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THERMAL, MECHANICAL, AND TRIBOLOGICAL PROPERTIES OF PTFE COMPOSITE WITH 20% GRAPHITE CONTENT IRRADIATED WITH AN ELECTRON BEAM

WŁAŚCIWOŚCI TERMICZNE, MECHANICZNE I TRIBOLOGICZNE KOMPOZYTU PTFE Z 20% ZAWARTOŚCIĄ GRAFITU NAPROMIENIOWANEGO STRUMIENIEM ELEKTRONÓW

Key words: PTFE, radiation modification; thermal properties; wear.

Abstract The paper investigated the effect of irradiation with an electron beam of energy 10 MeV in doses of 26–156 kGy on polytetrafluoroethylene with a 20% graphite additive. The tests have shown that changes in thermal properties of the composite (heat of crystallization, melting point, and degree of crystallinity) directly affected mechanical properties and contributed to the significant improvement of tribological properties. Tribological tests were performed on a pin-on-disc (T-01) test stand and counter-specimens were made of 1H18N9T steel. The load applied in the friction pair was 1 and 2 MPa (20 and 40 N). A nearly fourfold reduction in linear wear compared to the initial state for a load of 1 MPa has been shown. On the other hand, a more than 20-fold decrease in wear was found during tribological tests when the load was increased to 2 MPa. The most advantageous results were obtained for specimens irradiated with a dose of 104 kGy, and irradiation with a higher dose led to the degradation of the polymer and caused its wear to increase again. The obtained results hold promise for a significant improvement of the operational life of friction couples that do not require lubrication used, for example, in air compressors and engines, and for the possible application of thus modified polymers in nuclear and space industries.

Słowa kluczowe: PTFE, modyfikacja radiacyjna, właściwości termiczne, zużycie.

Streszczenie W artykule zbadano wpływ napromieniowania strumieniem elektronów o energii 10 MeV i dawkach 26–156 kGy na politetrafluoroetylen z 20% dodatkiem grafitu. Badania wykazały, że zmiany właściwości termicznych kompozytu (ciepło krystalizacji, temperatura topnienia, stopień krystaliczności) miały bezpośredni wpływ na właściwości mechaniczne oraz znaczną poprawę właściwości tribologicznych. Badania tribologiczne przeprowadzono na stanowisku trzpień-tarcza (T-01) przeciwpróbki wykonano ze stali 1H18N9T. Nacisk w węźle tarcia wynosił 1 i 2 MPa (20 i 40 N). Wykazano blisko 4-krotne ograniczenie zużycia liniowego w porównaniu do stanu wyjściowego dla nacisku 1 MPa. Przy zwiększeniu nacisku do 2 MPa podczas badań tribologicznych stwierdzono natomiast ponad 20-krotne zmniejszenie zużycia. Najkorzystniejsze wyniki uzyskano dla próbek napromieniowanych dawką 104 kGy; napromieniowanie większą dawką prowadziło do degradacji polimeru i ponownego wzrostu zużycia. Otrzymane wyniki rokują na znaczną poprawę trwałości eksploatacyjnej węzłów tarcia niewymagających smarowania stosowanych np. w sprężarkach powietrza, silnikach, a także możliwość zastosowania tak zmodyfikowanych polimerów w przemyśle jądrowym oraz kosmicznym.

INTRODUCTION AND RESEARCH METHODOLOGY

Discovered in 1938 by Roy Plunkett, polytetrafluoroethylene (PTFE) is a thermoplastic widely used mainly in the chemical and electronic industries and in household articles. The popularity of this polymer is mainly the result of its unique properties, such as chemical inertness, high electrical resistance, low dielectric constant, high melting point, and low friction coefficient during dry friction **[L. 1]**.

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The unique properties of this plastic result from its structure. PTFE is subject to linear polymerization with very high molecular mass Mn, in the range from 106 **[L. 2]** to 108 **[L. 3]**. Because polytetrafluoroethylene is not soluble in the majority of known solvents, the heat of crystallisation measured using differential scanning calorimetry is usually used to determine the molecular weight **[L. 3]**. The linear and smooth structure of PFFE particles is conducive to the formation of crystalline areas **[L. 4, 5]**. Depending on the polymerization process, the degree of the crystallinity of PFTE ranges from 40% **[L. 1]** to 70% **[L. 5]**, which directly affects mechanical and tribological properties. An alternative way to improve polymer properties is the use of electron beam and gamma ray beam irradiation **[L. 6–8]**. Research conducted so far focuses on PFTE without filler additives, and the majority of results concern gamma radiation due to the unavailability of electron radiation sources in the order of MeV necessary to penetrate PFTE to a depth of several centimetres, which enables changes in the structure of the polymer **[L. 9]**. This paper investigated the influence of irradiation with an electron beam of energy of 10 MeV on thermal, mechanical, and tribological properties of PTFE with 20% graphite content.

Commercially available polytetrafluoroethylene with 20% graphite content (SM-G20, Inbras, Poland), in the form of rods with a diameter of 20 mm, from which 20-mm high cylindrical samples were cut out, was used in the tests. The modification through radiation 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. In order to eliminate free radicals, the irradiated samples were stabilized through oxidation by means of thermal processing in a vacuum: heating to a temperature of 200°C for 4 hours, soaking for 2 hours, and cooling down to ambient temperature for 10 hours. Next, all the samples were vacuum wrapped.

Thermal properties of PTFE with 20% graphite content were tested using differential scanning calorimetry (DSC) by means of a Mettler-Toledo DSC-1 device. Samples for DSC tests that weighed approximately 15 mg and were selected from the central part of the cylinders were closed in standard aluminium cells. The heating rate was 10°C/min and the temperature ranged from -40°C to 400°C. Liquid nitrogen flowed through the chamber at a rate of 2 ml/min. Next, thermograms were analysed and the degree of the crystallinity of the composite was calculated **[L. 10]** based on the following dependence (1):

$$\chi_C = \frac{\Delta H_m}{\Delta H_c} \cdot 100 \quad [\%], \tag{1}$$

where ΔH_m – the heat of phase transition (melting) of the investigated polymer sample, determined from a DSC thermogram [J/g]; ΔH_c – the heat of completely crystalline polytetrafluoroethylene phase transition (empirically determined value = 82 J/g).

The hardness of PTFE composite with graphite in its initial state and after electron-beam irradiation was determined using a Vickers microhardness tester from Wolpert Wilson Instruments, model 401MVD. The load on the indenter during the test was 2.94 N (300gf), and the time of its work under full load was 10 seconds.

Tribological tests of polytetrafluoroethylene with 20% graphite content were performed using a pin-on-disc friction couple on a T-01 device (manufactured by ITeE Radom, Poland). In each case, 3 samples were prepared (pins, 5 mm in diameter). Discs made of 1H18N9T steel were used as counter-specimens. The surface roughness of the disks was R_a = 0.2 μm, which enabled the formation of a thin PTFE film that reduced the friction coefficient and wear. The tests were carried out with the following contact parameters: dry friction, pin diameter: 5 mm; friction distance diameter: 24 mm, sliding speed: 0.1 m/s; load: 20 and 40 N (stress 1 and 2 MPa); friction distance: 1000 m. Ambient parameters: temperature – 21±1°C, and humidity – 50±5%, were in compliance with the recommendations of VAMAS and standard ASTM G-99 **[L. 11, 12]**. The linear wear W_L was determined as a difference between the indications of the micrometric sensor before and after the test (and after the cooling stage). The friction coefficient was determined as a quotient of the recorded friction force, F_t and the normal force applied F_n.

RESEARCH RESULTS AND ANALYSIS

At first, the impact of electron-beam irradiation on thermal properties of PTFE with 20% graphite content was investigated by means of differential scanning calorimetry (DSC). Electron-beam irradiation caused a gradual increase in the temperature of the melting peak maximum of the polymer, T_m (**Fig. 1**).

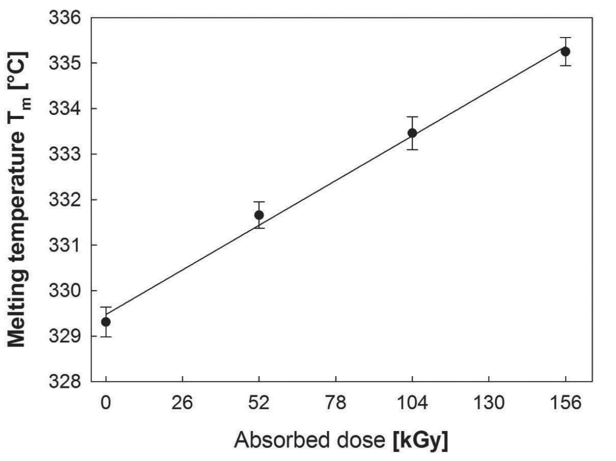

Fig. 1. Changes in melting point T_m of polytetrafluoroethylene with 20% graphite content as a function of the absorbed dose of the electron beam

Rys. 1. Zmiany temperatury topnienia T_m politetrafluoroetylenu z 20% zawartością grafitu w funkcji pochłoniętej dawki strumienia elektronów

The linear increase in melting point T_m directly contributed to the increase in melting heat ΔH_m, and consequently the degree of crystallinity χc determined based on it (**Fig. 2**).

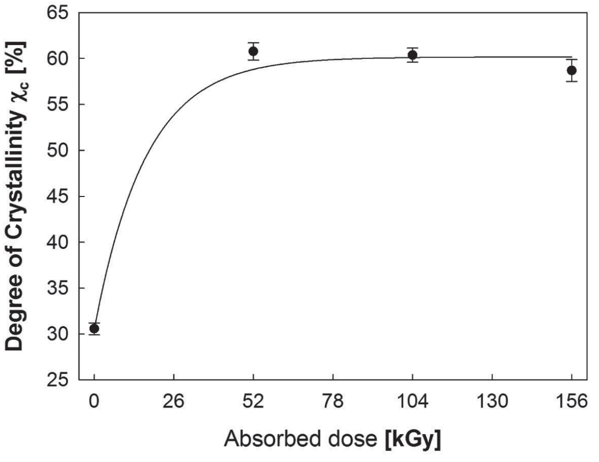

Fig. 2. Changes in the degree of crystallinity χc of polytetrafluoroethylene with 20% graphite content as a function of the absorbed dose of the electron beam
Rys. 2. Zmiany stopnia krystaliczności χc politetrafluoroetylenu z 20% zawartością grafitu w funkcji pochłoniętej dawki strumienia elektronów

When analysing changes in the degree of crystallinity as a function of the increasing irradiation dose, one can notice a large increase in the crystallinity degree, i.e. from 30.57% for the initial samples to more than 60% for samples irradiated with a dose of 104 kGy. A large increase in the degree of crystallinity was caused by the process of the destruction of polymer chains, which progressed as the irradiation dose increased. Due to their better mobility, smaller polymer chains facilitate the process of orientation of crystalline areas. The authors of papers **[L. 13, 14]** reached similar conclusions, but their research was conducted only on pure PTFE and the electron beam energy was 1.7 MeV, which is not sufficient to penetrate the material and only causes structural changes on its surface.

A change in the polymer structure, and, in particular, a large increase in the degree of crystalline, was very important from the point of view of functional properties, because it caused an improvement in mechanical and tribological properties of the examined composite. The course of changes in microhardness μHV is shown in **Figure 3**. According to this data, irradiating PTFE with 20% graphite content with an electron beam causes a significant increase in hardness as the absorbed electron beam increases.

Microhardness changes show a linear dependence (2) with a correlation ratio R = 0.91:

$$\mu HV = 0.004d + 5.49 \qquad (2)$$

where d is the absorbed electron beam dose [kGy].

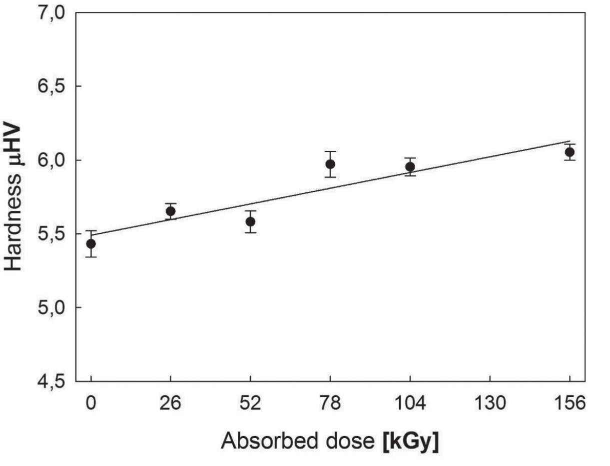

Fig. 3. Changes of microhardness μHV as a function of the absorbed dose of the electron beam
Rys. 3. Zmiany mikrotwardości μHV w funkcji pochłoniętej dawki strumienia elektronów

An increase in the irradiation dose absorbed by PTFE also directly affects the tribological properties of the examined composite. **Figure 4** shows changes in linear wear W_L as a function of the absorbed electron-beam irradiation dose. The linear wear for PTFE with 20% graphite content in its initial state was 416.25 for a load of 40 N and 85.85 μm for a load of 20 N. Electron-beam irradiation caused a gradual reduction in linear wear. The most advantageous results were obtained for the absorbed dose of 104 kGy. Wear reduction was nearly fourfold (to 22.88 μm) for a load of 20 N. On the other hand, tribological tests with load increased to 40 N showed a more than 13-fold decrease in tribological wear (to 20.25 μm). Irradiation with a larger dose caused the material to degrade (significant increase in brittleness) and the linear wear to increase again. This effect was particularly noticeable for greater loads, where an increase in wear to a level of 171.25 μm was recorded. The average value of friction coefficient μ at a load of 20 N was 0.169±0.02, and at a load of 40 N it was 0.197±0.01.

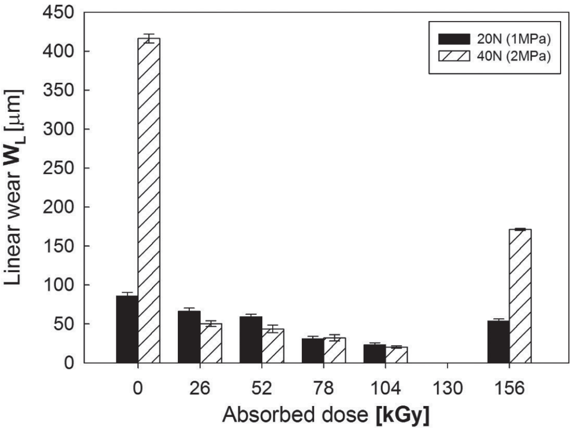

Fig. 4. Linear wear of PTFE with 20% graphite content as a function of the absorbed dose of the electron beam
Rys. 4. Zużycie liniowe PTFE z 20% zawartością grafitu w funkcji pochłoniętej dawki strumienia elektronów

CONCLUSIONS

- Irradiating polytetrafluoroethylene with 20% graphite content caused an increase in the temperature of the melting peak maximum of the polymer, Tm, increase in polymer melting point ΔHm, and consequently a twofold increase in the degree of crystallinity χc, from 30 to 60%.
- The change in the polymer's structure caused by the absorbed electron beam dose caused a linear increase in microhardness μHV, proportional to the increase in the absorbed irradiation dose.
- Tribological tests showed a nearly fourfold reduction in linear wear at a load of 20 N and more than a 20-fold decrease in wear at a load of 40 N. The most advantageous results have been obtained for an absorbed dose equal to 104 kGy. Increasing the radiation dose above that value caused a degradation of the material and an increase in wear.
- The significant improvement of thermal, mechanical, and especially tribological properties holds promise for a longer service life of elements made of PTFE irradiated with an electron beam.

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