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MECHANICAL AND TRIBOLOGICAL ANALYSIS OF MONOLITH AND COATING POLYETHERETHERKETONE

ANALIZA WŁAŚCIWOŚCI MECHANICZNYCH I TRIBOLOGICZNYCH POLIETEROETEROKETONU W POSTACI MONOLITYCZNEJ I POWŁOKI

Key words: PEEK, hardness, coefficient of friction, wear rate, Micro Mar Resistance.

Abstract: In this work, a comparative analysis of the micromechanical and tribological properties of polyetheretherketone (PEEK) in bulk and coating form was performed. The PEEK 708 coating was applied on a Ti6Al4V titanium alloy flat specimen using the electrophoretic deposition method. The micromechanical properties were determined through indentation tests performed using the Vickers method and scratch tests. Based on research work, the Vickers hardness (HV), elastic modulus (E), scratch hardness (HS), and Micro Mar Resistance (MMR) were determined. The tribological properties were defined by the coefficient of friction (f_s and f_w), which was obtained in scratch tests and ball-on-disk tests. The results of this research indicate, despite the slightly higher Vickers hardness (HV) of the PEEK 708 coating (HV = 350 MPa, HS = 300 MPa) relative to PEEK bulk (HV = 300 MPa, HS = 210 MPa), that there is an almost 40% difference between the scratch hardness (HS) values of these PEEK forms. It appears from the result analysis in this paper that testing methods to determine the micromechanical and tribological properties of PEEK in monolith form can be used for both PEEK coatings. Under certain test conditions, the impact of the substrate properties on the results of the PEEK 708 coating was not found.

Słowa kluczowe: PEEK, twardość, współczynnik tarcia, wskaźnik zużycia objętościowego, odporność na mikrouszkodzenia.

Streszczenie: W pracy dokonano analizy porównawczej właściwości mikromechanicznych oraz tribologicznych polieteroeteroketonu (PEEK) w postaci monolitycznej i powłoki. Powłoka PEEK 708 została osadzona metodą elektroforezy na płaskim podłożu ze stopu tytanu. Właściwości mikromechaniczne zostały zbadane metodą indentacyjną przy użyciu wgłębnika Vickersa oraz w teście zarysowania. Na podstawie badań wyznaczono twardość Vickersa (HV), moduł sprężystości (E), twardość zarysowania (HS) oraz odporność na mikrouszkodzenia (MMR). Właściwości tribologiczne zdefiniowano poprzez współczynnik tarcia (f_s i f_w), który wyznaczono zarówno w teście zarysowania oraz podczas tarcia w układzie typu kula–tarcza. Wyniki badań wskazują, że pomimo niedużo większej twardości Vickers'a (HV) powłoki PEEK 708 (HV = 350 MPa, HS = 300 MPa) względem monolitycznego PEEK (HV = 300 MPa, HS = 210 MPa), występuje niemal 40% różnica w ich twardościach zarysowania (HS). Z przeprowadzonej analizy wynika, że metody wyznaczania parametrów mikromechanicznych oraz tribologicznych stosowane dla materiałów monolitycznych PEEK sprawdzają się w badaniach powłok polimerowych PEEK. W określonych warunkach badań nie stwierdzono wpływu materiału podłoża na otrzymane wyniki dla powłoki PEEK 708.

INTRODUCTION

Polymers and polymer composites are a common group of materials widely used in industry. In machine construction, they often act as construction materials of the responsible elements, e.g., bearing nodes. The development of polymer production and moulding technology also enables their use as coatings. For

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instance, bearings are usually made as units of sliding polymer material but also in the form of multi-layer sleeves **[L. 1**, **2]**. Designing wear-resistant kinematic nodes involves the selection of materials whose properties are well characterized in a wide range of changes under external excitation. Due to differences in the behaviour of polymer coatings and bulk, correlation is sought between their physicochemical, mechanical, and/or tribological properties under mechanical, thermal, and environmental impact.

Among the many types of polymers used in machine construction, polyetheretherketone (PEEK) can be distinguished. The PEEK polymer was invented in 1979 and has become a widely used material in many sectors of industry **[L. 3]**. In the early 1980s, it was used, among others, in the construction of responsible elements – turbine blades for the aviation industry **[L. 4]**. Due to the properties of PEEK, it is used in many different areas, from jack sockets in smartphones, through bushes of rolling bearings, to attachments in dental implants **[L. 5–8]**.

Such great interest in PEEK is mainly due to the high mechanical properties and high temperature resistance compared to other polymers. The elastic modulus (E) of PEEK bulk, determined in tensile tests, reaches the value of 3.5–3.6 GPa, while the tensile strength (T_s) is 90–100 MPa **[L. 9–12]**. The basic mechanical parameters of construction material bulk, such as yield strength (R_e), ultimate limit strength (R_m) and elastic modulus (E), are usually determined in tensile tests. Nevertheless, the elastic modulus (E) can also be determined by the indentation method, which is the classic method for measuring hardness. The most common indentation test methods are Vickers, Rockwell, or Brinell. However, there are also other methods to determine the material resistance against the pressing of an indenter. For instance, polymer hardness can be determined in a scratch test using a Rockwell indenter, which is called scratch hardness (HS). According to the research of Sampaio et al. and Goyal et al., the Vickers hardness (HV) of PEEK bulk is the range of 30–40 HV (about 300–400 MPa), and, based on the analysis of Friedrich et al. the scratch hardness (HS) is approximately 420 MPa **[L. 9, 11, 13]**. It should be noted that the values of the obtained results are influenced by the test parameters and the type of device, as well as the performance and preparation of the used material. These factors are the boundary conditions of the test. The above values of Vickers hardness (HV) were determined for a normal load (F_n) of 1 N, while the scratch hardness (HS) at a progressive normal load (F_n) was in the range of 5–90 N. Furthermore, the mechanical properties of polymers as well as PEEK are strongly related to temperature. PEEK bulk has a melting point (T_m) in the range of 343–345°C, a glass transition temperature (T_g) in the range of 143–150°C, and an operating temperature (T_o) up to 200°C **[L. 12–16]**. Research performed by Briscoe et al. shows that, above the glass transition temperature (T_m> 143°C), there is a significant decrease in the mechanical properties of PEEK, including tensile strength and Young's modulus **[L. 14]**.

The PEEK polymer also has very good tribological behaviour and corrosion resistance **[L. 17]**. In laboratory conditions, the coefficient of sliding friction (f_w) of PEEK bulk is most often determined in flat contact as a *pin-on-disc* friction node and less often in point contact as a *ball-on-flat* friction node. One specific method to determine the coefficient of friction is a scratch test using a Rockwell indenter. In this method, the motion resistance is the result of the interaction in the concentrated sliding contact. In polymers, the value of the coefficient of scratch friction (f_s) is strongly dependent on the deformation of plastic polymer in contact with the indenter. According to the research of Lin et al. and Sumer et al., the coefficient of sliding friction (f_w) of PEEK bulk in dry flat contact is in the range of 0.35–0.43, and, in the presence of water, it is the range of 0.13–0.17 **[L. 18**, **19]**. However, according to the analysis of Friedrich et al. and Lin et.al, the limit values of the coefficient of scratch friction (f_s) are in the range of 0.24–0.46 **[L. 9**, **19]**. The values of the research results obtained by the above authors are affected by the boundary conditions of the tribological tests. The coefficient of sliding friction (f_w) in the mentioned tests were determined for normal loads (F_n) in the range of 16–150 N, while the coefficient of scratch friction (f_s) at a progressive normal load (F_n) was in the range of 0.3–60 mN and 5–90 N. The low values of coefficients of sliding and scratch friction make PEEK a great tribological pair compared to other polymers. In addition, PEEK is very resistant to most chemical solutions; therefore, it can be used in aggressive environments **[L. 17**, **20]**. Furthermore, PEEK is characterized by biocompatibility, as confirmed in clinical trials **[L. 10, 21]**.

Simultaneously, PEEK is increasingly used in coatings deposited on metallic substrates. This creates the need to perform research into the properties of formed coatings and to search for methods for their implementation **[L. 4, 11, 22]**. The popularity of PEEK coatings probably comes from the high price of PEEK itself, which is up to 8 times higher than the prices of other polymers. Moreover, the deposited PEEK coating provides corrosion protection and sliding properties while maintaining the high mechanical properties of the metallic substrate. A rich material database containing the properties of many polymers and polymer composites of component bulk can be an important source in obtaining technological or construction information in relation to components in coating form. This eliminates the need for special techniques to analyse polymer coatings, which are required due to the restrictions on their thickness. This is the reason for difficulties in the research of mechanical and tribological properties. Based on publications, PEEK coatings usually have a thickness of 10–100 μm and require adequate adhesion to the substrate **[L. 9, 11, 16, 22–27]**. All of these strongly limit the operability of available methods for researching the properties of such polymer coatings.

The finite thickness of the PEEK coating creates a geometrical barrier for the sample in tensile tests to determine elastic modulus (E) and tensile strength (T_s). A partial solution to this problem seems to be using the indentation method with different indenter geometries. This enables the elastic modulus (E) and, at the same time, the hardness of the coating to be determined, assuming that the penetration of the indenter does not exceed 10% of the coating thickness. Based on the research of several scientists, the Vickers hardness (HV) for the PEEK coating is in the range of 10–27.5 HV (about 100–275 MPa) **[L. 23–25, 27]**. The values of the obtained results differ due to the boundary conditions of tests and the method of deposition for PEEK coatings, which influences the degree of crystallinity and the uniformity of coatings, among others. The above Vickers hardness (HV) tests were performed at normal loads (F_n): 20 mN, 100 mN, 100 N. The hardness of thin coatings can also be determined in scratch tests (HS). In studies developed by Tharajak et al., the scratch hardness (HS) of the PEEK coating using a Rockwell indenter is 113 MPa **[L. 26]**. The test was performed at a progressive normal load (F_n) in the range of 50–250 N.

The popularity of increasingly thinner coatings being deposited also generates problems in tribological tests. Tribological research into coatings, including polymer coatings, is most often performed in sliding contact against a ball. Hence, methods were developed to determine the coefficient of sliding friction in point contact using balls, usually ceramic, but also on steel, as a *ball-on-flat* friction node. According to the researchers, the coefficient of sliding dry friction is in the range of 0.19–0.47, and this is reduced in wet contact. **[L. 16, 23, 25, 27, 28]**. For instance, in the presence of Ringer's solution, the coefficient of sliding wet friction in contact with an aluminium ball-PEEK coating is 0.13 **[L. 27]**.

In all the above research, the authors of publications used 6 mm diameter balls regardless of the material; therefore, the generators of the differences between the obtained results are the boundary conditions of the tests. The normal load (F_n) applied in the tests is in the range of 2–20 N. The scratch test, apart from testing the adhesion of polymer coatings, can also be used to analyse the deformation of the *coating-substrate* system and to determine the scratch hardness (HS), as well as to measure the friction force and, on this basis, to determine the coefficient of scratch friction (f_s). Moreover, geometrical analysis of the scratch trough can be used to determine the coating resistance to micro-damage (MMR – Micro Mar Resistance) **[L. 29, 30]**.

Due to the measurement limitations posed by the thickness of polymer coatings, including PEEK, it is reasonable to search for methods which are able to determine their micromechanical and tribological properties, other than those used for polymer bulk. Despite the rich material database for PEEK bulk, it is necessary to determine the properties of the *coating-substrate* system in terms of coating adhesion to the substrate and its deformation, which are due to the different forms of polymer. In addition to the classic methods for determining micro-mechanical and tribological parameters, using scratch tests seems to be the most favourable solution. Scratch tests make it possible to relatively quickly obtain the results of tests enabling the characterization of the mechanical and tribological properties of coatings and their comparison between other laboratories and existing material databases. Due to the above, in this publication, a comparative analysis of the elastic modulus (E), hardness (HS and HV), the coefficient of friction (f_s and f_w), and Micro Mar Resistance (MMR) of PEEK bulk and PEEK of grade 708 as coatings, deposited on a Ti6Al4V titanium alloy substrate, was performed.

MATERIALS AND SAMPLE PREPARATION

The research samples are polyetheretherketone (PEEK) of the following forms:

- Bulk in the shape of discs with a diameter of 16.5 mm and a height of 2.7 mm made of PEEK, and
- PEEK 708 coating deposited on a Ti6Al4V titanium alloy substrate in the shape of discs with a diameter of 22 mm and a height of 2.7 mm.

According to the specifications provided by the producer, the PEEK in monolith form is characterized by the following **[L. 16]**:

- An elastic modulus (E) of 4.2 GPa, which was determined in a tensile test in accordance with DIN EN ISO 527-2 norm at a crosshead speed of 1 mm / min; and,
- A Brinell hardness (HB) of 253 MPa, which was determined based on the ISO 2039-1 norm.

First, the surface of the monolithic sample was prepared by dry sanding using sandpaper with a grain size of P500 and P1000. Subsequently, it was water polished using sandpaper with a grain size of P2000. Due to the preparation of the sample, the surface roughness determined by the Ra parameter of 127 ±13 nm was obtained.

A 100 μm thick PEEK 708 coating was deposited by an electrophoretic process (EPD). In the electrophoretic deposition process, the colloidal suspension consists of the following:

- PEEK polymer particles, grade 708, with a grain size of 10 μm, which, according to the company's catalogue is characterized by the following **[L. 31]**:
  - Elastic modulus (E) of 4.3 GPa,
  - Shore D hardness of 85D.
  - Ethanol, and
  - Surfactants.

The sample and electrode immersed in the colloidal suspension were spaced 10 mm apart. Deposition of the polymer coating was performed at 70 V for 20 s. After the electrophoretic deposition process, the coating was annealed at 380°C for 20 min and then cooled down at a rate of 2°C/min. Due to the electrophoretic deposition process, a PEEK 708 coating was obtained with its surface roughness determined by the Ra parameter of 52 ±3 nm. The Ti6Al4V titanium alloy substrate is characterized by a elastic modulus (E) of 142 ±11 GPa and a Vickers hardness (HV) of 347 ±14 MPa.

The geometrical parameters of the samples surface structure were measured with a Filmetrics PROFILM 3D optical profilometer (USA).

METHODS

Research into the micromechanical properties and scratch resistance of both PEEK samples was performed at room temperature (approx. 21°C) using a Micro-Combi Tester (MCT) of CSM Instruments (Switzerland).

Indentation test

The Vickers hardness (HV) tests were performed in accordance with the ISO 14577-4: 2016 norm at normal loads (F_n): 50, 100, and 200 [mN] (**Fig. 1**) **[L. 32]**. Normal loads (F_n) increased linearly until reaching the maximum value after 30 s, and the time of maintaining the maximum value was 15 s. Based on the test, the location of the indenter was determined depending on the normal load (Fn) (**Fig. 2**). Analysis of load/unload deformation curves obtained in the indentation tests enables the elastic modulus (E) and Vickers hardness (HV) to be determined, which was the subject of previous mathematical models (eq. 1, 5) **[L. 33–37]**. The basis for determining the above parameters (E and HV) are dependencies describing the following: reduced elastic modulus (E_r), projected contact area (A_p) and contact depth (d_c) of the indenter to the surface of the sample (eq. 2–4). The calculated parameters (E and HV) are the arithmetic mean of the values in a series of tests performed for each of the normal loads (F_n) assumed in the indentation test.

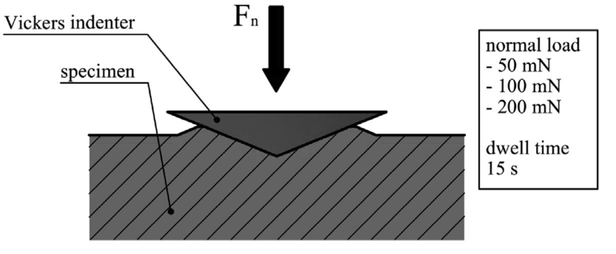

Fig. 1. Vickers hardness test
Rys. 1. Test twardości Vickersa

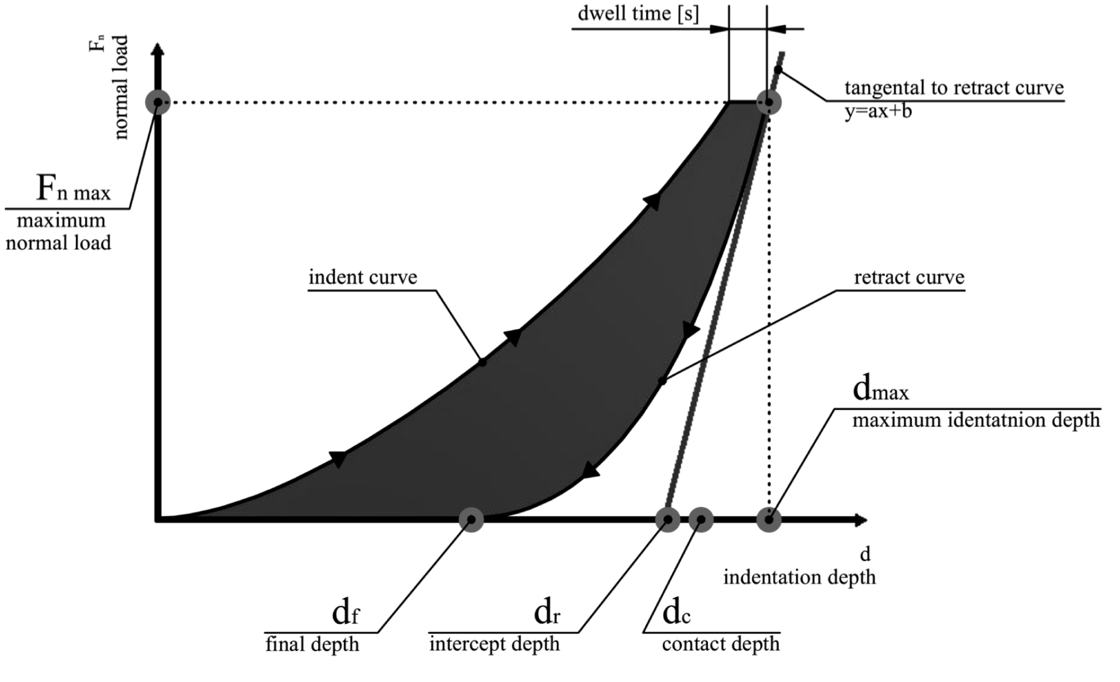

Fig. 2. A typically load/unload curve generated by Micro-Combi Tester (MCT)
Rys. 2. Typowa krzywa dociążania/odciążania wygenerowana przez Micro-Combi Tester (MCT)

$$E = \left(1-\upsilon^2\right)\cdot\left[\frac{1}{E_r}-\frac{1-(\upsilon_i)^2}{E_i}\right]^{-1} \tag{1}$$

$$E_r = \frac{2}{\pi}\cdot\frac{a}{\sqrt{A_p}} \tag{2}$$

$$A_p = 4\cdot(d_c)^2\cdot\left[tan\left(\frac{\alpha}{2}\right)\right]^2 \tag{3}$$

$$d_c = d_{max} - \epsilon\cdot\frac{F_{nmax}}{a} \tag{4}$$

from (1), (2), (3), (4)

$$E = \left(1-\upsilon^2\right)\cdot\left[\frac{4\cdot(10)^6}{\sqrt{\pi}}\cdot\frac{1}{a}\cdot\left(d_{max}-\epsilon\cdot\frac{F_{nmax}}{a}\right)\cdot tan\left(\frac{\alpha}{2}\right)-\frac{1-(\upsilon_i)^2}{E_i}\right]^{-1} \quad [\text{GPa}]$$

$$HV = \frac{F_{nmax}}{A_p} \tag{5}$$

from (3), (4, (5)

$$HV = \frac{1}{4\cdot(10)^9}\cdot\frac{F_{nmax}}{\left(d_{max}-\epsilon\cdot\frac{F_{nmax}}{a}\right)^2\cdot\left[tan\left(\frac{\alpha}{2}\right)\right]^2} \quad [\text{MPa}]$$

F_{nmax} – maximum normal load [mN]
d_{max} – maximum indentation depth [nm]
ϵ – constant of indenter geometry (for Vickers tip = 0.75) **[L. 32]**
a – gradient of the tangent [mN/nm]
α – angle of the indenter tip (for Vickers tip = 136°)
υ – Poisson's ratio of the specimen (for PEEK = 0.413÷0.427) **[L. 7]**
υ_i – Poisson's ratio of the indenter tip (for diamond tip = 0.07) **[L. 36]**
E_i – Elastic modulus of the indenter tip (for diamond tip = 1140 GPa) **[L. 36]**

Scratch test

The scratch tests were performed in accordance with the ASTM D7027-13 norm at a progressive normal load (F_n) in the range of 0–30 mN, with the velocity of the Rockwell indenter of 4.75 mm/min and a scratch length of 5 mm (**Fig. 3**) **[L. 38]**.

Based on the scratch, a 3D model of the scratch (troughs) was created using a Filmetrics PROFILM 3D profilometer (USA). A 3D model of the scratch was divided into 6 cross-sections at equal distances along its length (**Fig. 4**). These cross-sections correspond to the normal load (F_n) obtained in these places which belong to the set i ϵ {5, 10, 15, 20, 25, 30} N. The geometric parameters of the trough were determined for each cross-section of the scratch using Gwyddion software: depth (d), width (w) (**Fig. 6**). On this basis, the trough cross-sectional areas (A_s) were calculated as the sum of the trapezoid areas with the following definitions (6):

- Height is the absolute value of the difference between two consecutive horizontal coordinates belonging to the trough width ($|w_k-w_{k+1}|$), and
- Bases are the corresponding vertical coordinates belonging to the trough depth ($|d_k|$ and $|d_{k+1}|$).

Consequently, equations were developed which describe: mean value of the scratch hardness (HS), Micro Mar Resistance (MMR) and the coefficient of scratch friction (f_s) (eq. 7-9).

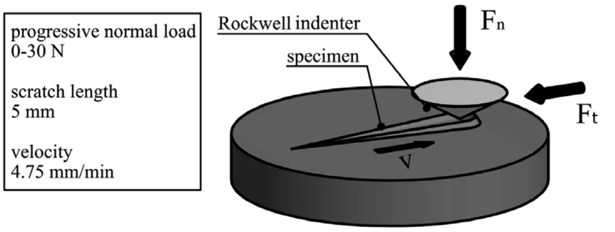

Fig. 3. Scratch test
Rys. 3. Test zarysowania

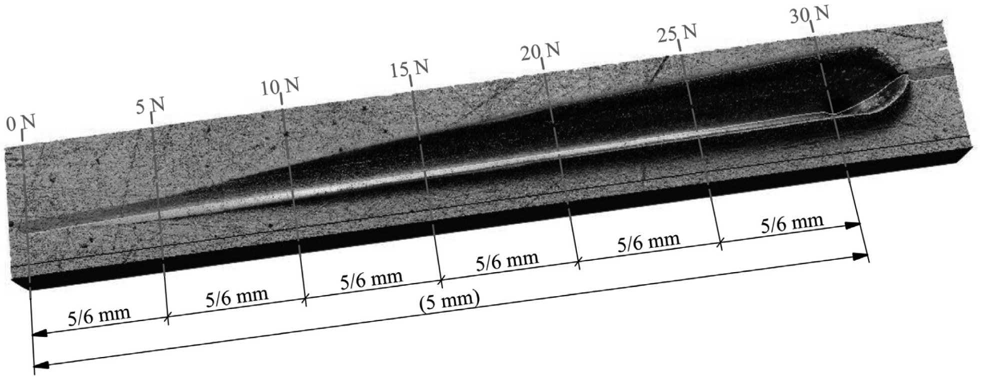

Fig. 4. Scratch's 3D model
Rys. 4. Model 3D zarysowania

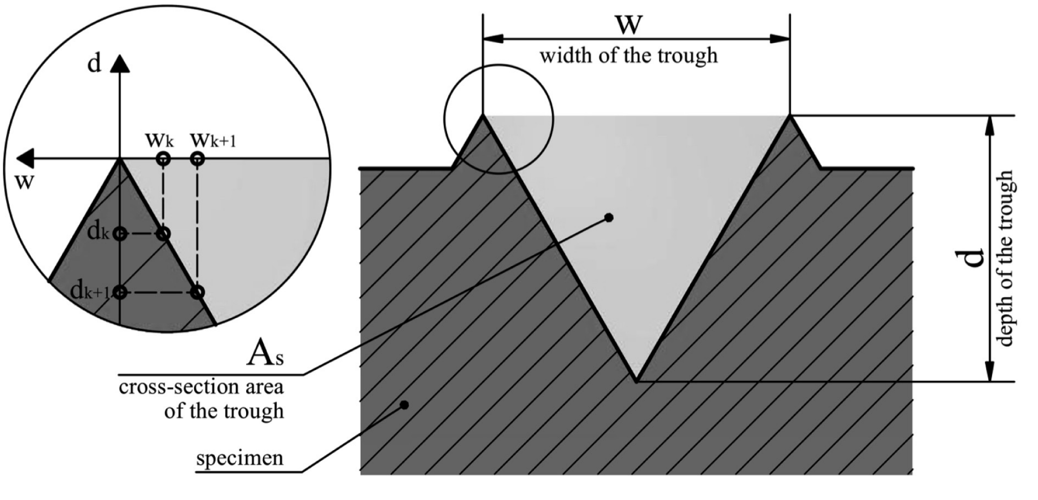

Fig. 5. Cross-section of the scratch
Rys. 5. Przekrój poprzeczny zarysowania

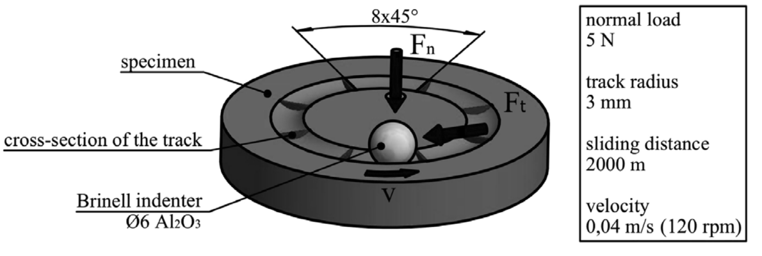

Fig. 6. Scheme of a ball-on-disc friction pair
Rys. 6. Schemat pary tarciowej typu kula–tarcza

$$A_s^i = \sum_{k=0}\left[\frac{1}{2}\cdot\left(\left|d_k^i\right|+\left|d_{k+1}^i\right|\right)\cdot\left|w_k^i - w_{k+1}^i\right|\right] \tag{6}$$

$$H_s = \frac{1}{card(i)}\cdot\sum_{i=1}^{6}\left(\frac{4}{\pi}\cdot\frac{F_n^i}{(w^i)^2}\right) \quad [\text{MPa}] \tag{7}$$

$$MMR^i = \frac{F_n^i}{A_s^i} \tag{8}$$

$$f_s^i = \frac{F_t^i}{F_n^i} \tag{9}$$

from (6), (8)

$$MMR^i = \frac{1}{(10)^3}\cdot\frac{F_n^i}{\sum_{k=0}\left[\frac{1}{2}\cdot\left(\left|d_k^i\right|+\left|d_{k+1}^i\right|\right)\cdot\left|w_k^i - w_{k+1}^i\right|\right]} \quad [\text{MPa}]$$

F_n^i – normal load achieve din the *i*-th cross section area of the scratch [N]
F_t^i – tangential load achieve din the *i*-th cross section area of the scratch [N]
w^i – width of the trough observed in the *i*-th cross section area of the scratch [mm]
d_k^i / d_{k+1}^i – *k*-th vertical coordinate in the *i*-th cross section area of the scratch [μm]
w_k^i / w_{k+1}^i – *k*-th horizontal coordinate in the *i*-th cross section area of the scratch [mm]

Tribological test

The tribological tests were performed in accordance with the ASTM G 138-05 and ISO 20808:2004 norms at a constant normal load (F_n) of 5 N in a non-lubricated contact point against an Al_2O_3 ball with a diameter of 6 mm on a track radius (r) of 3 mm and velocity of about 0.04 mm/s (120 rpm) (**Fig. 6**) **[L. 39**, **40]**. The sliding distance (s) of the test was 2000 m. The profile of the track formed after the test was measured by the contact method at 8 cross-sections in steps of 45¡. On this basis, the trough cross-sectional area (A_t) was determined in the *n*-th track cross-sections, where n ϵ {1, 2, 3, 4, 5, 6, 7, 8}, analogously to the equation of the trough cross-sectional area (A_s) in the scratch test (eq. 10, **Fig. 6**). In addition, according to the test parameters, the wear rate (K) was calculated as the mean value of 8 track cross-sections (eq. 11).

The coefficient of sliding dry friction (f_w) was determined at all track (s) lengths with a sampling time of 1 s (eq. 12).

$$A_t^n = \sum_{k=0}\left[\frac{1}{2}\cdot\left(\left|d_k^n\right|+\left|d_{k+1}^n\right|\right)\cdot\left|w_k^n - w_{k+1}^n\right|\right] \tag{10}$$

$$K^n = 2\pi\cdot\frac{A_t^n\cdot r}{F_n^n\cdot S} \tag{11}$$

F_n^n – normal load achieve din the *n*-th cross section area of the scratch [N]
F_t^n – tangential load achieve din the *n*-th cross section area of the scratch [N]
d_k^n / d_{k+1}^n – *k*-th vertical coordinate in the *n*-th cross section area of the scratch [μm]

w_k^n / w_{k+1}^n – k-th horizontal coordinate in the n-th cross section area of the scratch [mm]
r – radius of the track 3 mm
S – sliding distance 2000 m

$$f_w = \frac{F_t}{F_n} \tag{12}$$

F_n – normal load set in test (F_n = 5 N)
F_t – tangential load achieve din every 1 sec. of test [N]

RESULTS

Measurements in the indentation test performed using the Vickers method enabled curves of indenter depth (d) to be determined as a function of normal load (F_n). Based on the above data measurements, Vickers hardness (HV) and elastic modulus (E) were determined for each of the samples. The maximum penetration of the indenter (d_{max}) for PEEK bulk was approx. 6.4 µm, and for the PEEK 708 coating it was approx. 5.4 µm.

The analysis of cross-sections in the scratch test (A_s) enables the width (w) and depth (d) of the trough to be determined in the *i*-th cross-section of the scratch. Based on the measured geometrical parameters of the trough, the mean value of scratch hardness (HS) and Micro Mar Resistance (MMR) were calculated in the *i*-th cross-sections for each of the samples. The coefficient of scratch friction (f_s) was calculated for the assumed normal loads (F_n) and the corresponding measured tangential loads (F_t). The trough depth (d) at the maximum normal force (F_n=30 N) for PEEK bulk was approx. 33 µm, and for the PEEK 708 coating, it was approx. 50 µm.

Based on the tribological tests, the width (w) and depth (d) of the trough were measured in the *n*-th cross-section of the track. Due to the determined geometric parameters of the troughs, the mean value of the wear rate (K) was calculated for each of the samples. The mean value of the sliding friction coefficient (f_w) in non-lubricated contact against an Al_2O_3 ball was calculated for the assumed normal force (F_n) test and the tangential force measured in every 1 sec of the test (F_t). The maximum trough depth (d) for PEEK bulk was approx. 13 µm, and, for the PEEK 708 coating, it was approx. 7 µm.

Vickers and scratch hardness

The Vickers hardness (HV) values at the loads (F_n) of 50, 100, and 200 [mN] and scratch hardness (HS) at a progressive normal load (F_n) in the range of 0-30 N for PEEK bulk and the PEEK 708 coating are shown in **Fig. 7**.

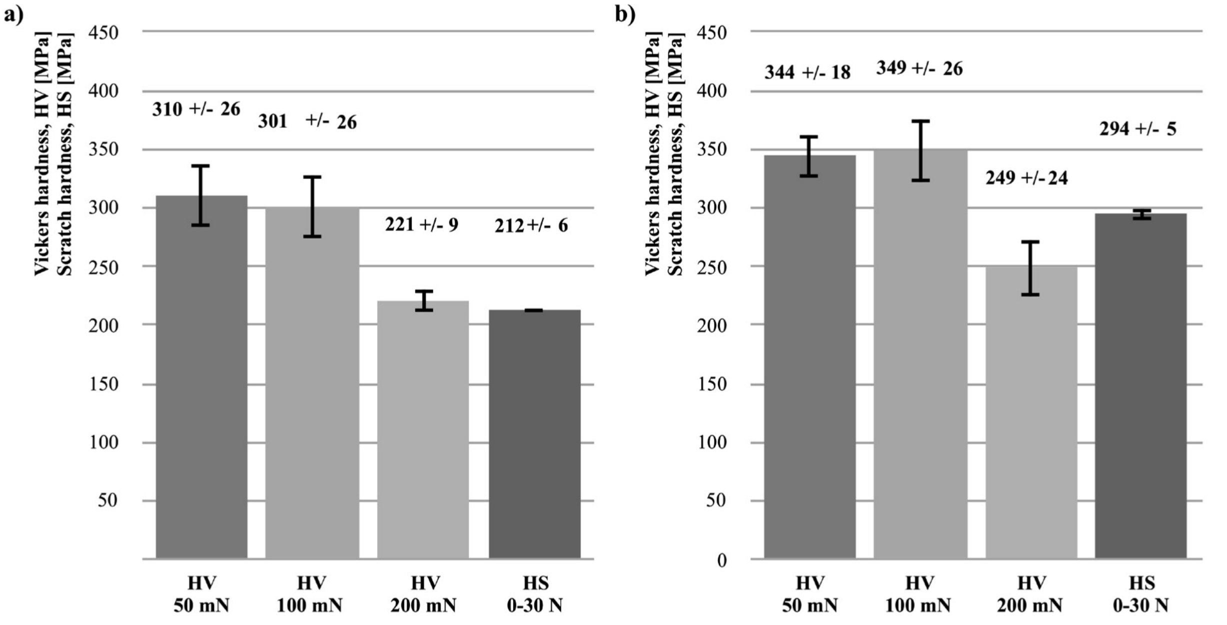

Fig. 7. Results of Vickers and scratch hardness: a) PEEK bulk, b) PEEK 708 coating
Rys. 7. Wyniki badań twardości Vickers'a i zarysowania: a) PEEK w postaci monolitycznej, b) powłoki PEEK 708

In both PEEK bulk and the PEEK 708 coating, Vickers hardness (HV) is similar under normal loads (F_n) of 50 and 100 [mN]. For the PEEK 708 coating, the above values are approx. 50 MPa higher. Under the normal load (F_n) of 200 mN, there is a decrease in Vickers hardness (HV), which is characteristic for both forms of PEEK, but the value for the coating is approx. 30 MPa higher than for the bulk. Nevertheless, the determined value indicates the non-influence of the substrate material on the obtained Vickers hardness (HV) results of the PEEK 708 coating.

The scratch hardness (HS) of the PEEK 708 coating is relatively higher than PEEK bulk despite a decrease in Vickers hardness (HV) with an increase in normal load (F_n). The scratch hardness (HS) difference between the above PEEK forms is over 80 MPa.

Elastic modulus

Elastic modulus (E) values at the loads (F_n) of 50, 100, and 200 [mN] for PEEK bulk and the PEEK 708 coating are shown in **Fig. 8**.

Result analysis of the elastic modulus (E) for the PEEK 708 coating and PEEK bulk indicates slight differences in the determined values. Regardless of the PEEK form, the above values are in a narrow range of 5 to 5.7 GPa. Therefore, the obtained results of elastic modulus (E) indicate the non-influence of the substrate material on the PEEK 708 coating in the indentation test.

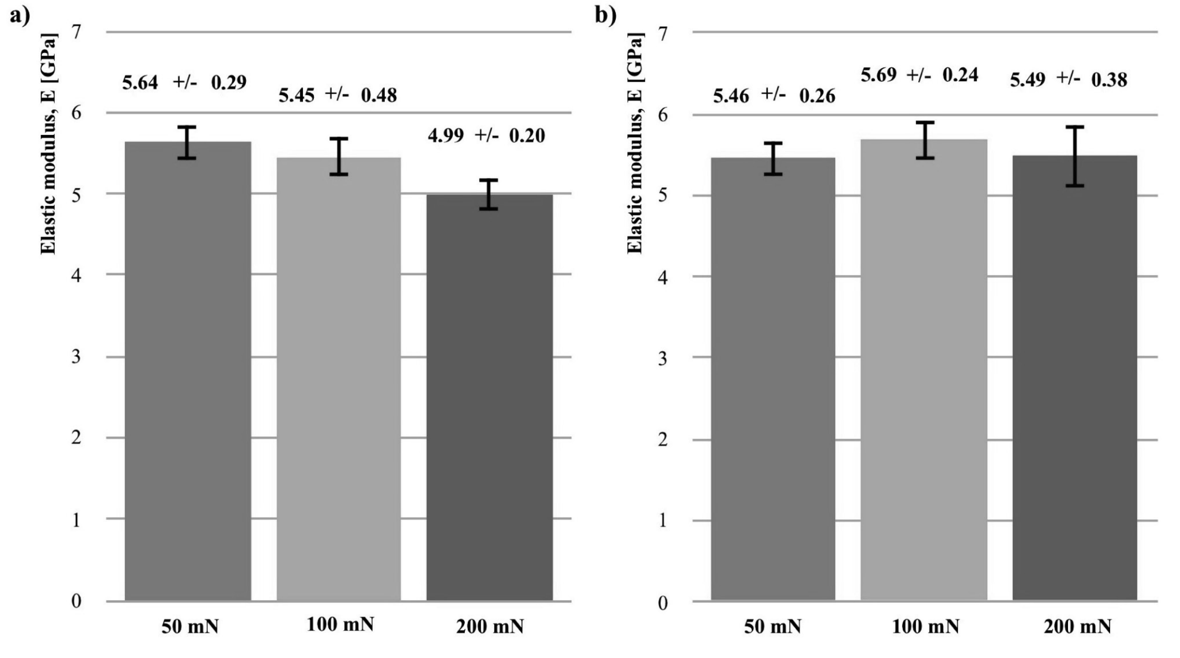

Fig. 8. Results of elastic modulus: a) PEEK bulk, b) PEEK 708 coating

Rys. 8. Wyniki badań modułu sprężystości: a) PEEK w postaci monolitycznej, b) powłoki PEEK 708

Micro Mar Resistance

Micro Mar Resistance (MMR) values at a progressive normal load (F_n) in the range of 0-30 N for PEEK bulk and the PEEK 708 coating are shown in **Fig. 9**.

Micro Mar Resistance (MMR) is a parameter which describes the scratch resistance of soft coatings in the case of slight surface damage **[L. 29**, **30]**. It is used to evaluate the potential usage of such coatings in industrial applications.

Micro Mar Resistance (MMR) for PEEK bulk is characterized by a gradual but small decrease in the value with an increase in normal load (F_n). In the case of the PEEK 708 coating, the change in the value of the above parameter is more abrupt. For a normal force (F_n) less than 10 N, the Micro Mar Resistance (MMR) of the PEEK 708 coating is greater than for PEEK bulk. However, for normal loads (F_n) more than 20 N, the above trend is reversed, which continues as the normal load (F_n) increases.

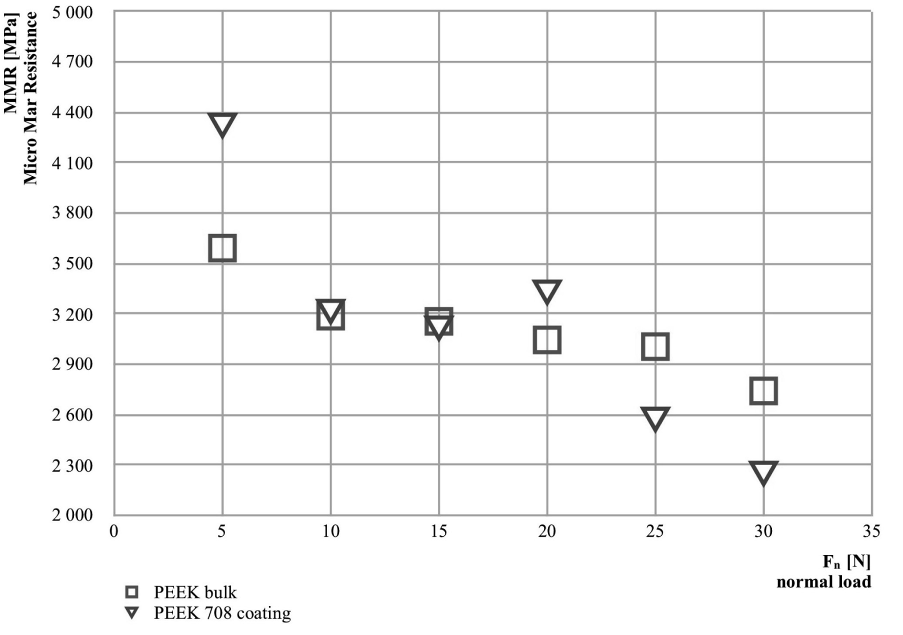

Fig. 9. Results of Micro Mar Resistance (MMR)
Rys. 9. Wyniki badań odporności na mikrouszkodzenia (MMR)

Coefficient of sliding and scratch friction

Tribological tests show that the PEEK 708 coating has good adhesion to the substrate and is distinguished by milder wear and less deformation of the worn surface relative to PEEK bulk (**Fig. 10**). The worn PEEK 708 surface is also smoother than the worn surface of PEEK bulk.

The coefficient of sliding dry friction (f_w) values against an Al_2O_3 ball at a constant normal load (F_n) of 5 N for PEEK bulk and the PEEK 708 coating are shown in **Fig. 11**.

Result analysis of tribological tests indicates significant differences in the coefficients of sliding dry friction (f_w) between both forms of PEEK. The coefficient of sliding dry friction (f_w) of the PEEK 708 coating (f_w = 0.22–0.25) is 36% lower than PEEK bulk (f_w= 0.35–0.4). Similar differences can be observed for wear rates (K). The wear rate (K) of PEEK 708 (K = $3.12 \cdot 10^{-6}$ mm^3/Nm) is 38% lower than PEEK bulk (K = $5.09 \cdot 10^{-6}$ mm^3/Nm).

The coefficient of scratch friction (f_s) values at a progressive normal load (F_n) in the range of 0–30 N for PEEK bulk and the PEEK 708 coating are shown in **Fig. 12**.

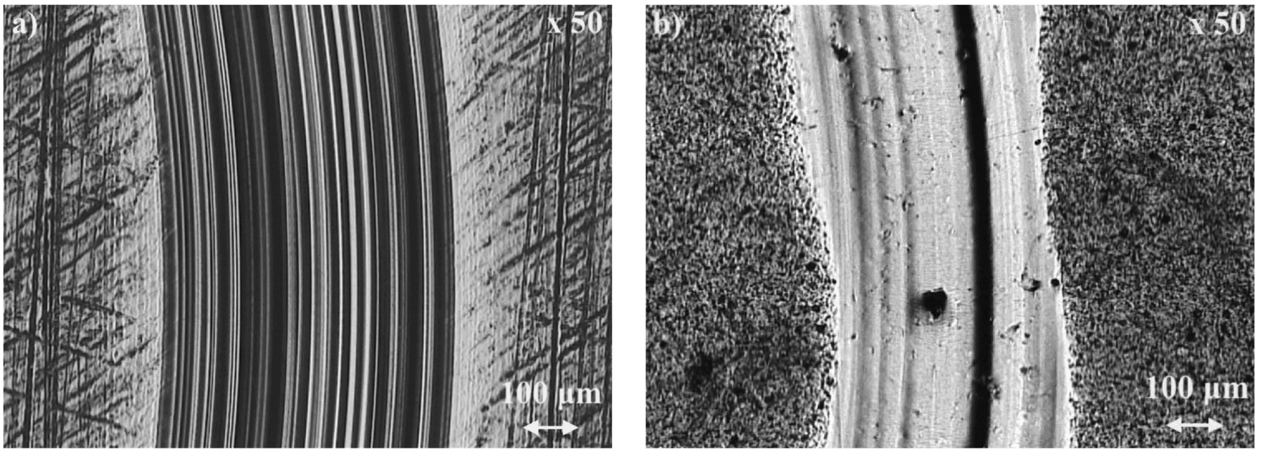

Fig. 10. Worn surfaces of the: a) PEEK bulk, b) PEEK 708 coating, after dry friction against Al2O3 ball (LM, mag. 50x)
Rys. 10. Zużyta powierzchnia: a) monolitu PEEK, b) powłoki PEEK 708, po współpracy z kulą Al2O3 w styku niesmarowanym (LM, pow. 50x)

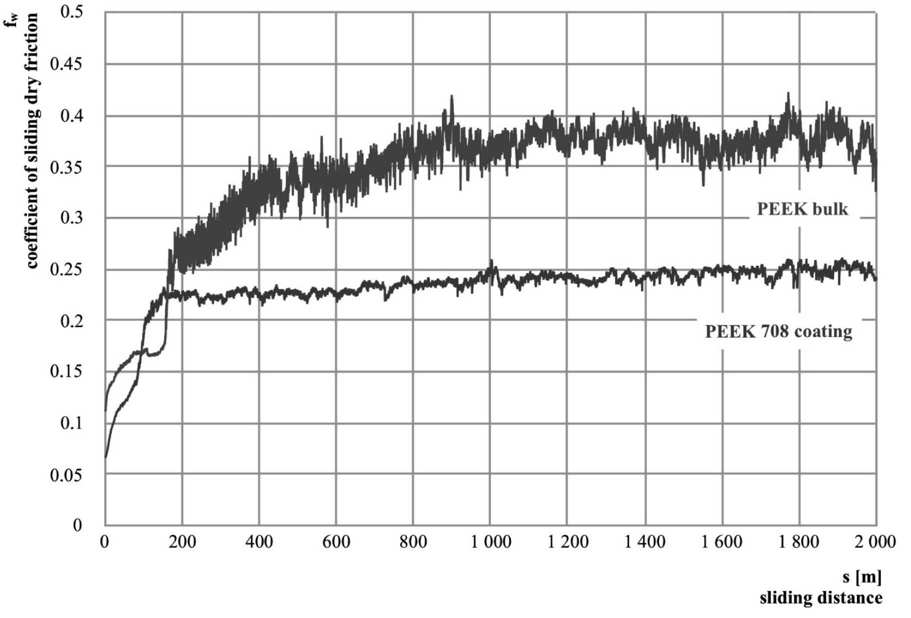

Fig. 11. Coefficient of sliding dry friction of PEEK bulk and PEEK 708 coating against Al2O3 ball
Rys. 11. Współczynnik tarcia ślizgowego suchego PEEK w postaci monolitycznej i powłoki PEEK 708 w styku z kulą Al2O3

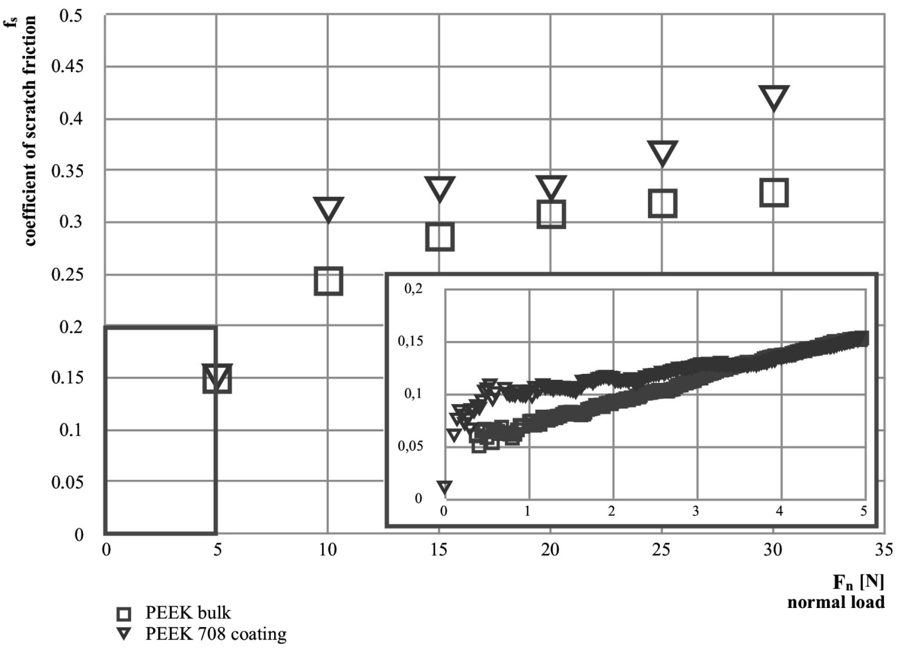

Fig. 12. Coefficient of scratch friction determined in scratch tests
Rys. 12. Współczynnik tarcia zarysowania wyznaczony w testach zarysowania

The coefficient of scratch friction (f_s) is used to qualitatively compare the adhesion of coatings to the substrate **[L. 41]**. Generally, it can be applied in the classification of coatings in industrial practice.

The coefficient of scratch friction (f_s) of PEEK bulk is less than or equal to the PEEK 708 coating, regardless of the normal load (F_n) value. Under a normal load (F_n) in range of 0-5 N, the coefficients of scratch friction (f_s) of both PEEK forms converge to a common value of 0.15. Over the value of 0.15, both coefficients of scratch friction (f_s) increase with normal load (F_n), but the increase is more intensive for the PEEK 708 coating.

CONCLUSIONS AND DISCUSSION

The Vickers hardness (HV) tests show that the obtained values for PEEK bulk at normal loads (F_n) of 50 and 100 [mN], which are about 300 MPa, correspond with other research, according to which the values are in the range of 300–400 MPa **[L. 11, 13]**. Nevertheless, the above results deviate from the value determined by the producer due to a different indentation method (Brinell's method), according to which the Brinell hardness (HB) is 265 MPa. In accordance with the performed analysis, the Vickers hardness (HV) of the PEEK 708 coating at normal loads (F_n) of 50 and 100 [mN] is approx. 350 MPa and deviates from the values in the range of 100––275 MPa obtained based on other research **[L. 23, 25, 27, 28]**. The ambiguity of the above results is most likely caused by the degree of polymer crystallinity. Moreover, the difference in the compared research results is related to the polymer structure, which is formed depending on the method of coating deposition. Nevertheless, the Vickers hardness (HV) of PEEK bulk and the PEEK 708 coating indicates an analogously downward trend at a normal load (F_n) of 200 mN. This proves that the substrate material does not affect the indentation test of the PEEK 708 coating. This behaviour is confirmed by the safe penetration depth of the indenter, which is 6.4% of the PEEK 708 coating thickness. The above thesis is also verified by the results of the elastic modulus (E), with values for both forms of PEEK being almost the same: for PEEK in monolithic form, it is approx. 5.4 GPa, and for the PEEK 708 coating, it is approx. 5.5 GPa. According to of other research, the elastic modulus (E) value of PEEK bulk determined in the tensile test is in the range of 3.5–3.6 GPa, while, based on the specification card, it is 4.2 GPa **[L. 9, 10]**. In the case of the PEEK 708 coating, the polymer company only provides the value of elastic modulus (E), which is 4.3 GPa. The above dissonance of comparable values is caused by the type of test.

The studies indicate that the tests of the elastic modulus (E) and Vickers hardness (HV) determined in the indentation method of PEEK bulk can be used to obtain the mentioned parameters for PEEK coatings. One condition for this is the fulfilment of the indenter penetration criterion, which should not exceed 10% of the coating thickness. Due to the dedicated mathematical relationships used to obtain the elastic modulus (E) and Vickers hardness (HV) in this publication, values with a smaller standard deviation were determined than in the case of the Olivier-Phar model. The reason for the difference in the determined values is probably a better fit of the tangent to the unloaded deformation curve in the indentation test.

Semi-crystalline thermoplastic polymers, including PEEK, are characterized by high elastic deformation. According to Xiang, the elastic deformation in the scratch test is related to the yield strength (Re), elastic modulus (E) and the coefficient of scratch friction (f_s) **[L. 42]**.

Therefore, soft and flexible coatings such as PEEK are characterized by high scratch resistance, which can be described by scratch hardness (HS) and Micro Mar Resistance (MRR). The above feature is characteristic of polymers and is related to elastic recovery after deformation due to scratches. In the case of polymer coatings, this is one of the most important features that matter due to the durability of the coating-substrate system and the areas of application. At the same time, polymers as a group of engineering materials are characterized by low mechanical properties. This is explained by low elastic modulus (E) of polymers and often relatively high plasticity in comparison with, for example, hard ceramic coatings.

Therefore, the scratch hardness (HS) and Micro Mar Resistance (MMR) of PEEK bulk and the PEEK 708 coating in the scratch test were determined in this publication. The study shows that, despite the 15% higher Vickers hardness (HV) of the PEEK 708 coating (HV = 350 MPa, HS = 300 MPa) relative to PEEK bulk (HV = 300 MPa, HS = 210 MPa), scratch hardness (HS) is almost 40% higher. The above difference is most likely influenced by the degree of the crystallinity of the PEEK 708 coating, which is directly related to the deposition method and elastic recovery. This explains the difference with the research of other authors where the scratch hardness (HS) of PEEK coatings is 113 MPa **[L. 26]**. This behaviour is also confirmed by Miro Mar Resistance (MMR). The biggest difference in the above parameter is for the normal load (F_n) of 5 N and reaches an almost 20% higher value for the PEEK 708 coating than PEEK bulk. This trend is maintained up to the normal load (F_n) of 20 N. Above the normal load (F_n) of 20 N, Micro Mar Resistance (MMR) of the PEEK 708 coating is lower than PEEK bulk.

Based on scratch tests, the coefficient of scratch friction (f_s) was also determined, and, for PEEK bulk, the maximum value is 0.33. The obtained value is consistent with the research of other authors where the maximum coefficient of scratch friction (f_s) value is in the range of 0.24–0.46 **[L. 9, 19]**. In the case of the PEEK 708 coating, the maximum coefficient of scratch friction (f_s) value is 0.42. The obtained value is also consistent with the research of other authors where the maximum coefficient of scratch friction (f_s) value is in the range of 0.19–0.47 **[L. 16, 23, 25, 27]**. Nevertheless, the coefficient of scratch friction (f_s) of the PEEK 708 coating is almost always higher than PEEK bulk, regardless of the normal force (F_n) value. This indicates a higher movement resistance of piled up material against the pressing of an indenter. Therefore, the PEEK 708 coating is characterized by a wider range of elastic deformability relative to PEEK bulk. The above relationship is confirmed by differences in the values of Vickers hardness (HV), scratch hardness

(HS), and Micro Mar Resistance (MMR), which are related to the crystallinity degree of the polymer and the deposition technology of the PEEK 708 coating. Hence, the coefficient of scratch friction (f_s) depending on normal load (F_n) can be an additional factor when comparing polymer coatings.

Tribological tests in non-lubricated contact against an Al_2O_3 ball enable the coefficient of sliding dry friction (f_w) to be determined, with a mean value for PEEK bulk in the range of 0.35–0.4 at a constant normal load (F_n) of 5 N. The above value is consistent with the research of other authors (0.35–0.43) despite the flat contact configuration used by them in tribological tests **[L. 18, 19]**. In the case of the PEEK 708 coating, the coefficient of sliding dry friction (f_w) value is in the range of 0.22–0.25. The above value is also consistent with the work of other researchers (0.19–0.47) where the contact configuration applied in tests are the same **[L. 16, 23––25, 27, 28]**. Therefore, the discrepancy between the coefficients of sliding dry friction (f_w) of these two forms of PEEK should be attributed to the difference in the mechanical properties of the PEEK 708 coating caused by a different crystallinity degree. In order to reliably compare the coefficients of sliding dry friction (f_w) of PEEK in bulk and coating form, both forms of PEEK must be formed so as to achieve convergent crystallinity degrees. Moreover, due to the constraint imposed by the coating thickness and the wide range in the elastic deformation of PEEK, tribological tests should be performed in a *ball-on-disc* friction node.

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REFERENCES

1. Koike H., Honda T., Kida K., Santos E.C., Rozwadowska J., Houri K., Uryu M., Kashima Y., Kanemasu K.: Influence of Radial Load on PEEK Plastic Bearings Life Cycle under Water Lubricated Conditions. Advanced Materials Research. 217–218, 2011, pp. 1260–1265.
2. Koike H., Kida K., Santos E.C., Rozwadowska J., Kashima Y., Kanemasu K.: Self-lubrication of PEEK polymer bearings in rolling contact fatigue under radial loads. Tribology International. 49, 2012, pp. 30–38.
3. Eschbach L.: Nonresorbable polymers in bone surgery. Injury. 31, 2000, D22-D27.
4. Tekin S., Cangül S., Adıgüzel Ö., Değer Y.: Areas for use of PEEK material in dentistry. International Dental Research. 8(2), 2018, pp. 84–92.
5. Cousins K.: Polymers for electronic components. Rapra Technology Limited, 2001.
6. Zsidai L., Kátai L.: Abrasive Wear and Abrasion Testing of PA 6 and PEEK Composites in Small-Scale Model System. Acta Polytechnica Hungarica. 13, 2016, pp. 1–6.
7. Wang J., Zhou Q., Chao D., Fangfei l., Cui T.: In situ determination of mechanical properties for poly(ether ether ketone) film under extreme conditions. RSC Advances. 7(14), 2017, pp. 8670–8676.
8. Kumar A., Yap W.T., Foo S.L., Lee T.K.: Effects of Sterilization Cycles on PEEK for Medical Device Application. Bioengineering. 5(1), 2018, pp. 1–10.
9. Friedrich K., Sue H. J., Liu P., Almajid A.: Scratch resistance of high performance polymers. Tribology International. 44(9), 2011, pp. 1032–1046.
10. Schwitalla A., Mueller W.-D.: PEEK dental implants: A review of the literature. International Journal of Oral Implantology. 39(6), 2013, pp. 743–749.
11. Sampaio M., Buciumeanu M., Henriques B., Silva F., Souza J.C.M., Gomes J.R.: Tribocorrosion behavior of veneering biomedical PEEK to Ti6Al4V structures. Journal of the Mechanical Behavior of Biomedical Materials. 54, 2016, pp. 123–130.
12. Sampaio M., Buciumeanu M., Henriques B., Silva F., Souza J.C.M., Gomes J.R.: Comparison between PEEK and Ti6Al4V concerning micro-scale abrasion wear on dental applications. Journal of the Mechanical Behavior of Biomedical Materials. 60, 2016, pp. 212–219.
13. Goyal R.K., Tiwari A.N., Negi Y.S.: Microhardness of PEEK/ceramic micro- and nanocomposites: Correlation with Halpin–Tsai model. Materials Science and Engineering: A. 491(1–2), 2008, pp. 230–236.
14. Cebe P., Chung S.Y., Hong S.-D.: Effect of thermal history on mechanical properties of polyetheretherketone below the glass transition temperature. Journal of Applied Polymer Science. 33(2), 1987, pp. 487–503.
15. Briscoe B.J., Stuart B., Stuart B., Rostami S.: A comparison of thermal- and solvent-induced relaxation of poly(ether ether ketone) using Fourier transform Raman spectroscopy. Spectrochimica Acta Part A: Molecular Spectroscopy. 47(9–10), 1991, pp. 1299–1303.

16. Victrex VICOTE peek coating technology. Victrex, 2017.
17. Chemical Resistance Victrex PEEK Polymers. Victrex, 2012.
18. Sümer M., Ünal H., Mimaroğlu A.: Evaluation of tribological behaviour of PEEK and glass fibre reinforced PEEK composite under dry sliding and water lubricated conditions. Wear. 265(7–8), 2008, pp. 1061–1065.
19. Lina L., Peib X.-Q., Bennewitzb R., Schlarb A. K.: Friction and wear of PEEK in continuous sliding and unidirectional scratch tests. Tribology International. 122, 2018, pp. 108–113.
20. Schweitzer P. A.: Mechanical and Corrosion-Resistant Properties of Plastics and Elastomer. CRC Press, 2000.
21. Solvay's Zeniva PEEK Passes Biocompatibility Testing in China. Versatile thermoplastic biomaterial to meet growing demand for implantable medical devices in Asia. 2016.
22. Lan P., Polychronopoulou K., Zhang Y., Polycarpou A. A.: Three-body abrasive wear by (silica) sand of advanced polymeric coatings for tilting pad bearings. Wear. 382–383, 2017, pp. 40–50.
23. Li J., Liao H., Coddet C.: Friction and wear behavior of flame-sprayed PEEK coatings. Wear. 252(9–10), 2002, pp. 824–831.
24. Zhang G., li W., Cherigui M., Zhang C., Liao H., Bordes J.-M., Coddet C.: Structures and tribological performances of PEEK (poly-ether-ether-ketone) based coatings designed for tribological application. Progress in Organic Coatings. 60(1), 2007, pp. 39–44.
25. Zhang C., Zhang G., JI V., Liao H., Costil S., Coddet C.: Microstructure and mechanical properties of flame-sprayed PEEK coating remelted by laser process. Progress in Organic Coatings. Progress in Organic Coatings. 66(3), 2009, pp. 248–253.
26. Tharajak J., Palathai T., Sombatsompop N.: Scratch Resistance and Adhesion Properties of PEEK Coating Filled with h-BN Nanoparticles. Advanced Materials Research. 747, 2013, pp. 303–306.
27. Moskalewicz T., Zimowski S., Zych A., Łukaszczyk A., Reczyńska K., Pamuła E.: Electrophoretic Deposition, Microstructure and Selected Properties of Composite Alumina/Polyetheretherketone Coatings on the Ti-13Nb-13Zr Alloy. Journal of The Electrochemical Society. 165(3), 2018, D116-D128.
28. Zhang G., Li W.-Y., Cherigui M., Zhang C., Liao H., Bordes J.-M., Coddet C.: Structures and tribological performances of PEEK (poly-ether-ether-ketone)-based coatings designed for tribological application. Progress in Organic Coatings. 60(1), 2007, pp. 39–44.
29. Weidian S.: Characterization of Mar/Scratch Resistance of Polymeric Coatings: Part I. Surface Science and Nano-Tribology Laboratory, Coatings Research Institute. 2006, pp. 54–60.
30. Weidian S.: Characterization of Mar/Scratch Resistance of Polymeric Coatings: Part II. Surface Science and Nano-Tribology Laboratory, Coatings Research Institute. 2006, pp. 44–51.
31. TECAPEEK natural – półwyroby. Ensinger Polska, 2018.
32. Metallic materials. Instrumented indentation test for hardness and materials parameters. Part 4: Test method for metallic and non-metallic coatings. ISO 14577-4:2016, 2016.
33. Briscoe B.J., Fiori L., Pelillo E.: Nano-indentation of polymeric surfaces. Journal of Physics D: Applied Physics. 31(19), 1998, pp. 2395–2405.
34. Mussert K.M., Vellinga W.P., Bakker A., Zwaag S.V.D.: A nano-indentation study on the mechanical behaviour of the matrix material in an AA6061 – Al2O3 MMC. Journal of Materials Science. 37(4), 2002, pp. 789–794.
35. Roa J.J., Oncins G., Diaz J., Sanz F., Segarra M.: Calculation of Young's Modulus Value by Means of AFM. Recent Patents on Nanotechnology. 5(1), 2011, pp. 27–36.
36. Guillonneau G., Kermouche G., Bec S., Loubet J.-L.: Determination of mechanical properties by nanoindentation independently of indentation depth measurement. Journal of Materials Research. 27(19), 2012, pp. 2551–2560.
37. Kim G., Elnabawi O., Shin D., Pae E.K.: Transient Intermittent Hypoxia Exposure Disrupts Neonatal Bone Strength. Front Pediatr. 4, 2016, p. 15.
38. Standard Test Method for Evaluation of Scratch Resistance of Polymeric Coatings and Plastics Using an Instrumented Scratch Machine. ASTM D7027-13, 2013.
39. Fine ceramics (advanced ceramics, advanced technical ceramics). Determination of friction and wear characteristics of monolithic ceramics by ball-on-disc method. ISO 20808:2004, 2004.
40. Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear. ASTM G133 – 05(2016), 2016.
41. Jiang C., Jiang H., Zhang J., Kang G.: Analytical model of friction behavior during polymer scratching with conical tip. Friction. 7(5), 2018, pp. 466–478.
42. Xiang C., Sue H.J., Chu J., Coleman B.: Scratch behavior and material property relationship in polymers. Journal of Polymer Science Part B: Polymer Physics. 39(1), 2001, pp. 47–59.