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Effect of electron irradiation on mechanical, tribological and thermal properties of polytetrafluoroethylene

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The article presents the study results of the electron irradiation effect on the mechanical, tribological and thermal properties of polytetrafluoroethylene (PTFE). The results allow a better understanding of the processes occurring in the structure of PTFE under irradiation and reveal potential applications of the modified material with improved tribological characteristics, high thermal resistance and mechanical strength. In this work the samples were tested for wear resistance and thermal stability. It was found that the effect of electron irradiation leads to a significant increase in the microhardness of the material by 1.5 times compared to the initial state. However, degradation of the thermal properties of the polymer due to the breakage of molecular chains is observed, which may affect its resistance to high temperatures and mechanical stresses. Such studies are important to advance the knowledge of the effects of irradiation on the structures and properties of polymeric materials. These results highlight the complex interaction between electron irradiation and the properties of polytetrafluoroethylene, which is important for understanding and optimising the application of this polymer in various engineering and industrial applications.

Keywords: PTFE; electron beam treatment (EBT); differential scanning calorimetry (DSC); friction; wear; hardness

1. Introduction

Polytetrafluoroethylene, also known as PTFE, is a synthetic polymer composed of fluorine and carbon atoms. PTFE is a versatile material with a unique combination

of properties including chemical resistance, non-stickiness, and high temperature resistance [1]. Due to these properties, PTFE is widely used in various industries such as aerospace, automotive, medical, and electrical. PTFE is used in the manufacture of various products such as seals, gaskets, bearings, wire insulation and non-stick cookware [2–4]. PTFE has become an indispensable material in modern industry due to its exceptional properties and versatility.

However, PTFE has its own disadvantages such as relatively low wear resistance and poor mechanical properties. Therefore, to improve the tribo-mechanical properties of PTFE, processing methods by adding fillers and surface treatment by concentrated energy flow are widely used.

One of the types of modification is electron irradiation, which can be used to change the properties of PTFE. The essence of this method is to expose a PTFE material to a high-energy electron beam that can cause cross-linking of polymer chains. Such crosslinking can improve the mechanical properties of the material, including its strength, stiffness, and resistance to wear and creep. Electron irradiation can also improve the thermal stability of PTFE. The degree of modification can be controlled by adjusting the dose and energy of the electron beam.

In [5, 6], it was shown that mechanical characteristics are closely related to the modification of the structure formed after electron irradiation. The increase in wear resistance of polymeric materials is associated with the creation of a large number of cross-links during electron beam irradiation. The results obtained in [7] confirmed that cross-linking at significant doses prevails over depolymerisation, even if irradiation was performed in air.

Thus, the study of the effect of irradiation on the mechanical and tribological properties of PTFE is important because it can help in understanding the behaviour of the material under radiation exposure, improving its performance and service life, and developing new radiation-resistant materials for various industrial applications. For example, in the aerospace industry, materials used in space environments are exposed to various types of radiation, including ionising radiation, which can affect the performance of materials.

The aim of this work was to investigate the effects of electron irradiation in the properties of PTFE polymer.

2. Materials and Methods

2.1 Material

PTFE samples in the form of plates with dimensions of 30×30 mm and thickness of 3 mm were selected as the material for the study.

2.2 About electron beam irradiation

Electron-beam treatment (EBT) of polymer was performed on pulsed linear accelerator ILU-10, installed in JSC "Nuclear Technology Park" (Kurchatov, Kazakhstan) The required irradiation doses were obtained by adjusting the parameters

of electron beam. The irradiation dose was 100 and 120 kGy per pass, therefore, for high doses several passes were required. Parameters of electron irradiation are given in Table 1.

Table 1.
Parameters of electron irradiation of polymers.

Sample	Beam energy, E, MeV	Beam current, I, mA	Dose per pass, kGy	Quantity runs	Radiation dose, kGy
PTFE-a	2.7	6.84	100	4	400
PTFE-b	2.7	6.84	120	5	600
PTFE-c	3.2	6.84	120	5	600
PTFE-d	3.7	6.84	120	5	600

2.3 Thermogravimetric analysis (TGA)

Studies were carried out in the temperature range of 20–800 °C at a heating rate of 10 °C/min in air atmosphere using TGA-1250. The samples were weighed on microbalance and crimped in a ceramic cuvette. The thermogram, i.e., a plot of percentage as a function of temperature, was used to study the variation in the heat resistance of the polymer. The error in recording thermograms was ± 2 °C.

2.4 Differential scanning calorimetry (DSC)

A TGA-1250 analyser was used for differential scanning calorimetry. Samples were weighed and compressed as described for TGA measurements. Sealed samples were scanned over a temperature range of 20 °C to 800 °C at a rate of 10 °C/min. Thermograms were obtained for the heat flux versus temperature curve. The maximum possible error associated with the measurement was ± 2 °C.

2.5 Microhardness

Hardness and modulus of elasticity of the samples were measured on a FISCHER-SCOPE HM2000S hardness tester according to DIN EN ISO 14577-1 and ASTM E 2546 by Helmut Fischer GmbH Institut fur Elektronik und Messtechnik. The dwell time of the sample under a load of 1 N for the polymer was 20 s. At least 10 hardness measurements were carried out at different places of the sample surface.

2.6 Roughness

The surface roughness of PTFE polymers before and after electron beam treatment was measured on a profilometer model HY2300 Anytester.

2.7 Wear testing

Testing of samples on wear in the dry friction mode was carried out according to the scheme "ball-disk" at load $P = 12N$ and sliding velocity $V = 0.1$ m/s on the tribometer Anton Paar T R B 3 in accordance with international standards ASTM G99-959, DIN50324 and ISO 20808. In tribological tests a 6 mm diameter ball (counterbody steel SHX15) was used. The test path was 250 metres. The volumetric wear was evaluated from the friction track profile using a model 130 contact profilometer. The friction track profile was measured after the test 5 times in different places of the specimen, and then the average values were found. The sliding wear was calculated using the following formula (1):

$$I = \frac{2\pi rS}{d \cdot P} = \frac{V}{d \cdot P'} \tag{1}$$

where r – the radius of the counterbody, S – the cross-sectional area of the wear groove, V – the volume of material removed, d – the total test distance and P – the applied load.

3. Results and discussion

3.1 Thermogravimetric analysis

Thermogravimetric analyses of the initial PTFE and irradiated samples for different dosages are shown in Figure 1.

The irradiation dose does not affect the thermal properties of high density polyfluoroethylene due to immobilisation of the formed free radicals in the crystalline region with hindered chain mobility [8, 9].

The decomposition of the pure polymer starts at 440 °C and ends at 580 °C. This shows that increasing the level of crosslinking did not contribute to the thermostability. It is also seen that the degradation tendency of PTFE-a sample is similar to the original sample, which shows radiation-induced changes in the crystallinity of PTFE at irradiation doses of 400 kGy does not affect the rate of thermal decomposition. However, there is a difference in the residual mass values of the samples. The original PTFE and PTFE-a have higher residual masses than the others. The other samples PTFE-b, PTFE-c and PTFE-d have comparatively low residual masses and have about the same value.

Figure 1 shows how the unirradiated PTFE and PTFE-a, e samples are stable up to 505 °C and its decomposition occurs in a one-step process, while the irradiated PTFE-b sample decomposes in a two-step process. Note that low molecular weight decomposition products are released from the material already as a result of irradiation at elevated temperature. Consequently, the mass loss of these radiation-modified PTFEs does not begin until the temperature of 385 °C. The first stage peaks at around 450 °C. The weight loss in the first stage increases with increasing dose. Therefore, it can be concluded that some chemical formations occurring during irradiation initiate and complete the degradation step.

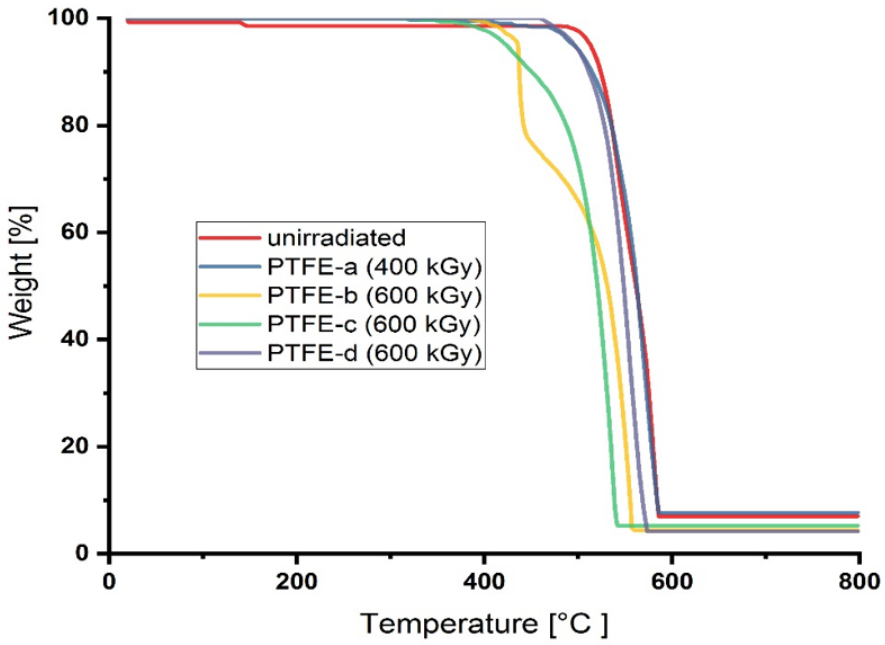

Figure 1. TGA weight loss curves of PTFE at irradiation doses of 400, 600 kGy and initial decomposition curves.

3.2 Differential Scanning Calorimetry

DSC scans of heating and cooling of PTFE samples were used to determine the melting temperature (T_m) and crystallization temperature (T_k) peaks, respectively, and the percentage of crystallinity (X_c) was calculated (using formula 2) [10] based on the melting enthalpy values from the polymer sample in J/g. Thus, X_c is calculated as a percentage value as the ratio of ΔH_k obtained from the peak thermogram to the area with ΔH_m.

$$X_c = \frac{\Delta H_c}{\Delta H_m} \cdot 100\%, \tag{2}$$

where X_c – the degree of crystallinity, ΔH_c – the heat of crystallization, ΔH_m – the heat of fusion.

The exothermic and endothermic curves are shown in Figure 2. Accordingly, from the exothermic heating peaks, it can be seen that T_m decreases slightly at 400 kGy, indicating that cross linking of molecular chains is the dominant process and the melting temperatures of the remaining samples decrease where chain breaking dominates and the peaks shift further to the left, where the lowest T_m is observed in the PTFE-c sample at a dose of 600 kGy. From the endothermic scan in Figure 2, the crystallization peak T_c decreases with increasing irradiation dose and beam energy. The peaks shift further to the left of the thermogram where the crystallization process occurs at significantly lower temperatures compared to the unirradiated PTFE sample.

Heating and cooling scans from the DSC thermogram provide information on the effect of irradiation on the molecular chain crystallization process and final crystallinity [11]. When the molecular weight of PTFE decreases, it leads to a thermally less stable semi-crystalline structure that melts at lower temperature due to unravelling of the polymer chains, resulting in a more disordered structure.

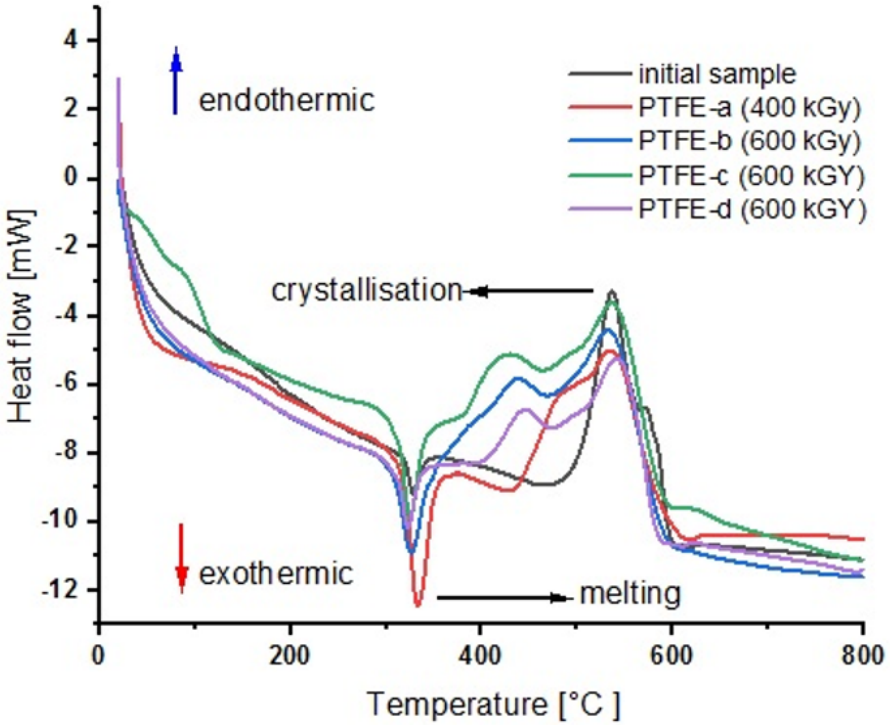

Figure 2. DSC cooling thermogram of PTFE with different irradiation doses.

Table 2 shows that the heat of crystallization, ΔH_k and the percentage of crystallinity, X_k (%), calculated from the area of the cooling peak thermogram, have maximum values at the initial state and decrease with irradiation. However, according to Lappan [12] et al, the average molecular weight decreases with increasing irradiation dose because PTFE undergoes preferential chain breaking at higher doses, resulting in shorter molecular chains.

Table 2.
Thermal transitions of PTFE samples before and after electron-beam treatment.

Sample	Melting temperature, T_m, °C	The heat of fusion, ΔH_m, J/g	Crystallization temperature, T_c, °C	The heat of crystallization, ΔH_c, J/g	The degree of crystallinity, X_c, %
PTFE-initial	328	330	548	184	56
Irradiated PTFE-a	333	585	478	163	28
Irradiated PTFE-b	326	480	435	142	29
Irradiated PTFE-c	325	525	537	71	13
Irradiated PTFE-d	323	462	434	125	27

3.3 Microhardness

Figure 3 describes the change of sample hardness depending of the increase in beam energy. Significant increases in microhardness in the irradiated samples are observed, as well as an increase in Young's modulus from 1.5 GPa to 1.8 GPa. This is attributed to the fact that radiation-induced cross-linking contributed to the resistance to surface deformation.

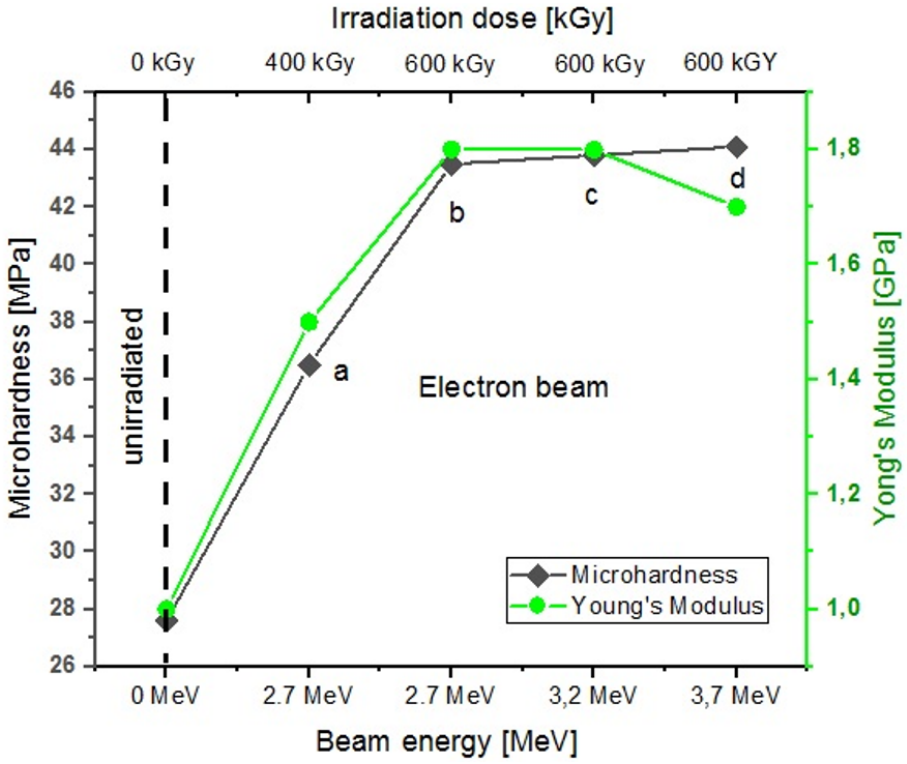

Figure 3. Evolution of PTFE mechanical properties with different irradiation doses.

Figure 3 shows the microhardness and Young's Modulus for five PTFE samples (unirradiated, a, b, c, d). We can see microhardness increase from 28 MPa for initial PTFE sample to 36 MPa for irradiated PTFE-a at 400 kGy dose and 2.7 MeV energy. For PTFE-b microhardness also increased up to 43 MPa for 600 kGy dose and 2.7 MeV. Further we can observe that microhardness remains the same (around 43 MPa) for 600 kGy dose when beam energy increase from 2.7 to 3.7 MeV. Approximately we can also see the same behavior for Young's modulus distribution for different samples. In this graph points a–d refer to different PTFE sample.

Based on the conducted studies, it was found that the mechanical properties of PTFE change and depend on the irradiation parameters, which can be seen in the improvement of hardness. This is probably due to better dispersion of PTFE particles, which gives a hardening effect. In addition, it has been shown [13] that electron-beam treatment of PTFE leads to a change in the degree of crystallinity of the surface layer, which is also a factor in changing its microhardness.

3.4 Roughness

3D morphological images of untreated (a) and irradiated (b–e) PTFE are shown in Figure 4. The roughness of the unprocessed surface and irradiated PTFE were analyzed for a scan area of 120, 156 μm2, respectively. Uneven grooves and irregularities were observed on the sample surface before irradiation (Figure 2 a). Apparently, these grooves were formed as a result of polishing the sample. The average surface roughness (R_a) of the original PTFE was relatively high and was 2.65 μm (see Table 2). Irradiation of PEEK with a dose of 400 Gy resulted in a significant decrease in the number of bumps. At the same time, the length of the bumps changed and the depth increased. The average surface roughness (R_a) of irradiated PFTE-c at 600 kGy significantly decreased and was 0.47 μm. We believe that the decrease in surface roughness of the sample is caused by radiation damage during irradiation. When the irradiation dose was increased up to 400 kGy, the surface of the sample smoothed out and the average surface roughness decreased to 0.27 μm. This is most likely due to evaporation and partial melting of the sample surface.

The roughness values are given in Table 2. The roughness of irradiated samples is smaller in contrast to the original unirradiated PTFE. Irradiation promoted smoothing of microscopic irregularities on the PTFE surface and resulted in the roughness reduction.

Table 3.
Values of roughness parameters of initial and irradiated PTFE.

PTFE samples	R_a, [μm]	R_{ms}, [μm]	R_z, [μm]
Initial PTFE	2.65	0.25	19.80
Irradiated PTFE-a, 400 kGy	0.86	0.27	6.93
Irradiated PTFE-b, 600 kGy	1.73	0.27	12.45
Irradiated PTFE-c, 600 kGy	0.47	0.26	4.79
Irradiated PTFE-d, 600 kGy	1.51	0.28	11.43

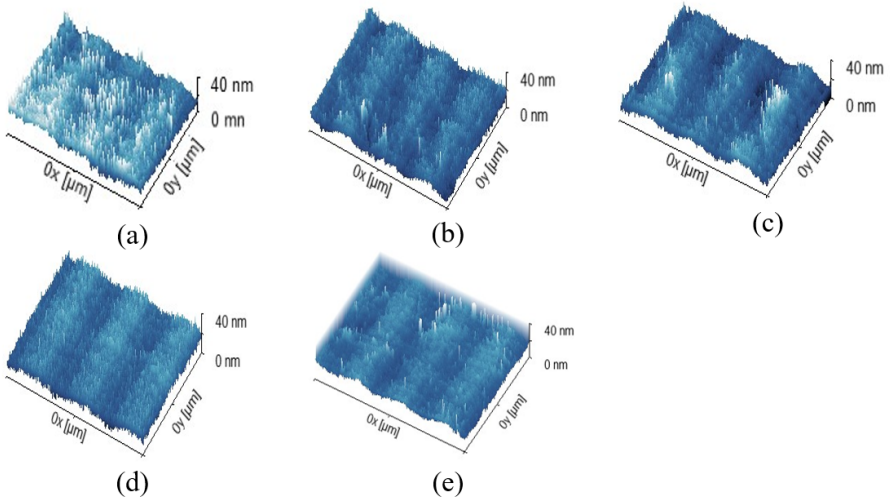

Figure 4. 3D surface morphology of pristine (a) and irradiated PTFE: (b) 400 kGy, (c, d, e) 600 kGy.

3.5 Wear testing

Polytetrafluoroethylene has a low coefficient of friction, which is determined by the low intermolecular force, which slightly attract other substances [13–15]. The asymmetry of PTFE caused by the effect of concentrated energy on the surface can lead to an increase in the coefficient of friction. The results of friction coefficient measurement for the original (untreated) and for irradiated specimens are shown in Figure 5. The friction coefficient of the original sample is $\mu \approx 1.65$. After training to a dose of 400 kGy (PTFE-a), a decrease in the coefficient of friction to $\mu \approx 1.50$ is observed. And after irradiation with a dose of 600 kGy, an increase in the coefficient of friction to $\mu \approx 1.75$ is observed. However, during the first 400–500 seconds the abrasion line of the untreated sample is much lower than for the treated samples. This is probably due to the fact that the surface layer of irradiated samples has high hardness.

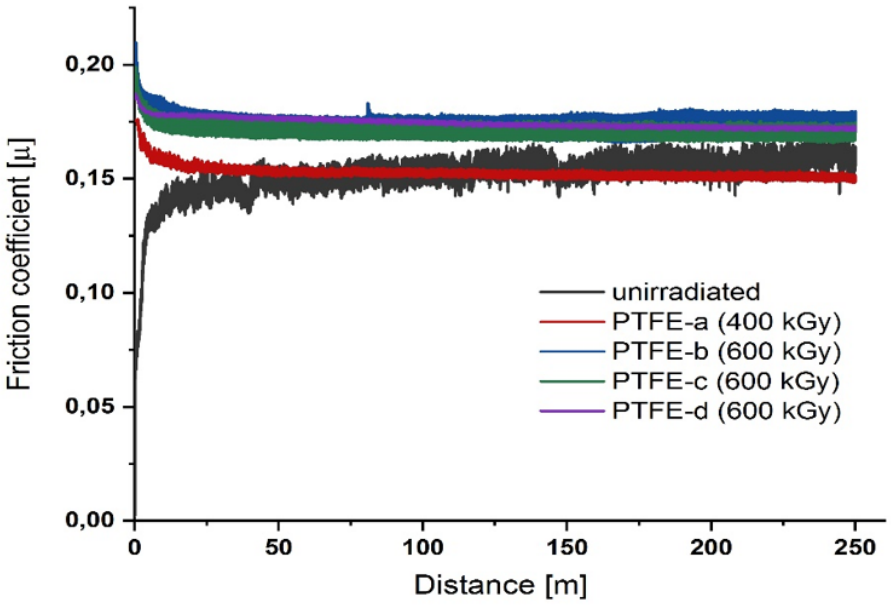

Figure 5. Graph of friction coefficient of PTFE samples at different irradiation parameters.

As shown in Figure 6, the wear volume of the original sample was 0.015 mm^3. For the modified samples by electron irradiation the wear volume decreases by 4–5 times. It was found that the wear resistance was affected by both irradiation dose and electron beam energy. Among the irradiated samples, the lowest sliding wear volume index was observed for the sample irradiated with a beam energy of 3.7 MeV.

The high wear resistance of the PTFE-d sample explains the fact that this sample has high hardness like other PTFE-b and PTFE-c samples, while having comparatively lower modulus of elasticity than PTFE-b and PTFE-c. Materials with high hardness and low elasticity are commonly used in applications where stiffness, durability, resistance to wear and deformation are required.

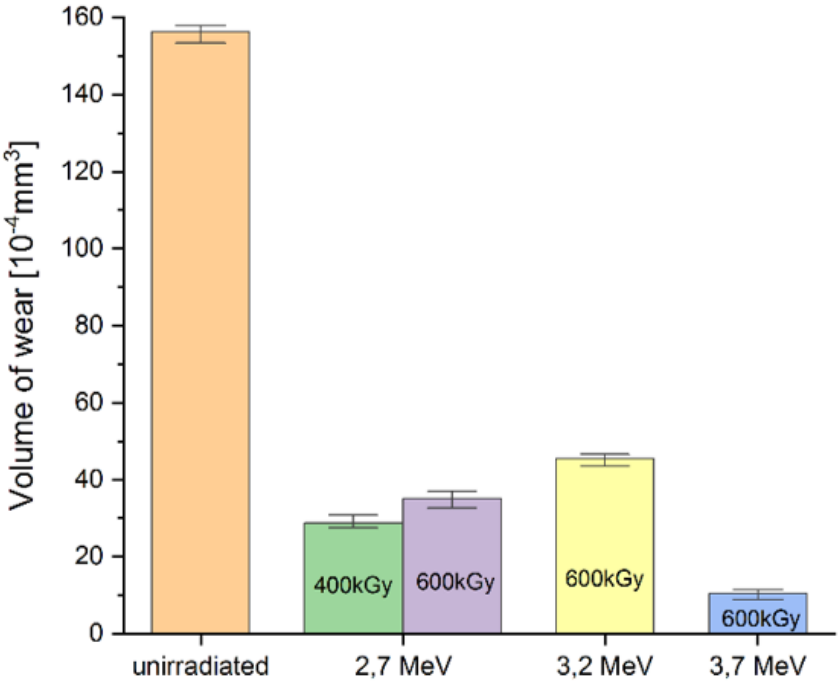

Figure 6. Sliding wear volume of PTFE specimens with regard to irradiation doses.

Conclusion

In the course of the work carried out, the results obtained were:

1. Radiation-induced changes in crystallinity at irradiation doses up to 400 kGy do not affect the decomposition rate of PTFE, but the values of residual masses differ between different samples. The irradiated PTFE exhibits two-step decomposition starting from about 385 °C, and it is suggested that radiation-induced chemical structures play an important role in this process. Analysis of the DSC data also indicates a decrease in crystallization temperature (T_c) with increasing irradiation dose, which leads to crystallization at lower temperatures compared to the unirradiated PTFE sample.

2. The study of the effect of electron irradiation on the mechanical characteristics of polytetrafluoroethylene (PTFE) showed that the microhardness of the material increased 1.5 times compared to the initial state. In addition, Young's modulus increased by 1.8 times, indicating an increase in the elasticity of the material. This indicates the formation of new strong bonds in the structure of PTFE, improving its mechanical properties.

3. It was found that electron irradiation led to an increase in the wear resistance of PTFE samples. The values of friction coefficients increased insignificantly in comparison with the initial sample, except for the sample irradiated at a dose of 400 kGy, the friction coefficient of which was insignificantly reduced. Such behaviour of tribological characteristics is explained by the formation of stronger carbon bonds in the material under the influence of irradiation, which contributes to the reduction of wear without a significant change in the coefficient of friction.

Overall, the study showed the nature of the relationship between electron irradiation and properties of PTFE (mechanical, tribological and thermal).

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