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CONNECTION BETWEEN STRUCTURAL CHANGES OF IRRIADIATED POLYETHER ETHER KETONE AND MECHANICAL PROPERTIES

KORELACJA POMIĘDZY ZMIANAMI STRUKTURALNYMI NAPROMIENIOWANEGO POLIETEROETEROKETONU A JEGO WŁAŚCIWOŚCIAMI MECHANICZNYMI

Key words: differential scanning calorimetry, gamma irradiation, polyether ether ketone.

Abstract

The article presents the results of research on the impact of structural changes in polyether ether ketone (PEEK) on its mechanical properties. The polymer was exposed to gamma radiation at a dose of 50 and 150 kGy, and the radiation energy was 4 MeV. Changes in the degree of crystallinity and the related changes in the glass transition and melting temperature for the polymer were determined by differential scanning calorimetry (DSC). Mechanical properties were determined using the micro-mentoring method. The tests showed a change in the degree of crystallinity in the range of several degrees and a significant increase in the glass transition temperature. In terms of mechanical properties, the reduction of hardness and Young's modulus was observed. Observed changes, especially in terms of changes in the structure of the polymer under the influence of radiation, are difficult to explain, which requires conducting further research, especially in the range of irradiation parameters used. Further research is important because PEEK is used in many fields, especially in conditions conducive to corrosion and the influence of radiation.

Słowa kluczowe: różnicowa kalorymetria skaningowa, promieniowanie gamma, polieteroeteroketon.

Streszczenie

W artykule przedstawiono wyniki badań wpływu zmian strukturalnych w polieteroeteroketonie (PEEK) na jego właściwości mechaniczne. Polimer został poddany działaniu promieniowania gamma w dawce 50 i 150 kGy, energia promieniowania wynosiła 4 MeV. Zmiany stopnia krystaliczności podobnie jak zmiany temperatury zeszklenia i topnienia dla polimeru zostały wyznaczone za pomocą różnicowej kalorymetrii skaningowej (DSC). Właściwości mechaniczne wyznaczono za pomocą metody mikrointendacji. Badania wykazały zmianę stopnia krystaliczności w zakresie kilku stopni oraz znaczne zwiększenie temperatury zeszklenia. Pod kątem właściwości mechanicznych zaobserwowano zmniejszenie twardości i modułu Younga. Zaobserwowane zmiany, szczególnie pod kątem zmian w strukturze polimeru pod wpływem promieniowania, są trudne do wyjaśnienia, co wymaga prowadzenia dalszych badań szczególnie w zakresie zastosowanych parametrów napromieniowania. Dalsze badania są o tyle istotne, że PEEK znajduje zastosowanie w wielu dziedzinach, szczególnie w warunkach sprzyjających korozji oraz wpływu promieniowania.

INTRODUCTION

Polyether ether ketone (PEEK) is a thermoplastic polymer, due to a low coefficient of friction (COF) and wear resistance. Because of those two parameters, PEEK has been widely applied in aerospace and automotive components since entering the market. This polymer is one of special engineering plastics used in industry and the requirements for the characteristics of these materials are becoming increasingly stringent. In pure PEEK, it is hard to meet the needs of industry, which is why surface modification and composite strengthening of PEEK has been one of the crucial themes of research. Methods mainly include plasma and gamma modification, mixed modification, which can improve its performance in self-lubricating, high temperature, high load, and other

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harsh conditions, reduce material costs and expand applications [**L. 1**].

PEEK is an aromatic polymer, characterized by glass transition temperature (T_g) and a melting point temperature (T_m) of 143°C and 334°C, respectively (T_m depending on the relative proportion of ether-ketone group linking the phenylene rings). It has good mechanical properties in a temperature range of 196°C to 260°C and works close to the temperature of 260°C in a long term operation. It has excellent thermal stability, and the degree of crystallinity is generally 20% to 30% but can be up to 48%. The density of PEEK is 1.265 g/cm^3 in the amorphous state [**L. 2**]. It can be processed by conventional methods, such as injection moulding, extrusion, compression moulding, and powder coating. The structure of a repeat unit of PEEK (**Fig. 1**) contains a large number of aromatic rings, polar ketone groups, and an ether bonds. The chemical structure of this polymer influences its excellent properties compared to other specialty engineering plastics, such as flame resistance, workability, excellent dimensional stability, fatigue resistance, and high fracture toughness. Moreover, this material has an excellent corrosion and moisture resistance and very good mechanical properties at high temperature under various organic and inorganic corrosion solutions. PEEK is resist to water, and its products can keep constant performance under a temperature that exceeds 250°C steam or high pressure water immersion, and it can continue working in these conditions for thousands of hours. PEEK is non-toxic and is approved for using in contact with food. Thanks to its properties, this polymer is widely used in medical, food, electronics, chemical, semiconductor, and other fields of production [**L. 3–4**].

Polymers are extensively employed in a radiation environment, from industry to health to daily consumer products that they are commonly used in. High energy radiation can bring major changes in the molecular structure and macroscopic properties of the polymers [**L. 5**].

The radiation dose brings changes in physical properties of polymers, but it is considerably less than that required to cause any significant change in glass, ceramic or metals. However, in numerous applications, polymers are specifically needed in environments of ionizing radiation, because of its specific properties such as elasticity, light weight, and formability. Because of this, the polymer is required to be as radiation resistant as possible [**L. 6–7**]. The radiation effects are demonstrated as changes in appearance, physical and chemical states, and electrical, thermal, and mechanical properties. Not all properties of polymer can be affected to the same degree by radiation, because radiation-induced excitation is not coupled to the entire chemical system, but it is located at a specific bond [**L. 8**]. Polymers like PEEK contain aromatic rings, which absorb energy and are characterised by significantly increasing the radiation stability by aiding in the redistribution of the excitation energy through the material. Conversely, polymers with highly aliphatic structures are least resistant to radiation. Polyether ether ketone has the highest radiation resistance of 10 MGy [**L. 9–10**].

The radiation damage of PEEK was evaluated by measuring mechanical properties before and after irradiation as well as the effect of radiation on the thermal properties.

EXPERIMENTAL DETAILS

Material

Commercially available, linear aromatic, semi-crystalline, colour natural and unreinforced polyether ether ketone (**Fig. 1**) was used in this study. The cylindrical specimens (diameter of 30 mm, 20 mm in height), were irradiated with gamma rays from a ^{60}Co source in a gamma chamber. The irradiation was carried out by delivering the following radiation doses: 50 and 150 kGy (gamma rays of energy 4 MeV).

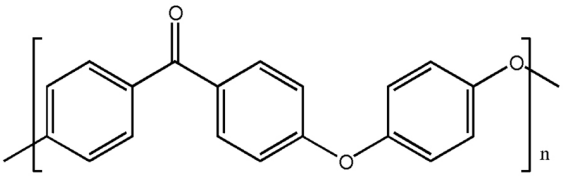

Fig. 1. Structure of repeat unit of PEEK
Rys. 1. Struktura meru PEEK

Polymer's crystallinity degree

The degree of crystallinity was measured by differential scanning calorimetry (DSC). Sections 10 mg in weight were cut out from the central part of specimens in the initial state after irradiation with gamma rays. Examination was performed using a dynamic differential calorimetry while enclosing the specimens in aluminium cells. The rate of heating was 10°C/min and the temperature range was −40°C to 400°C. Next, the thermograms were analysed and the calculations of the crystallinity degree χc were made in accordance with the following formula (1) [**L. 11**]:

$$\chi_c = \frac{\Delta H_m}{\Delta H_c} \cdot 100 \tag{1}$$

where

ΔH_m – the heat of phase transition (i.e. melting) of the investigated polymer sample determined from a DSC thermogram [J/g];

ΔH_c – the heat of phase transition of completely crystalline polyether ether ketone (empirically determined value amounting to 130 J/g [**L. 12**]).

Micro-indentation tests

Tests of micromechanical properties were performed using a Micron-Gamma tester, equipped with a self-levelling table. In micro-indentation tests, a Berkovich penetrator was used. The maximum load was P = 1 N, the time of loading and unloading was 30 s, and the time of holding the specimen under the maximum load was 10 s. Measurements were made in accordance with ISO 14577 standard. To determine hardness and Young's modulus, E, a standard Oliver-Phare method was used [**L. 13**].

Measurement results were averaged for 6 indents. Measurements were made at room temperature.

Examination of tribological properties

Friction is governed by the surface interaction in moving contact. Friction coefficient μ was determined as a quotient of the recorded friction force F_t and the normal force applied F_n (25 N). The tribological wear tests were conducted on a pin-on-disc test stand T-01. Discs were made of carbon steel C45, the surface of which was mechanically polished and had an average profilometric parameter of roughness Ra = 0.5 μm, and a hardness of 50 HRC. The diameter of the pin at contact was 8 mm. Before each test, the polymer pin and steel disc were thoroughly cleaned with alcohol. The pressure in the friction couple was 0.5 MPa (normal force F_n = 25 N). The tribological tests were carried out at a sliding speed of 0.5 m/s at a friction distance of 1000 m. An ambient temperature around 21 ±1°C was kept constant for all tests. The tribological evaluations were done in technical dry friction conditions. The coefficient of friction was determined as a quotient of the normal force applied F_n and the recorded friction force F_t. Wear of the pin was evaluated by measuring dimension loss after completing the test using a precision equipment. The specific linear wear rate W_r was calculated from the following relationship:

$$W_r = \frac{\Delta l}{L} \left[\mu m/km\right] \tag{2}$$

where
Δl − length loss [μm],
L − sliding distance [km].

RESULTS AND DISCUSSION

Thermal studies

Based on the DCS run, it has been determined that gamma irradiation of PEEK induced a change in the thermal properties of polymer. The tests were performed in accordance with the methodology described in previous section. The enthalpies of melting and crystallization of the unirradiated and irradiated samples were determined from the peak area of the corresponding transitions in DSC scans. The effect of radiation on the crystallinity of PEEK was examined based on DSC measurements and the results are shown in **Figure 2**.

The isothermal crystallization behaviour of PEEK was studied by DSC over a wide temperature range of 238–345°C. The melting endotherms display a small peak at 238–240°C with the predominant melting peak at 335–345°C.

Gamma radiation increases ΔH_c for the examined specimens (**Tab.1**). No significant differences of crystallization heat values were observed between them after irradiation. For the sample irradiated with 50 kGy, the heat of crystallization ΔH_c was approximately 4% higher than for unirradiated sample. For 150 kGy, the results presented less than 1% differences in ΔHc compare to the unmodified sample. The decreasing tendency of ΔH_c of PEEK with an increasing radiation dose has also been shown, which can be attributed to the increasing chain scission reaction of PEEK under increased doses.

Tab. 1. Values of ΔH_m [J/g], crystallization temperature (Tc) and T_m [°C] measured from DSC curves for PEEK before and after irradiation

Tabela 1. Zmiana wartości ciepła topnienia ΔH_m [J/g], temperatur krystalizacji T_c i topnienia T_m [°C] dla PEEK dla różnych dawek promieniowania

Radiation dose [kGY]	T_c [°C]	T_m [°C]	ΔH_m [J/g]
0	240	345	44.27
50	239	343	46.15
150	238	335	43.94

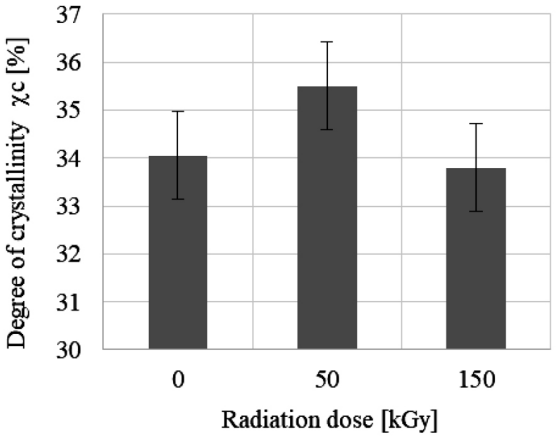

Fig. 2. Changes in the crystallinity of PEEK with radiation dose

Rys. 2. Zmiana stopnia krystaliczności w zależności od dawki promieniowania gamma

A polymer with a higher radiation dose is characterized by significantly lower crystallinity and ΔH_c. After gamma radiation of polyether ether ketone, an increase in the degree of crystallinity χ_c was observed (**Fig. 2**).

Data analysis of the calculated crystallinity percentage anticipated by DSC measurements is reported in **Fig. 2**. The crystallinity increased as the radiation dose increased to 50 kGy, and then it decreased for 150 kGy. The data indicated an increase from 34% to 35.5% and a decrease to 33.8% for 0, 50, and 150 kGy, respectively. The results showed less than 5% differences in crystallinity. A slight decrease in all of the unit cell parameters for the annealed samples was already reported in previous studies [**L. 14**]. This indicates that the unit cell density increases with the annealing temperature. A higher corresponding crystal density is expected, indicating a closer packing of the lamellae or a greater crystal perfection induced by the thermal treatment [**L. 15**].

After irradiating the polymer with gamma radiation of energy doses of 4 MeV and 50–150 kGy, the energy may permeate through the entire volume of material and cause decrease in degree of crystallinity. Authors of papers who examined linear thermoplastic polymers with no additives indicated that the absorption of higher radiation doses by the polymer is conducive to a decrease in the molecular mass due to the chain decomposition reaction [**L. 16–18**].

Whether one or more physical, mechanical, and chemical properties will be noted depend on the amount crosslinking and/or scission on changes in crystallinity. Polymers change their microstructure and molecular structure when they are subjected to gamma ray irradiation [**L. 19**]. During gamma ray irradiation in air, chain scission occurs mainly on the surface, and cross linking occurs inside the polymer [**L. 20**].

A change of thermal properties after gamma radiation has a direct effect on mechanical properties of PEEK as well as on wear resistance.

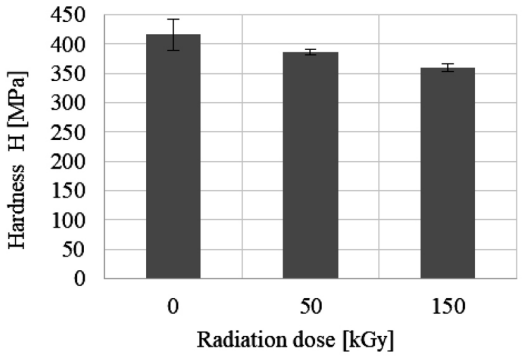

Fig. 3. Changes in hardness of PEEK as a function of the radiation dose

Rys. 3. Zmiana twardości w funkcji dawki promieniowania gamma

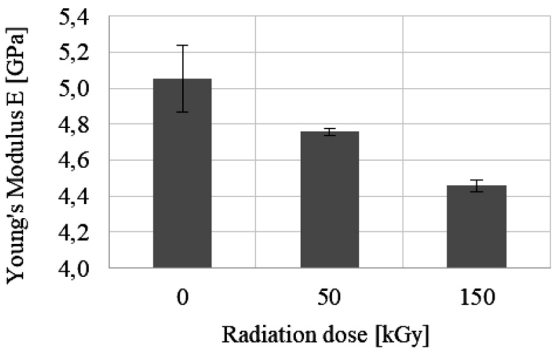

Fig. 4. Changes in Young's Modulus of PEEK as a function of the radiation dose

Rys. 4. Zmiana wartości modułu Younga w funkcji dawki gamma promieniowania gamma

Mechanical properties

Significant differences in the mechanical properties of irradiated PEEK are noticeable compared to the unmodified polymer. Gamma radiation of PEEK causes changes in hardness and Young's modulus E. Both of them increase proportionally to the absorbed radiation dose (**Figs. 3−4**). The change in the crystallinity has a direct influence in the hardness and Young's modulus of PEEK. Both parameters were subject to decrease in the range of 0−150 kGy.

Fig. 3 reports the reduced hardness approximately by 16%. In addition, Young's Modulus values were decreased by 13% in relation to the unirradiated sample.

The effects of gamma radiation on the mechanical properties are strictly correlated with the chemical structure of PEEK (**Fig. 1**). The aromatic rings and the ketone groups possess bonds with very high activation energies and are the less probable sites for radiation damage. The two C-C and four C-O bonds in the backbone repeating unit have the lowest activation energies, being 347 kJ/mole and 360 kJ/mole, respectively. This makes them the most probable sites for radicalization, which from the backbone and would create new active chain ends with added mobility that would recombine or crosslink on adjacent molecules. The twelve C-H bonds with an activation energy of 414 kJ/mole are located at the 2, 3, 5, and 6 sites on the three aromatic rings. From their respective positions, six of those bonds, when irradiated, favour the creation of new intramolecular bonds in the backbone between aromatic rings and the other six when irradiated favour intermolecular crosslinking with adjacent molecules. Intramolecular bond formation combined with some crosslinking caused the loss in backbone flexibility. Moreover, chain scission occurs and the appearance of additional chainends reduces the Young's modulus. Young's modulus seemed to be slightly affected by radiation, and a marked decreasing trend appeared for doses between 50−150 kGy; although, the molecular backbone movement in the amorphous phase seems to become more important at this dose range. Probably, it was caused by an increase in lower molecular weight products resulting from chain scission. On a segmental scale of several repeating

units, the effect of chain scission in the amorphous phase becomes predominant over crosslinking at higher doses. Moreover, it contributes more effectively to the reduction of the mechanical properties of irradiated PEEK. In unirradiated specimens, the Young's modulus of the semicrystalline PEEK is attributed to the presence of crystals in its morphology where molecules can transfer stress from the tough amorphous phase to the hard crystalline phase. In spite of the slightly higher crystallinity content of the 50 kGy, it displays a lower Young's modulus [**L. 21**].

During micromechanical measurements, the load-unload curve was recorded. An analysis of them enables one to determination of the parameters of the work indentation. Measurements of the work of indentation allow one to assess the material's susceptibility to deformation.

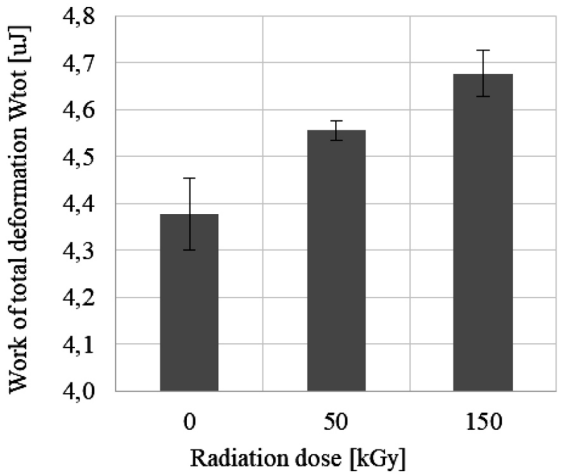

Fig. 5. Changes in total work of deformation of PEEK with radiation dose

Rys. 5. Zmiana całkowitej pracy indentacji w zależności od dawki promieniowania gamma

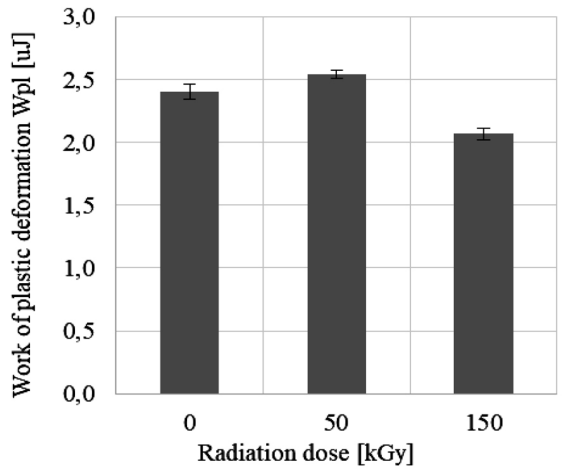

Fig. 6. Changes in the work of plastic deformation of PEEK with radiation dose

Rys. 6. Zmiana pracy odkształcenia plastycznego w zależności od dawki promieniowania gamma

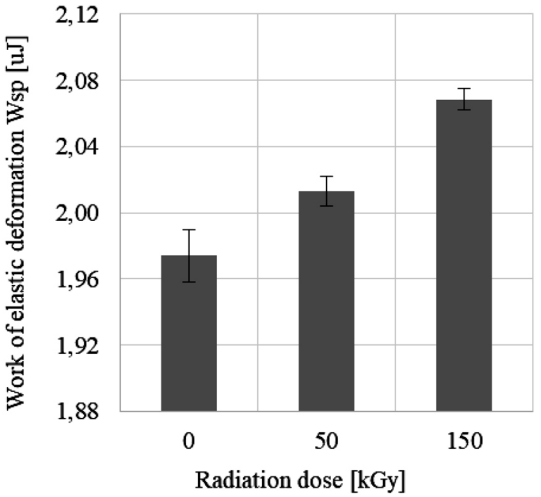

Fig. 7. Changes in the work of elastic deformation of PEEK with radiation dose

Rys. 7. Zmiana pracy odkształcenia sprężystego w funkcji dawki promieniowania gamma

The measure of the total work of indentation Wtot (**Fig. 5**) is the area under the load curve. Wpl (**Fig. 6**) is the sum of the work of plastic deformation, and Wel (**Fig. 7**) is the work of elastic deformation.

The test has shown an increase of the value of total work of indentation (**Fig. 5**) by approximately 7% with increasing radiation dose. Similar dependency occurs with the work of elastic deformation (**Fig. 7**). The work of plastic deformation (**Fig. 6**) reflects slight increase in the range of 0−50 kGy, followed by a decrease along with the growing radiation dose to 150 kGy. According to those results, the material should become more elastic and harder, which should significantly contribute to a reduction in the tribological wear.

For crystalline polymers, it is common to notice a milder gamma radiation effect on some mechanical properties, e.g., the elastic modulus, which is more intimately related to the crystalline content of the polymer. Crystalline polymers are less affected by radiation than the amorphous content, because the radiation is not able to destroy the crystalline portions responsible for the stiffness of the material [**L. 22**]. Gamma radiation primarily causes scissions and predominantly in molecules of the amorphous region; however, the highest losses in mechanical properties to a crystalline polymer are caused by scissions in the linked molecules [**L. 23**].

Tribological evaluation

Gamma radiation can affect the tribological performance of the polymer. **Fig. 8** presents a variation of the coefficient of friction (COF) as a function of irradiation doses.

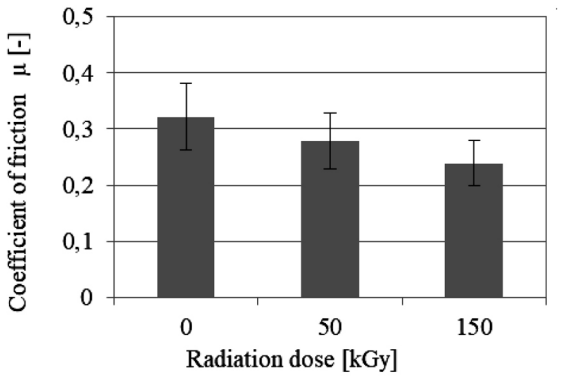

Fig. 8. Variation of coefficient of friction with radiation dose

Rys. 8. Zmiana współczynnika tarcia w zależności od dawki promieniowania gamma

Results show that the coefficient of friction decreases with an increase in radiation dose. The same tendency was observed for linear wear rate (**Fig. 9**). The best tribological behaviour of PEEK was obtained when the radiation dose equals 150 kGy.

Compared with neat PEEK, the coefficient of friction of irradiated polymer is reduced by 35%, and wear resistance is decreased by 16% for the sample of 50 kGy and is decreased by 13% for the sample of 150 kGy.

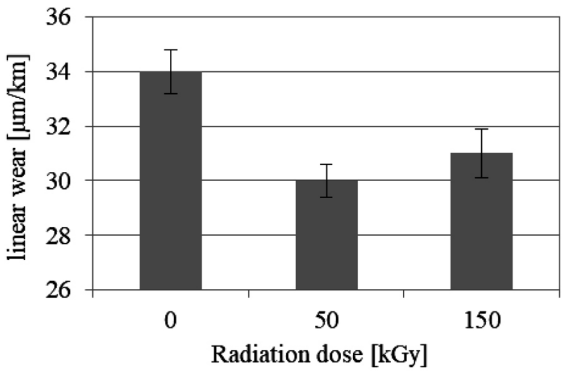

Fig. 9. Variation of wear rate with radiation dose

Rys. 9. Zmiana wartości zużycia liniowego w zależności od dawki promieniowania

Figure 9 shows the intensity of the tribological wear of the studied polymers recorded before and after irradiation. Generally, samples after irradiation indicated a significant increase of the tribological wear intensity of the polymer. Wear rate may change with the change in hardness. In general, increased hardness is responsible for the increase of the wear resistance of a material. In the current work, the hardness of irradiated material at all selected doses decreased as well as wear intensity.

CONCLUSIONS

The effects of gamma radiation on the thermal and mechanical properties of PEEK were studied. When exposed to radiation, the thermal properties, such as glass transition temperature, melting point temperature, enthalpy of melting, and degree of crystallization were found to be affected due to radiation damage.

DSC measurements were undertaken on specimens in order to investigate the thermal properties of material. Further crystallinity measurements should be done using techniques such as FTIR, WAXD, or X-ray diffraction.

Radiation was found to have an impact on PEEK mechanical properties, indicating that the increase in crystallinity had a strengthening effect. It was found that the hardness and Young's modulus decreased proportionally to the applied radiation dose. The decrease in mechanical properties may be caused by the degradation of the polymer. It may also result in a slight increase in wear intensity at radiation doses above 150 kGy but with decrease at a dose of 50 kGy. Tribological analysis of PEEK showed a reduction in the coefficient of friction with an increase in the radiation dose.

The analysis of the work of indentation has shown that not only the total work of indentation but also its components increased with increasing radiation dose.

The crosslinking reduces the plastic deformation of the surface layer during interaction with the moving disc, which reduces the intensity of wear and also limits the susceptibility to operational deformation. Radiation crosslinking reduces the mobility of the chains, which decreases the plastic deformability of the polymer. According to the literature, this is manifested by a decrease in elongation at the breaking point and a resistance to fatigue cracking. As the radiation dose increases, there is a decrease in ductility and strength, which reaches saturation at a dose where the crosslink density reaches its maximum. Morphological studies showed a slight decrease in the degree of crystallinity, which results in the increase in the polymer susceptibility to deformation, which is desirable in bearing applications, because it reduces the contact stress.

Further studies are needed to evaluate more properties of PEEK, both static and dynamic, and to obtain more information on its structure and stability over time.

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