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THE ANALYSIS OF THE INFLUENCE OF GAMMA IRRADIATED POLYSULFONES ON THE STATIC FRICTION COEFFICIENT

ANALIZA WPŁYWU PROMIENIOWANIA GAMMA NA WSPÓŁCZYNNIK TARCIA STATYCZNEGO POLISULFONÓW

Key words: static coefficient of friction, gamma irradiation, polysulfones.

Abstract The paper presents the results of studies on the effects of gamma irradiation on the static friction coefficient of thermoplastic polymer – polysulfone. These polar polymers belong to the group of amorphous thermoplastics and are widely used for various applications, e.g., automotive and electronic industries (dielectrics in capacitors), waste water recovery, medical uses (hemodialysis membranes), requiring autoclave, and steam sterilization. Polysufones are known for their toughness and stability at high temperatures.

The aim of this study is to analysed changes in the static coefficient of friction in association with a contact pressure (in the range 0.2 – 0.8 MPa) depending on the ionizing radiation dose of PSU (in the range 50-150 kGy). Additionally, microhardness, and wear intensity were measured, because tribological properties of polymers as well as mechanical properties that influence their durability and applications. The studies confirmed that the static coefficient of friction increases with an increase in contact pressure (in the test range). The research has shown that mechanical (microhardness) and tribological (static coefficient of friction and tribological wear) improve as the radiation dose of irradiated material increase. Moreover, the tribological wear increases with increasing the sliding velocity. This gamma irradiated polymer is characterized by higher microhardness, a static coefficient of friction, and a higher wear rate compared to PSU in the initial state, because of changes in structure. It requires further research.

Słowa kluczowe: współczynnik tarcia statycznego, promieniowanie gamma, polisulfony.

Streszczenie W artykule przedstawiono wyniki badań wpływu promieniowania gamma na właściwości tarcia statycznego polisulfonu. Ten polarny polimer należący do grupy termoplastów o budowie amorficznej został wybrany z uwagi na jego szerokie zastosowanie w różnych dziedzinach, w tym w przemyśle samochodowym, elektronicznym (dielektryki w kondensatorach), oczyszczaniu wody, medycynie (membrany do hemodializy), autoklawach. Polisufony są znane ze swojej wytrzymałości i stabilności wymiarów w wysokich temperaturach. Celem przeprowadzonych badań była analiza wpływu promieniowania gamma (w zakresie 50–150 kGy) na zmiany wartości współczynnika tarcia statycznego (w zakresie 0,2÷0,8 MPa). Dodatkowo wykonano badania mikrotwardości oraz intensywności zużywania z uwagi na to, że właściwości tribologiczne polimerów takie jak właściwości mechaniczne mają wpływ na ich trwałość i właściwości użytkowe. Analiza wyników wykazała, że wraz ze wzrostem dawki promieniowania gamma zwiększała się wartość pomiarów mikrotwardości, współczynnika tarcia statycznego oraz intensywności zużywania. Wyniki wykazały wpływ prędkości poślizgu na zużycie liniowe materiału. Przyczyną zaobserwowanych zmian są zmiany zachodzące w strukturze polimeru pod wpływem promieniowania, co wymaga prowadzenie dalszych badań.

INTRODUCTION

Ionizing radiation is widely used in our daily life, from industry to health to daily consumer products, commonly used. International use of radiation in industry, health, and power production is increasing rapidly. Radiation sources are utilized daily in hospitals, factories, educational institutions, and many other establishments, such as food processing and preservation. Fifty years of research in polymer radiation chemistry has led to numerous applications of commercial and economic importance, and work remains active in the application of radiation for practical uses involving polymeric materials. Today, a substantial commercial industry is in place based on the processing of polymers with radiation. Ionizing radiation (gamma rays, X-rays, accelerated electrons,

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ion beams) has been found to be widely applicable in modifying the structure and properties of polymers, and it can be used to tailor the performance of either bulk materials or surfaces **[L. 1]**. One of type of radiation is gamma rays. Gamma radiation is the most energetic, highly penetrating electromagnetic radiation with an extremely high frequency. High energy radiation can bring major changes in the molecular structure and macroscopic properties of polymers. The radiation dose required to bring changes in physical properties of polymers is considerably less than that required to cause any significant change in ceramics or metals **[L. 2]**. Radiation can bring changes in appearance, chemical and physical states, and thermal, mechanical, and tribological properties **[L. 3]**. Aromatic polysulfones (PSU) are a family of amorphous thermoplastics that possess unique high performance properties as engineering materials, with the high strength, the highest service temperature of all melt-processable thermoplastics, low creep, good electrical characteristics, and transparency. Polysulfones are highly resistant to aqueous mineral acids, bases, oils, greases, and oxidizing agents, and they are fairly resistant to many non-polar solvents. However, polysulfones are not resistant to low polar solvents, such as esters, ketones, and aromatic and chlorinated hydrocarbons **[L. 4]**. Polysulfones are resistant to many forms of electromagnetic radiation frequency, including microwave, visible, and infrared. They also show a good resistance to X-rays and electron beams under practical application conditions. PSUs exhibit poor resistance to ultraviolet (UV) light, as do most aromatic polymers **[L. 5]**. Polysulfones are highly resistant to degradation by gamma radiation **[L. 6]**. Synthetic polymers used in the biomedical field such as polyolefins, poly(tetrafluoroethylene), poly(vinyl chloride), polyesters, polyethers, polyamides, polyurethanes, and polysulfones, should be tolerant to several sorts of sterilizations procedures for production of medical devices. There is a demand for medical polymers free from hazardous chemicals in order to be safe for humans. Biosafety and biocompatible characteristics are additionally required for safety healthcare products production **[L. 7]**. Sulfone-based polymers offer a number of features that make them attractive for a wide variety of applications. In addition, many applications are made possible by the excellent hydrolytic stability, chemical resistance, flame resistance, excellent thermal stability, and toughness **[L. 5]**. The excellent hydrolytic stability of PSU makes them an ideal choice for use in a variety of medical and dental devices, e.g., devices and components that have to be sterilized in steam autoclaves, sometimes hundreds of times over the life of the component. Such components include sterilization trays, as well as parts of surgical instruments themselves, such as the instrument handles. Traditionally, metals such as stainless steel have been used for this purpose, but metals are being replaced by thermoplastics materials. PSU is generally regarded as the plastic material for durable sterilizable trays and devices **[L. 5]**. Polysulfones, because of their ability to be repeatedly sterilized and their excellent solution processing behaviour and biocompatibility, are widely used in membranes for hemodialysis **[L. 8]**. They are also used in devices such as binocular opthalmoscopes, and dental syringe guns. What is more, because of their superior resistance to chemicals and high temperatures, polysulfones are an excellent choice for components that are exposed to high temperatures and corrosive media. Examples include printer cartridges, internal components of coffee machines, and battery containers. Polysulfones are also used in the automotive and aerospace industries for applications where superior thermal and mechanical properties relative to conventional resins are required **[L. 4]**. The mechanical properties exhibited by a polymer after irradiations are a complex function. Therefore, it is hard to draw structure/radiation resistance conclusions only from the change in the mechanical or tribological properties. However, the changes in mechanical properties are direct indications of the ultimate usefulness of the polymer in a radiation environment. Polymers cooperate with others surfaces that include sliding interfaces (metallic, ceramic, polymeric), which is why friction becomes an important factor. Friction is governed by the surface interaction in moving contact. Based on classical theory of adhesion, friction coefficient μ is given as follows **[L. 9]**:

$$\mu = \frac{F_t}{F_n} \tag{1}$$

where F_t – friction force [N], F_n – normal force [N].

The static friction force must be overcome by an applied force before an object can move. The maximum possible friction force F_t between two surfaces before sliding begins is the product of the coefficient of static friction and the normal force F_n. A force larger than F_t overcomes the force of static friction and causes sliding to occur. The instant sliding occurs, static friction in no longer applicable and kinetic friction becomes applicable. The coefficient of static friction μ_s is usually higher than the coefficient of kinetic friction μ_k.

In this paper, the effect of gamma radiation on the static (μ_s) coefficient of friction, tribological wear, and mechanical property measurements of irradiated polysulfone is investigated.

MATERIALS

Commercial polysulfone (**Fig. 1**) was used in this study, because of its high thermal, oxidative, and hydrolytic stability. Moreover, polysulfones have good resistance to many acids, solutions, oils, and greases. Their high biocompatibility and ability to be sterilized makes them highly suitable for medical applications. Due to these properties, PSU is widely used for various applications, e.g., automotive, electronic, and medical uses **[L. 10]**.

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, 100 and 150 kGy (gamma rays of energy 4 MeV).

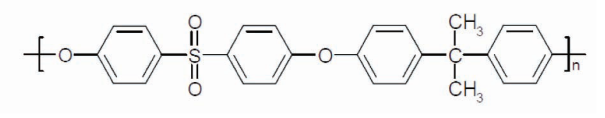

Fig. 1. Structure of the repeat unit of PSU
Rys. 1. Struktura meru PSU

EXPERIMENTAL DETAILS

Mechanical properties

Mechanical analysis was performed on a Micro- Hardness SHIMADZU hardness tester. The microhardness measured was performed using Vickers's method, before and after irradiation. The tests were conducted at room temperature. For analysis, samples of analysis thermoplastics having a 30 mm diameter and a 20 mm length were prepared. Testing was performed by forcing the indenter into the surface of a sample using a specified load (1 N) with a dwell time of 20 s. To find accurate results, at least four readings at different locations on samples were determined and the average value was reported.

Tribological evaluation

The static friction tests were conducted on an experimental device for static friction measurement of two friction couples (metal (steel C45, 20-25 HRC)-polymer) was describe in article **[L. 11]**. The device measures an angle of repose (the angle when the specimen starts moving on the counter-sample). The tester has a laser indicator which points on the scale. The friction angle is defined as follows:

$$tan\,\rho = \mu_s \tag{2}$$

where ρ is the angle from horizontal [°].

According to Formula 1 and knowing the value of normal force F_n, the static COF value was calculated (Formula 2). During testing, the samples was loaded with a normal force of 25 N (0.2–0.8 MPa). Each test was repeated 6 times.

The tribological wear tests were conducted on a *pin-on-disc* test rig **[L. 12]**. Samples cooperated during the test with a flat surface made of carbon steel C45, the surface of which was mechanically polished and had an average of the profilometric parameter of roughness Ra = 0.5 μm and a hardness of 50 HRC. The diameter of the pin at the 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 and 1 m/s at a friction distance of 1000 m. An ambient temperature was around 21 ±1°C was kept constant for all tests. The tribological evaluations were done in the technical dry friction conditions on a testing machine. The wear of the pin was evaluated by measuring dimension loss after completing the test using a precision equipment. The specific wear rate *Wr* was calculated from the following relationship:

$$W_r = \frac{\Delta l}{L}\left[\text{mm/km}\right] \tag{3}$$

where Δl – length loss [mm], L – total sliding distance [km].

RESULTS AND DISCUSSION

Measurement of surface microhardness

The microhardness was determined using Vickers's method. The measurement results are summarized in **Tab. 1**.

Table 1. Results of the microhardness measurements
Tabela 1. Wyniki pomiaru mikrotwardości [HV 0.1]

Gamma radiation dose [kGY]	Microhardness [HV 0.1]
0	14.3 ± 0.2
50	15.6 ± 0.6
100	16.3 ± 0.9
150	16.8 ± 0.5

Table 1 indicates that the exposure to radiation dose of 50. 100, and 150 kGy resulted in an increased microhardness of irradiated polysulfones. The microhardness value of PSU before irradiation increased from 14.3 ± 0.2 to 16.8 ± 0.5 HV 0.1 after exposure to gamma irradiation. At lower absorbed doses of 50 kGy, a slight increase in microhardness was observed. The effect may be explained by the crosslinking process as a consequence of the modification through radiation. The reason for increasing the microhardness materials may be the changes in the chemical structure of polymers and include the crosslinking process, which causes the curing of the polymer. With the increase in the dose of gamma radiation, further changes in the properties of materials are possible, e.g., an increase in their fragility **[L. 13, 14].** Whether one or more physical, mechanical, and chemical properties will be noted depends on the amount of crosslinking and/or scission on changes in crystallinity. Polymers change their microstructure and molecular structure when they are subjected to gamma ray irradiation **[L. 15]**. Radiation modification can be one

of the methods of strengthening the surface layer of the thermoplastics. Irradiated polymers were characterized by greater resistance to wear and were harder than their unmodified counterparts. High microhardness generally produces a wear resistant surface; however, other factors also influence this.

Tribological properties

Tribological tests were carried out on a device that allows one to determine the static coefficient of friction **[L. 11]** and on a *pin-on-disc* test rig to measure linear wear. **Figure 2** presents typical variation of static coefficient of friction (COF) with irradiation doses depending on the load. In each test, the highest COF was depicted by samples irradiated for 150 kGy irradiation dose. The tests show the impact of the radiation dose and pressure on the static coefficient of friction.

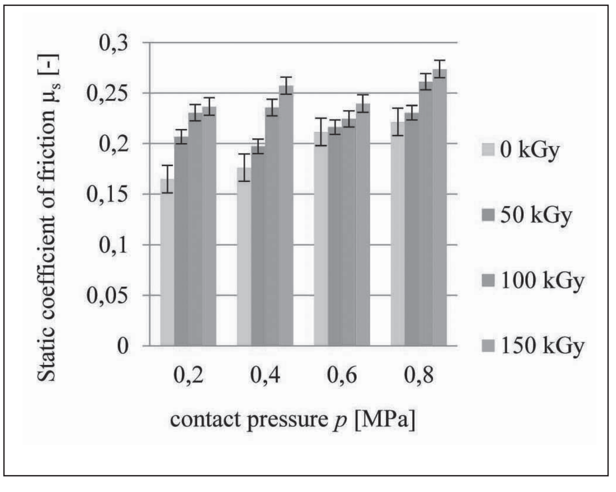

Fig. 2. Variations of the static coefficient of friction with radiation dose
Rys. 2. Zmiana statycznego współczynnika tarcia w zależności od dawki promieniowania gamma

Analyses of the results of the static coefficient of friction of PSU studies presented in **Fig. 2** indicated that, after irradiation, the COF increased with increasing pressure: 0.2 MPa: 43.64%, 0.4 MPa: 46.02%, 0.6 MPa: 13.21%, 0.8 MPa: 23.42%, respectively. Subsequently, the samples were irradiated with gamma radiation doses of 50, 100, and 150 kGy, respectively. The reason behind this may be that, at higher contact pressure, adhesion might be dominating, which results in higher COF. Results showed that the static coefficient of friction increases with an increase in microhardness. This indicated that changes in the surface generated due to gamma radiation of the polymer are responsible for the change in COF. However, at 0.4 MPa (50 kGy) and 0.6 MPa (100 and 150 kGy), contact pressure conditions showed a lower COF. There is nearly a 5% reduction in the coefficient of friction as against materials analyses at lower contact pressure (50 kGy at 0.2 MPa, 100 and 150 kGy at 0.4 MPa).

Sliding velocity has an impact on the wear rate. Linear wear rate changes depending on sliding speed (v = 0.5 and 1 m/s) and radiation dose. The results are summarized in **Fig. 3**.

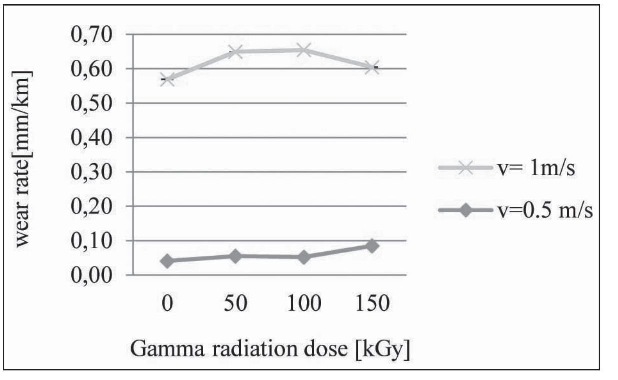

Fig. 3. Variation of wear rate with radiation dose
Rys. 3. Zmiana wartości zużycia liniowego w zależności od dawki promieniowania

Figure 3 shows the intensity of the tribological wear of the studied polymers recorded before (0 kGy) and after irradiation. The lowest value of the linear wear was observed for samples that were not irradiated for sliding velocity. The highest linear wears were characterized by samples irradiated with 50 and 100 kGy during test at 1 m/s sliding speed. It can be seen that the tests with a slower sliding speed caused more than a five times the reduction of wear compared to tests with a faster sliding speed. Generally, samples after irradiation indicated a sharp increase in wear rate with an increase in sliding speed. Such a significant increase of the tribological wear intensity of the polymer does not coincide with the results of microhardness measurements. The wear rate may change with a change in microhardness. In general, the increased microhardness is responsible for the increase wear resistance of the material. In the current work, the microhardness of irradiated materials at all of the selected doses increased; however, the wear rate is different. The reason behind this may be that radiation modification leads to changes in structure like crosslinking or degradation (very often both). The surface conditions are also changing **[L. 16, 17]**, which leads to a change in other properties of the polymer. The increased sliding velocity resulting in a high wear rate of irradiated polymer may be due to changes in the wear mechanism from abrasive to adhesive. However, it depends on the value of irradiation dose.

Wear mechanisms of irradiated and non-irradiated PSU

The polymer specimens were observed under a scanning electron microscope in order to investigate the wear surface after tribological tests. Examples of images from the scanning electron microscope (SEM) of surfaces of irradiated samples after tribological tests are shown in **Fig. 4**.

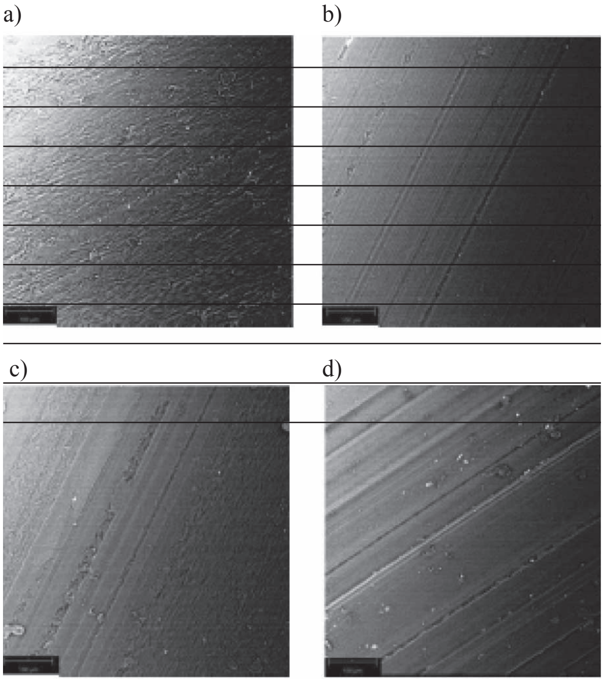

Fig. 4. Surface of PSU pins after tribological evaluation with radiation doses: a) 0 kGy, b) 50 kGy, c) 100 kGy, d) 150 kGy

Rys. 4. Powierzchnia PSU po badaniach tribologicznych napromieniowana dawkami: a) 0 kGy, b) 50 kGy, c) 100 kGy, d) 150 kGy

Surface topographies of worn surfaces supported wear performance trends of non-irradiated and irradiated samples of PSU. On the worn surface of non-irradiated PSU as shown in **Fig. 4(a)**, wear debris is not very visible nor are sliding marks. It might exhibit a lower wear rate than other samples. The main wear mechanism of non-irradiated PSU is abrasive wear caused by the hardness of the counterface. **Figures 4(b)** and **(d)** show wear marks in the form of continuous narrow cutting grooves, and a comparatively smooth topography. **Figure 4(b)** indicates the worn surface of the sample irradiated at 50 kGy. Wear performances indicated that the sample exhibited a very high wear rate at the higher sliding velocity of 1 m/s. **Figure 4(d)** indicates the worn surface of PSU irradiated at 150 kGy. It shows a smooth topography; however, sliding marks are more visible than the sample irradiated at 50 kGy. In **Figure 4(c)**, some small wear debris formed during the sliding process and are visible as well as in **Fig. 4(d)**. The surface was covered with plastically deformed wear debris, which might result in an increasing wear rate with an increase in sliding velocity.

CONCLUSIONS

The results of tribological tests led to the following conclusions and observations:

- Improvement of the mechanical properties of PSU as a result of radiation modification was substantiated with the results of microhardness tests. It was found that gamma irradiation of the analysed thermoplastic induces an increase in the microhardness with the increase of the absorbed irradiation dose. This tendency is often observed for irradiated materials **[L. 1–17]**.
- Tribological analysis of the PSU subjected to gamma irradiation showed a change in the static coefficient of friction. It also showed an increase in the static coefficient of friction with both an increase in pressure and the radiation dose. The highest COF was observed at the higher radiation dose of 150 kGy. The values of the static coefficient of friction are higher than for the unmodified material. The radiation dose could influence the mechanical properties of the polymer, which have an impact on the static coefficient of friction. Probably, surface energy studies would provide more information about that issue.
- An increase in the contact pressure within the test range should contribute to a decrease in the static coefficient of friction, which is typical of the phenomenon of friction for the metal-polymer couples and is consistent with the postulates of adhesion and molecular-adhesive friction theory. It is justified to verify if radiation doses have an impact on the effect of unit pressure.
- It should be noted that a slight increase in microhardness was observed in the irradiated material, but it had no effect on reducing the wear of the irradiated polymer. A similar conclusion was presented in article **[L. 17]**. Tribological tests showed a fivefold reduction of linear wear when the sliding speed was reduced from 1 m/s to 0.5 m/s.

The obtained results should confirm the positive effect of irradiation on the tribological properties of polysulfones, like the reduction of wear and the static coefficient of friction. Radiation can cause the crosslinking process as well as degradation, which manifests itself through a higher hardness and an increase in the linear wear. Related to presented results that show that the lowest linear wear was characterized by the non-irradiated sample, it is believed that irradiation of PSU with gamma radiation caused its degradation. However, this requires further studies.

- According to presented results, the optimal radiation dose irradiated material in order to improve mechanical and tribological properties cannot be determined.
- Exposure to gamma radiation caused modifications in surface conditions and in the molecular structure, which have an impact on all analysed properties of the material. Further studies of structural properties will help to explain how radiation modification influences mechanical and tribological properties.
- Radiation processing is a practicable and economical method for modifying the physical properties of polymeric materials, and the process will find a variety of applications.

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