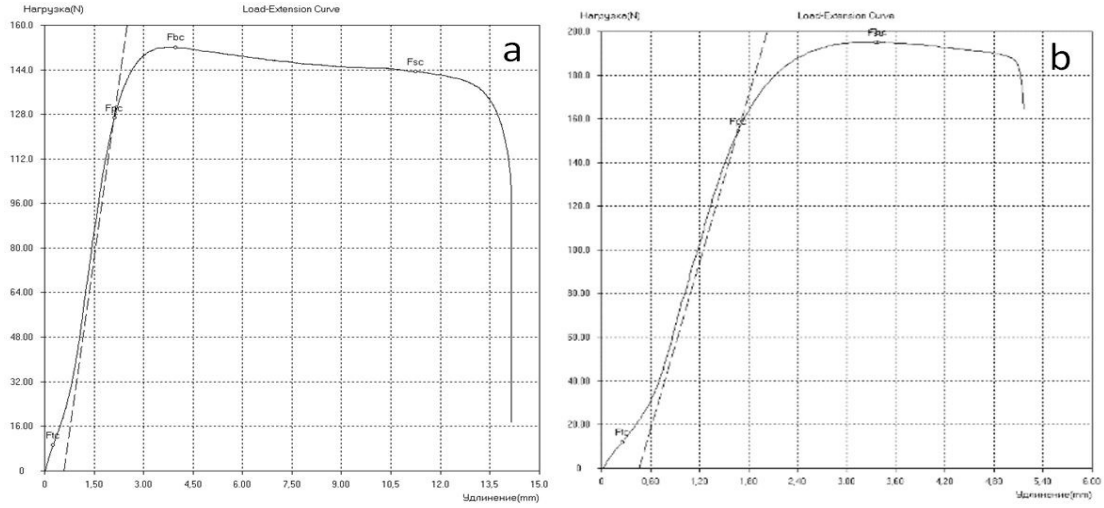
The results of mechanical experiments of PE-UHMW before and after EBT are shown in Table 3. The results were obtained on analysis base of tensile curves of polymers (Fig. 6). The tensile strength (σ_B) of the PE-UHMW polymer was 22 MPa, the yield strength ($\sigma_{0.2}$) was 17.9 MPa, after EBT it increased by

23.9 MPa and 18 MPa, respectively. In addition, the elongation was initially up to 300 %, and then sharply reduced after EBT to 10 %.

Table 3

Results of mechanical experiments before and after EBT

PE-UHMW	σ_B (MPa)	$\sigma_{0.2}$ (MPa)	δ (%)
Before irradiation	22	17.9	300
After irradiation	23.9	18	10



a — before irradiation; *b* — after irradiation (dose — 4MGy; energy — 4.5 MeV)

Figure 6. PE-UHMW polymer tensile curves

Conclusion

Analyzing the experimental results obtained in the work, we can do the following conclusions:

1. It was established that significant changes in the mechanical properties of the PE-UHMW polymer are not observed after EBT on the ILU-10 accelerator. However, a significant decrease in the elongation from 300 % to 10 % as a result of radiation aging was observed after EBT.

2. It was determined by the method of differential scanning calorimetry that the melting temperature of the PE-UHMW polymer practically does not change for all samples, regardless of the radiation dose.

3. It was revealed that during EBT oxidation occurs as a result of chemical reactions of the polyethylene chain with oxygen O_2. No new functional groups were created, apparently due to the fact that irradiation simply caused a break in bonds to form free radicals, and then rearrange to cause crosslinking.

The work has been implemented as part of the grant financing of scientific research for 2018–2020 by the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan.

References

1 Raghu, S., Archana, K., Sharanappa, C., Ganesh, S., & Devendrappa, H. (2015). The physical and chemical properties of gamma ray irradiated polymer electrolyte films. *Journal of Non-Crystalline Solids, 426,* 55–62.

2 Shailesh, M.K., & Kumar, A. (2007). Radiation-induced grafting of vinyl benzyl trimethyl ammonium chloride onto nylon-6 fabric. *Radiation Physics and Chemistry, 76(5)*, 901–906.

3 Tretinnikov, O.N., Ogata, S., & Ikada, Y. (1998). Surface crosslinking of polyethylene by electronbeam irradiation in air. *Polymer*, *39(24)*, 6115–6120.

4 Shifeng, Zhu, Meiwu, Shi, & Meifang, Zhu (2013). Effects of Electron-Beam Irradiation Crosslinking on PA6 Fibers. *Fibers and Polymer, 14(4)*, 525–529.

5 Feulner, R., Brocka, Z., Seefried, A., Kobes, M.O., Hülder, G., & Osswald, T.A. (2010). The effects of e^- beam irradiation induced cross linking on the friction and wear of polyamide 66 in sliding contact. *Wear*, *268*, 905–910.

Ж.Б. Сағдолдина, Б.К. Рахадилов, К. Акатан, П. Ковалевский, Д.Ж. Карабекова

Вакуумсыз электрондық-сәулелік өңдеудің асажоғарымолекулалық полиэтиленнің құрылымы мен қасиеттеріне әсері

Мақалада электрондық-сәулелік өңдеудің асажоғарымолекулалық полиэтиленнің құрылымына, механикалық қасиеттеріне, микроқаттылығына, термотұрақтылығына әсерін зерттеу жұмыстарының нәтижелері келтірілген. Электрондық-сәулелік өңдеу өндеу өндірістік ИЛУ-10 импульстік үдеткіште жүргізілген. Үлгілер энергиясы 2,5; 3,5; 4,5 МэВ болатын электрондар арқылы сәулелену дозасы 2–9 МГр аралығында өңделді. Дифференциалды сканерлеу калориметрия әдісін қолдану арқылы PE-UHMW полимерінің балқу температурасы сәулелену дозасына қарамастан барлық үлгілер үшін іс жүзінде өзгермейтіні анықталған. Электронды сәулемен өңдеуден кейін PE-UHMW полимерінің беттік морфологиясы едәуір жақсарды, микро деңгейде сферолиттер түзілуі радиацияның әсерінен болатын полимер молекулаларының жылжуын көрсетті. Полиэтилен тізбегінің оттегімен O_2 химиялық реакциясы нәтижесінде, электрондық-сәулелік өңдеу кезінде тотығу болады. Механикалық сынамалар нәтижесіне байланысты электрондық-сәулелік өңдеуден кейін PE-UHMW полимерінің механикалық қасиеттерінің өзгеруі айтарлықтай байқалмады. Бірақ электрондық-сәулелік өңдеуден кейін радиациялық қартаю нәтижесінде салыстырмалы ұзарудың мәнінің айтарлықтай, яғни 300 % пайыздан 10 % пайызға дейін төмендегені байқалды. PE-UHMW полимерінің қаттылығы зерттелген электронды-сәулелік өңдеу режимінде аздап өзгерген.

Кілт сөздер: электронды-сәулелік өңдеу, асажоғарымолекулалық полиэтилен, құрылым, механикалық қасиет, тотықтану.

Ж.Б. Сагдолдина, Б.К. Рахадилов, К. Акатан, П. Ковалевский, Д.Ж. Карабекова

Влияние вневакуумной электронно-лучевой обработки на структуру и свойства сверхвысокомолекулярного полиэтилена

В статье приведены результаты работ по исследованию влияния электронно-лучевой обработки на структуру, механические свойства, микротвердость, термостабильность сверхвысокомолекулярного полиэтилена PE-UHMW. Электронно-лучевая обработка проводилась на промышленном импульсном ускорителе ИЛУ-10. Образцы облучались электронами с энергией 2,5; 3,5 и 4,5 МэВ, доза облучения варьировалась от 2 до 9 МГр. Методом дифференциально-сканирующей калориметрии определено, что температура плавления полимера PE-UHMW практически не изменяется для всех образцах независимо от дозы облучения. После электронно-лучевой обработки морфология поверхностей полимера PE-UHMW значительно улучшается, на микроуровне формируются сферолиты, которые указывают на смещение молекул полимера под влиянием облучения. Выявлено, что во время электронно-лучевой обработки происходит окисление в результате химических реакций полиэтиленовой цепи с кислородом O_2. Согласно результатам механических испытаний после электронно-лучевой обработки не замечены существенные изменения механических свойств полимера PE-UHMW. Однако после электронно-лучевой обработки наблюдалось значительное снижение значения относительного удлинения от 300 % до 10 % в результате радиационного старения. Твердость полимера PE-UHMW незначительно изменилась в исследуемом режиме электронно-лучевой обработки.

Ключевые слова: электронно-лучевая обработка, сверхвысокомолекулярный полиэтилен, структура, механическое свойство, окисление.