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SCLEROMETRIC AND TRIBOLOGICAL PROPERTIES OF POLYTETRAFLUOROETHYLENE WITH 40% BRONZE CONTENT FORMED BY ELECTRON BEAM IRRADIATION

WŁAŚCIWOŚCI SKLEROMETRYCZNE I TRIBOLOGICZNE POLICZTEROFLUOROETYLENU Z 40% ZAWARTOŚCIĄ BRĄZU KSZTAŁTOWANEGO PRZEZ NAPROMIENIOWANIE STRUMIENIEM ELEKTRONÓW

Key words:	PTFE with a 40% bronze content, radiation modification, wear micromechanism, sliding wear resistance ratio, wear.
Abstract	The paper focuses on the improvement of sclerometric and tribological properties of polytetrafluoroethylene (PTFE) with 40% bronze content implied by irradiation with an electron beam of 10 MeV and a power of 10 kW, in a dose of 26–156 kGy. The results of the study confirm that radiation modification of the PTFE-bronze composite causes structural changes induced by breaking of bonds in long PTFE chains and the branching of the polymer structure. As a result, an increase in such properties as the wear resistance ratio, W_{β} , is observed. In addition, sclerometric tests have shown that, with an increase of the absorbed radiation dose, the groove-to-elevation area ratio changes during scratching, which indicates a change in the micromechanism of wear, i.e. the material undergoes ploughing. From the operating point of view, the most important were tribological tests, which were carried out on a pin-on-disc test stand (T-01). The tests showed a nearly fourfold reduction in wear at a load of 20 N and more than a threefold reduction at 40 N. Controlled radiation modification leads to improved properties of the PTFE-bronze composite, which may result in a wider range of its applications.
Słowa kluczowe:	PTFE z 40% zawartością brązu, modyfikacja radiacyjna, mikromechanizm zużycia, wskaźnik odporności na zużycie ściernie, zużycie.
Streszczenie	W pracy skoncentrowano uwagę na poprawie właściwości sklerometrycznych i tribologicznych politetrafluoroetyleny z 40% zawartością brązu implikowanych przez napromieniowanie strumieniem elektronów o energii wiązki 10 MeV i mocy 10 kW oraz dawce 26–156 kGy. Wyniki badań potwierdzają, że modyfikacja radiacyjna, jakiej poddany został kompozyt PTFE-brąz, powoduje zmiany strukturalne wywołane zrywaniem wiązań w długich łańcuchach PTFE oraz rozgałęzianiem się struktury polimeru. W konsekwencji obserwuje się wzrost takich właściwości jak wskaźnik odporności na zużycie W_{β} . Badania sklerometryczne wykazały ponadto, że wraz ze wzrostem pochłoniętej dawki promieniowania zmienia się stosunek powierzchni wyżłobienia i wypiętrzenia podczas zarysowania, co świadczy o zmianie mikromechanizmu zużycia – materiał ulega bruzdowaniu. Z punktu widzenia eksploatacyjnego najważniejsze było przeprowadzenie badań tribologicznych, które wykonano na stanowisku trzpień-tarcza (T-01). Badania wykazały blisko 4-krotne ograniczenie zużycia przy zastosowaniu obciążenia 20 N oraz ponad 3-krotne przy zwiększeniu obciążenia do 40 N. Kontrolowana modyfikacja radiacyjna prowadzi do poprawy właściwości kompozytu PTFE-brąz, co może prowadzić do poszerzenia spektrum jego zastosowań.

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INTRODUCTION AND RESEARCH METHODOLOGY

Polytetrafluoroethylene (PTFE) is currently one of the most important thermoplastics on the market. This material is characterized by such properties as low dielectric constant, high specific resistance, chemical inertness, high melting point, and low friction coefficient. These properties facilitate using this material in many areas of life, such as, inter alia, electronic and electrical systems, bearing components, chemical or medical apparatus components (including implants), or commonly used household items [L. 1–6].

PTFE is characterized by a banded crystalline-amorphous structure, where the band length can be from 10 to 100 μm and its width from 0.2 to 1 μm . The result of such a structure is a high, as for a polymer, density of 2.1 to 2.3 g/cm^3 [L.7].

Despite its good properties, PTFE shows quite poor functional properties, i.e. it is characterized by high wear and low abrasion resistance, although its friction coefficient is low (static 0.08 and dynamic 0.01) [L. 8]. These properties can be significantly increased by applying appropriate types of fillers in the PTFE matrix. Not only the type of fillers, but also the size and shape of their particles have a significant influence on the improvement of properties of the composite [L. 8]. The use of fillers is mainly aimed at improving mechanical properties (rigidity, strength) and tribological properties [L. 6]. Adding a bronze filler to the PTFE matrix results in a significant improvement of both mechanical and tribological properties. PTFE with a bronze additive shows a higher hardness, compression strength, and Young's modulus, as well as better resistance to abrasive wear and a lower friction coefficient. Moreover, the change of properties can be strictly controlled by changing the volume share of fillers, their type, shape, and distribution in the PTFE matrix [L. 8–10].

Another factor which affects the properties of PTFE, apart from fillers, is ionizing radiation. Even at relatively low doses, radiation influences such properties as crystallinity degree, and mechanical and tribological properties, thereby allowing control of mechanical, physical, and technological properties of PTFE [L. 11–18].

Most studies concern the effect of gamma radiation on PTFE without fillers. Therefore, it is advisable to determine the effect of electron beam irradiation on the PTFE-bronze composite. In this paper, attention is focused on the change of sclerometric and tribological properties of the investigated composite through the use of irradiation with a 10 MeV electron beam, which is necessary to penetrate the material to the thickness of several centimetres.

The research materials were 20 mm diameter bars made of polytetrafluoroethylene (PTFE) with a 40% bronze addition (SM-B40, Inbras, Poland). The

filler for PTFE was tin bronze without lead preparation (Sn – 10%, Zn – 2%, Pb<0.004%) with a grain size of 0–32 μm . Cylindrical samples, 20 mm in height, were cut out from the composite. Irradiation with an electron beam was performed using a linear accelerator Elektronika 10/10 (energy of electrons: 10 MeV, beam power: 10 kW). The absorbed dose ranged from 25 to 156 kGy. Next, the samples were stabilized through oxidation by means of thermal processing in a vacuum, which was heating to a temperature of 200°C for 4 hours, soaking for 2 hours, and cooling down to ambient temperature for 10 hours. After that, all the samples were vacuum wrapped.

The scratch tests were performed with a Micron-Gamma device using a Rockwell indenter (Y-275, 200 μm radius). During the scratch test, a normal force of 4 N and a scratching rate of 5.4 mm/min were applied for a ca. 4 mm long scratch. Measurements of the groove area A and the plastic elevation area B (Fig. 1) were taken by means of a Taylor Hobson profiler with the TalyMap Universal software.

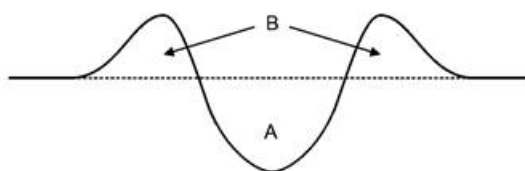


Fig. 1. Cross-section diagram of a scratch formed during a scratch test

Rys. 1. Schemat profilu powstałego podczas testu zarysowania

A scratch area of 4.5 x 1 mm was examined, maintaining a sampling distance of $x = 25 \mu\text{m}$ and $y = 1 \mu\text{m}$, which allows obtaining 180 cross-sections for each surface examined. The coefficient of polymers' resistance to sliding wear, W_{β} , was calculated from the following formula (1) [L. 19]:

$$W_{\beta} = \frac{1}{\frac{1}{n} \sum_{i=1}^n (\beta_i A_i)} \quad [\text{mm}^2] \quad (1)$$

where β_i – the micromechanism of sliding wear determined from dependence (2) [L. 20–21]:

$$\beta = \frac{1}{n} \sum_{i=1}^n \frac{A_i - B_i}{A_i} \quad [-] \quad (2)$$

where A_i – furrow area, B_i – elevation area.

Tribological tests of polytetrafluoroethylene with a 40% bronze content were performed using a T-01 device (manufactured by ITeE Radom, Poland). A pin-on-disc friction couple was applied. In each case, 3 samples were prepared (pins, 5 mm in diameter).

Discs made of 1H18N9T steel were used as counter-specimens, with a surface roughness $R_a = 0.2 \mu\text{m}$, which enabled the formation of a thin film reducing the friction coefficient and wear. Tests were performed in accordance with the recommendations of VAMAS Technical Note and the requirements of the ASTM G-99 standard [L. 22–23], with the following contact parameters: dry friction; pin diameter: 5 mm; friction distance diameter: 24 mm, sliding speed: 0.1 m/s; and, load: 20 N and 40 N (pressure: 1 and 2 MPa); friction distance: 1000 m. The ambient parameters were temperature – $21 \pm 1^\circ\text{C}$, and humidity – $50 \pm 5\%$. The linear wear W_L was determined as the difference between the indications of the micrometric sensor before and after the tests (and after the cooling stage).

RESEARCH RESULTS AND ANALYSIS

As a result of changes caused by electron beam irradiation, which include, inter alia, the reconstruction of the molecular structure (breakage of polymer chains, an increase in the degree of crystallinity, a significant decrease of average molecular weight, an increase of radiation stability, and a possibility of easier processing) of the PTFE–bronze composite, the sliding wear resistance coefficient, W_β , increases (Fig. 2). A combined application of both factors (the filler consisting of bronze and irradiation) shows their strengthened/synergistic effect. An increase of W_β is observed with an increasing absorbed radiation dose, especially in the range of 26–104 kGy. The application of a 156 kGy dose [L. 24–25] induces a reduction of this coefficient due to degradation of the material. It should be noted, however, that the reduction is not as intense as for the PTFE–graphite composite discussed in previous papers of the authors [L. 24–25], which may indicate higher radiation resistance in the case where bronze is used as a PTFE filler.

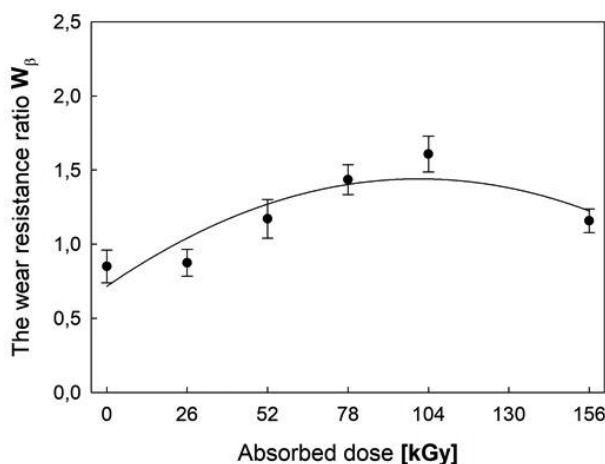


Fig. 2. The effect of electron-beam irradiation on the wear resistance ratio W_β of the PTFE–bronze composite

Rys. 2. Wpływ napromieniowania strumieniem elektronów na wskaźnik odporności na zużycie W_β kompozytu PTFE–brąz

Based on a stereometric analysis of scratch traces, the wear micromechanism β of the PTFE–bronze composite before and after electron-beam irradiation was also determined (Fig. 3a). The results show that, in the polymer subject to electron-beam irradiation, the ploughing micromechanism component (*parameter $\beta \rightarrow 0$*) predominates. This means that a larger part of the material is lifted up on the edge of the scratch formed during the test, which is reflected in the isometric 3D images of the scratched surface (Fig. 3b). Similarly to the wear resistance ratio, these changes occur within the absorbed dose ranging from 26 to 104 kGy, while the absorption of a 156 kGy dose leads to partial degradation of the material and shifting of the micromechanism of wear in the cutting direction, however, the changes are not intense.

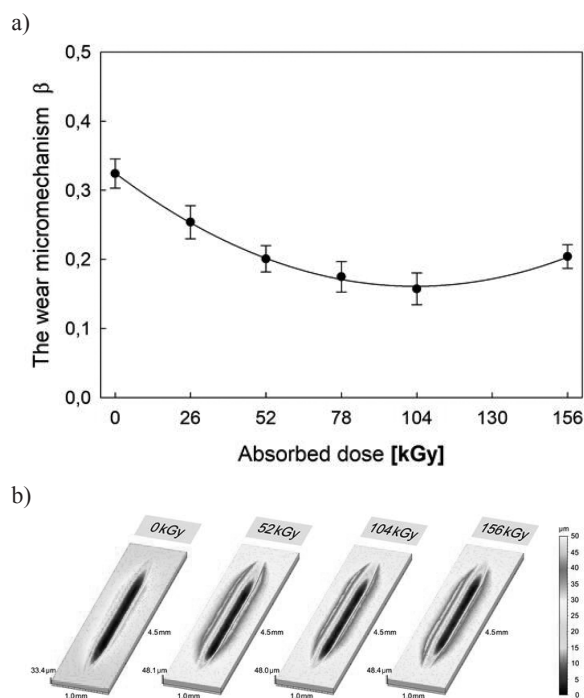


Fig. 3. The effect of electron-beam irradiation on the micromechanism of PTFE–bronze composite wear β – a), isometric 3D images of the scratched surface – b)

Rys. 3. Wpływ napromieniowania strumieniem elektronów na mikromechanizm zużycia kompozytu PTFE–brąz β – a), obrazy izometryczne 3D zarysowanej powierzchni – b)

From the operating point of view, the results of tribological tests are the most important, and the tests showed that, with an increase in the absorbed dose of electron beam irradiation, a significant decrease in the linear wear W_L of the studied composite is observed (Fig. 4) for both 20 N and 40 N loads. In the initial state, the linear wear at a 20 N load was $50 \mu\text{m}$, and at 40 N, it was $72.5 \mu\text{m}$. The most advantageous results were observed for the absorbed dose of 104 kGy ($15.125 \mu\text{m}$; $27.125 \mu\text{m}$) and 156 kGy ($11.875 \mu\text{m}$; $22.375 \mu\text{m}$), i.e. a three- to fourfold reduction in wear compared to the unirradiated material. In the case of the PTFE composite

with a graphite addition [L. 25], irradiation with the 156 kGy dose resulted in significant degradation and increased wear. In the case where bronze is applied, this effect is eliminated and the wear is the lowest in the case of the highest absorbed dose of 156 kGy. The mean value of the friction coefficient μ was identical for both loads and did not change as a result of electron beam irradiation. It amounted to 0.184 ± 0.01 . The results obtained show that the change of PTFE filler from graphite [L. 25] to bronze significantly reduces the wear of polytetrafluoroethylene.

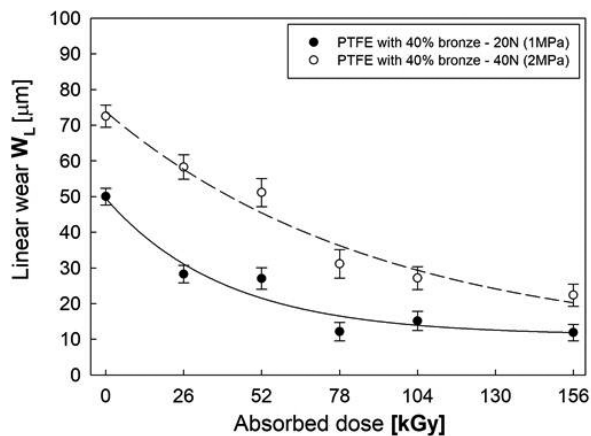


Fig. 4. Linear wear of PTFE with 40% bronze content as a function of the absorbed electron-beam irradiation dose

Rys. 4. Zużycie liniowe PTFE z 40% zawartością brązu w funkcji pochłoniętej dawki strumienia elektronów

CONCLUSIONS

- Electron beam irradiation induces a reconstruction of the polytetrafluoroethylene molecular structure (the process took place at room temperature, so destruction of polymer chains was the dominant mechanism of irradiation, which is confirmed, inter alia, by increased crystallinity), which has a direct impact on the increase in its thermal, mechanical, or sclerometric properties, and the resulting operational life achieved through reduced wear.
- Stereometric analysis of the scratched surface of PTFE with a 40% bronze addition subjected to electron-beam irradiation showed a change of the wear mechanism β in the direction of ploughing, and an increase in the resistance to sliding wear, W_{β} in particular, for the absorbed dose of 104 kGy.
- Tribological tests showed a three- to fourfold reduction in linear wear for 20 N and 40 N loads. The most advantageous results were obtained for the absorbed doses of 104 and 156 kGy.
- Increasing the radiation dose above the value of 104 kGy did not induce any considerable degradation of the PTFE-bronze composite, which was observed in the case of PTFE with a graphite filler.
- The significant improvement of properties, in particular tribological properties, holds promise for a longer service life of components made of PTFE with a bronze filler and irradiated with an electron beam.

REFERENCES

1. Olabisi O., Adewale K.: Handbook of thermoplastics, Boca Raton FL: CRC Press, 2016.
2. Rossa B.B., Fluorocarbon polymers in the Chemical Industry, Praktische Chemie 15, 1964, pp. 64–73.
3. Cox J.M., Wright B.A., Wright W.W.: Thermal degradation of fluorine-containing polymers, J Appl Polym Sci 8, 964, pp. 2935–2961.
4. Briscoe B.J., Ni Z.: The influence of γ -irradiation on the tribology of ptfе and high density polythene, Wear 100, 1984, pp. 221–242.
5. Perry H.R., Green D.W., Maloney J.O.: Perry's chemical engineers' handbook, 6th ed. New York: McGraw-Hill, 1984.
6. Tanaka K., Uchiyama Y., Toyooka S.: The mechanism of wear of polytetrafluoroethylene, Wear 23, 1973, pp. 153–177.
7. Ebnesajjad S.: Expanded PTFE Applications Handbook, Oxford UK: Elsevier, 2017.
8. Khedkar J., Negulescu I., Meletis E.I.: Sliding wear behavior of PTFE composites, Wear 252, 2002, pp. 361–369.
9. Pengpeng Y., Jian W., Liwen M., Dafang H., Xin F., Xiaohua L.: Tribological behaviors of carbon series additions reinforced CF/PTFE composites at high speed, Applied Polymer Science 133, 2016, pp. 43236–43245.
10. Unal H., Sen U., Mimaroglu A.: Study of abrasive wear volume map for PTFE and PTFE composites, Appl Compos Mater 14, 2007, pp. 287–306.
11. Tabata Y., Suzuki H., Ikeda S.: Radiation modification of PTFE and its application, Radiation physics and chemistry 84, 2013, pp. 14–19.
12. Lappan U., Geibler U., Hauber L., Jehnichen D., Pompe G., Lunkwitz K.: Radiation-induced branching and crosslinking of polytetrafluoroethylene (PTFE), Nuclear Instruments and Methods in Physics Research B 185, 2001, pp. 178–183.

13. Oshima A., Tabata Y., Kudoh H., Seguchi T.: Radiation induced crosslinking of polytetrafluoroethylene, *Radiation Physics and Chemistry* 45, 1995, pp. 269–273.
14. Forsythe J.S., Hill D.J.T.: The radiation chemistry of fluoropolymers, *Progress in polymer science* 25, 2000, pp. 101–136.
15. Barylski A., Maszybrocka J., Kupka M., Aniołek K., Kaptacz S.: Radiation-chemical modification of PTFE in the presence of graphite, *Journal of Applied Polymer Science* 132, 2015, pp. 42348–42355.
16. Lunkwitz K., Lappan U., Scheler U.: Modification of perfluorinated polymers by high energy radiation, *Journal of Fluorine Chemistry* 125, 2004, pp. 863–873.
17. Lunkwitz K., Lappan U., Lehmann D.: Modification of fluoropolymers by means of electron beam irradiation, *Radiation Physics and Chemistry* 57, 2000, pp. 373–376.
18. Khatipov S.A., Serov S.A., Sadovskaya N.V., Konova E.M.: Morphology of polytetrafluoroethylene before and after irradiation, *Radiation Physics and Chemistry* 81, 2012, pp. 256–263.
19. Samborski T.M.: Method of identifying stereometric wear. The doctoral dissertation. Cracow University of Technology, Faculty of Mechanical Engineering, Kraków, 2002.
20. Jardret V., Zahouani H., Loubet J.L., Mathia T.G.: Understanding and quantification of elastic and plastic deformation during a scratch test *Wear* 218, 1998, pp. 8–14.
21. Hokkirigawa K., Kato K.: An experimental and theoretical investigation of ploughing, cutting and wedge formation during abrasive wear. *Tribology Int.* 21, 1988, pp. 51–57.
22. Czichos H., Becker S., Lexow J.: Multilaboratory tribotesting: results from the VAMAS program on wear test methods, *Wear* 114, 1987, pp. 109–130.
23. ASTM G99-17, Standard Test Method for Wear Testing with a Pin-on-disk Apparatus, ASTM International, West Conshohocken, PA, 2017.
24. Barylski A., Kaptacz S., Aniołek K., Kupka M.: The effect of irradiation with an electron beam on mechanical, sclerometric and tribological properties of PTFE with a graphite additive. *Tribologia* 3, 2016, pp. 29–36.
25. Barylski A., Kaptacz S., Skoneczny W., Kupka M., Aniołek K.: Thermal, mechanical, and tribological properties of PTFE composite with 20% graphite content irradiated with an electron beam. *Tribologia* 4, 2017, pp. 17–20.