Tribology and Materials
Vol. 3, No. 3, 2024, pp. 96-107

ISSN 2812-9717
https://doi.org/10.46793/tribomat.2024.012

Radioactive tracers in industry: Thin layer activation of carbon-based materials for wear measurement

Alexander HOFER [1,*], Ferenc DITRÓI [2], Manuel ZELLHOFER [1], Sándor TAKÁCS [2], Thomas WOPELKA [1], Andreas KÜBLER [3], Martin JECH [1]

[1] AC2T research GmbH, Wiener Neustadt, Austria
[2] HUN-REN Institute for Nuclear Research, Debrecen, Hungary
[3] Robert Bosch GmbH, Stuttgart, Germany
*Corresponding author: alexander.j.hofer@gmx.at

Keywords
thin layer activation
carbon-based materials
RIC method
wear measurement
DLC
PEEK
EPDM

History
Received: 27-05-2024
Revised: 26-07-2024
Accepted: 31-07-2024

Abstract

Thin layer activation (TLA) is already routinely utilised for online wear monitoring of metallic components with the radioisotope concentration (RIC) method for various tribological applications. However, many components in tribological systems are made of carbon-based bulk material (e.g. polymers) or have carbon-based wear resistant coatings (e.g. diamond-like carbon). By utilising the nuclear reaction $^{12}C(^{3}He,x)^{7}Be$, TLA can thus be employed in carbon-containing components. To evaluate the applicability of this approach for TLA in combination with the RIC method, three materials EPDM (ethylene propylene diene monomer), PEEK (polyether ether ketone) and DLC (diamond-like carbon), which are vastly utilised in tribology, were activated. Subsequently, the modulus of elasticity and hardness of the activated specimens were measured and evaluated if the material works for TLA. As EPDM developed cracks after the irradiation process, it is regarded to be not applicable for TLA and subsequent wear measurements. While the PEEK material revealed small changes in hardness values compared to non-irradiated samples, the irradiated DLC coating showed no detectable material changes. Both irradiated materials have been applied to representative tribological wear studies, for which the RIC results showed a good correlation with optical wear measurements.

1. Introduction

Carbon-based materials have become integral to various mechanical systems in both industrial and everyday applications due to their advantageous properties such as low wear, low friction, low weight and low thermal conductivity compared to metals or metallic alloys. These benefits make them a key focus of current tribological research, aimed at improving efficiency, durability, reducing energy consumption and lowering maintenance costs.

Therefore, there is a strong need for efficient wear measurement with high resolution of these materials. An established approach for the wear measurement of metals is the thin layer activation (TLA) in combination with the radioisotope concentration (RIC) measurement method, which allows measuring wear continuously throughout the test with a resolution in the nanometer range. This paper investigates the feasibility of using TLA and RIC for selected carbon-based materials that are largely utilised for tribological purposes and cover a wide spectrum in terms of applications and tribological properties, namely: EPDM (ethylene propylene diene monomer), PEEK (polyether ether ketone) and DLC (diamond-like carbon).

This TLA and RIC combination relies on the detection of worn particles containing radioactive tracer isotopes and provides insights into time-dependent wear phenomena like running-in wear

and steady-state wear rates which for example allows evaluating different operating conditions [1]. To be able to detect radioactive particles radioactive isotopes must be generated in the components in advance. TLA is capable of producing radioactive particles in the top layers of the investigated material with sufficient yield for RIC wear measurements [2]. In this paper, "activation" refers to generating isotopes through irradiation. TLA for RIC measurements is usually designed so that activated samples do not exceed exempt radiation levels, known as the free handling limit (FHL). This restriction is chosen primarily for reasons of radiation protection and the associated, more versatile application possibilities due to fewer legal restrictions.

The RIC method, combined with TLA, is well-established for investigating wear in metallic materials, typically involving elements like Fe, Co, Ni, Ti, Cu and Zn which are excellent targets for producing proper radioisotopes by charged particle irradiation [3,4]. However, carbon-based materials like EPDM, PEEK and DLC usually do not contain these elements in significant quantities. Instead, carbon itself serves as the target for TLA, with ^{7}Be being the preferred tracer isotope due to its suitable production yield, half-life and gamma spectrometry characteristics suitable for the RIC method [5].

TLA implies exposure of the target material to ionising radiation and consequently energy deposition into the material. While ionising radiation can intentionally modify materials for specific applications [6], the goal in tribological testing is to maintain the properties of the irradiated material as close to its original state as possible. This is particularly challenging with carbon-based materials, which are generally more prone to radiation-induced degradation compared to metals which is, amongst other reasons, due to their difference in bonding structures and the corresponding physical properties [7].

Radiation effects on polymers are complex, often involving both chain scissioning and crosslinking, whereby one of the two mechanisms is predominant [8]. However, radiation-induced changes mainly depend on the chemical structure of the polymer chain. Aromatic structures in the backbone make polymers more resistant to ionising radiation. In contrast, aliphatic polyethers, aliphatic polysulfones and polymers containing C–Cl bonds in the macromolecular structure are highly sensitive to radiation [9,10]. Hence, the irradiation resistance of carbon-based materials varies significantly.

For EPDM crosslinking tends to be predominant in the absence of oxygen [11]. EPDM rubber starts showing significant changes in material properties at 5×10^{6} Gy when irradiated with gamma rays [12]. In PEEK material crosslinking is also the leading mechanism in an oxygen-free environment. Additionally, PEEK has aromatic structures in its backbone leading to a higher irradiation resistance compared to EPDM, which is given up to a gamma irradiation dose of 10^{7} Gy [13] or at least should keep the majority of its mechanical properties under oxygen-free conditions during irradiation [8]. DLC is generally very resistant to ionising irradiation. Only at high irradiation doses of greater than 10^{15} ions per cm^{2} tetrahedral amorphous carbon shows structural damages, which manifests in an increased concentration of sp^{2} [14]. However, Zellhofer et al. [15] reported that the DLC layer (used also in this publication) does not significantly change in roughness, hardness and modulus of elasticity after irradiation by the TLA technique.

Predicting the outcome of the activation for a specific sample depends on multiple factors beyond just considering the sheer total amount of induced energy. Dose rates, heat production, ambient conditions during and after the irradiation (oxidation and post-irradiation oxidation effects) and other influencing factors can also affect the outcome of the activation process [8]. Moreover, additives (which are often not known in commercial products) can significantly change the materials' behaviour under the influence of ionising radiation. For instance, aromatic hydrocarbons act as energy acceptors, also antioxidants and nanoparticles are routinely added for the purpose of enhancing the irradiation resistance of the materials [16].

The application of the investigated carbon-based materials in industry is broad. Amorphous carbon coatings like DLC are widely studied in space tribology, where the harsh, vacuum environment often lacks liquid lubrication [17-20]. Additionally, extensive research is ongoing into the use of DLC coatings in liquid-lubricated and non-lubricated applications, such as bearings, automotive components and cutting tools [21-25].

Polymers like EPDM and PEEK play a critical role in a broad spectrum of industries, necessitating intensive tribological research. Ren et al. [26] provide a comprehensive review of polymer

composite coatings research in tribology. Tahir et al. [27] reviewed research on carbon-based materials with a particular emphasis on wear mechanisms and interfaces. EPDM is widely used in the manufacture of seals, gaskets and tubing, particularly in the automotive industry and other sectors. Its extensive application makes it a significant subject of current tribological research [28,29]. Similarly, PEEK is extensively employed in bearings, bushings and medical implants. Given its critical role in these components, tribological research is dedicated to the improvement of this material [30-32].

This paper investigates the feasibility of using TLA for selected carbon-based materials (EPDM, PEEK and DLC), assesses their applicability in wear measurement using the RIC method and explores the influence of specific (tribological) conditions, like load and temperature, on their wear behaviour.

2. Activation

Activation of components for wear measurement is usually realised by three different "nuclear methods", namely neutron activation, isotope implantation and thin layer activation (TLA). Neutron activation in a (nuclear) reactor results in uniform activation of the whole component causing high activities and low sensitivity. In combination with a low cross-section of neutrons on carbon, neutron activation is inapplicable for the given task [33-36].

Implantation of ^{7}Be ions in the materials' surface for subsequent wear measurement was shown to be feasible for carbon-based and other materials [35,36]. However, this implantation technique has several drawbacks compared to the TLA activation with ^{3}He:

- the number of radioactive beam facilities is fewer and using them is more expensive than for direct activation;
- the isotopes for implantations (such as ^{7}Be) must be produced additionally and sometimes elsewhere;
- the beam intensity for implantation is low and consequently a sufficient long implantation time must be considered for a reasonable activity;
- the implementation depth is usually much lower and the distribution of the implanted ^{7}Be cannot be regarded to be constant in a designated surface layer as in the case of the thin layer activation method.

Nevertheless, the implantation technique may be applied in such a way, that the energy input is low enough for very damageable materials and as such reasonable for specific tasks that cannot be met by TLA. Due to the described scientific and economic aspects, this paper focuses on and investigates the feasibility of TLA with carbon-based materials EPDM, PEEK and DLC.

2.1 Thin layer activation (TLA) method

The irradiation of the samples was performed at the MGC-20E cyclotron of the HUN-REN Institute for Nuclear Research (Debrecen, Hungary). The irradiation parameters (beam energy, intensity, duration, beam spot size, possible scanning of the target surface, etc.) were calculated by the dedicated software tool developed for the International Atomic Energy Agency (IAEA) [37]. Carbon in the chemical structure is utilised in the nuclear reaction $^{nat}C(^{3}He,x)^{7}Be$, which allows the production of the proper tracer radioisotope for wear measurement related to gamma spectrometry. Depending on the energy of the incident particles during the activation process, the probability of the nuclear reaction above varies in a wide range. This probability is commonly referred to as cross-section with the unit millibarn (1 mb = 10^{-27} cm^{2}). Figure 1 shows cross-sections, taken from the IAEA EXFOR [38] and TLA database [37], which are measured by different research groups. In the context of this work, the data set from Ditrói et al. [5] ^{nat}C has been chosen for the nuclear reaction $^{12}C(^{3}He,x)^{7}Be$, as this data set is the most recently measured one and is also implemented in the IAEA TLA tool [37].

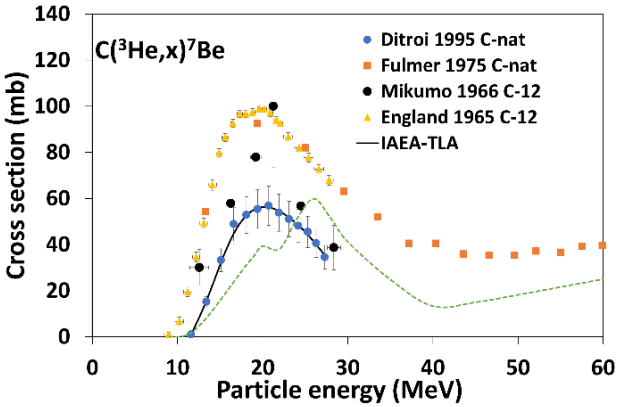

Figure 1. Measured cross-sections of the $^{12}C(^{3}He,x)^{7}Be$ nuclear reaction taken from the IAEA EXFOR and TLA database; different colours/labels show the cross-sections from different sources; the data from Ditroi 1995 are used in the IAEA TLA tool which is indicated by the solid line fit

To spare the expensive ^{3}He gas, the ^{3}He was diluted with ^{4}He with a ratio of 1:3. So it was possible to run the ion source effectively, but the consumption of ^{3}He was reduced. Finally, only the ^{3}He particles were extracted into the beam transport system. This dilution reduced the highest beam current at the target position to 500 nA, which we did not intend to exceed because of the thermal sensitivity of the material to be investigated. The calculated beam energy was 21.1 MeV considering the required homogeneous activity at the surface. The homogeneity depth (specific activity is constant within a given depth of a depth profile) with 21.1 MeV beam energy was different for the various target materials EPDM, DLC and PEEK, due to the different material densities. To prevent thermal damage on the irradiated samples and to reduce oxidation effects on polymers, all samples were cooled with nitrogen vapour ascending from a liquid nitrogen container.

With the help of the IAEA TLA tool and based on the chosen cross-section data set, activity depth profiles for materials can be calculated, considering material composition and density, the incident particle energy and the energy loss along their path through the material. The activities given in this publication were all measured with an HPGe detector immediately after TLA.

2.2 EPDM activation – Results and discussion

EPDM is a widely used elastomer in industrial applications, such as gaskets. According to the analysis found in the literature, EPDM material is expected to be damageable by the irradiation process [12]. Therefore, a first test sample (EPDM gasket) was irradiated on four spots (Fig. 2) with different beam currents of 400, 200, 100 and 50 nA for half an hour, which should result in a ^{7}Be activity of approximately 8, 4, 2 and 1 kBq, respectively.

The beam was targeted perpendicularly to the surface. An inspection of the four spots showed severe material damage for the positions irradiated with 400 and 200 nA. The spots irradiated with 100 and 50 nA showed only slight changes on the surface, the latter having the least damage. Based on these results, a new gasket sample was irradiated with a 50 nA beam current for later wear investigation in a sealing test rig.

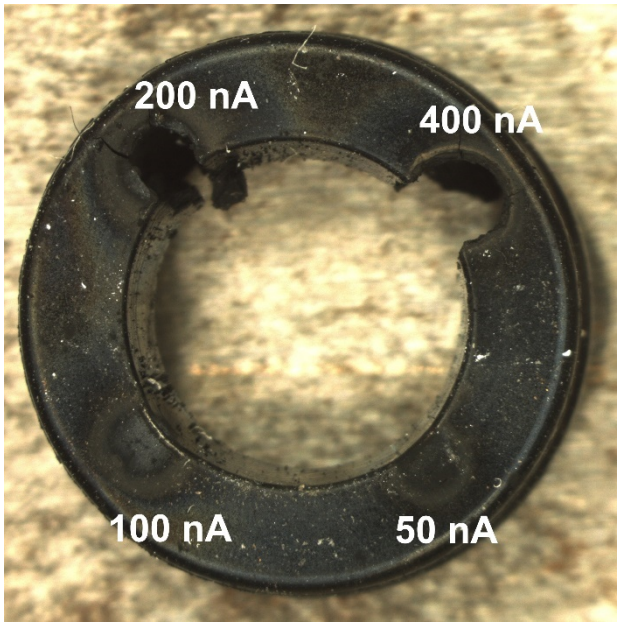

Figure 2. Test activations of EPDM gasket with 400, 200, 100 and 50 nA beam current

Different to the first test sample, the new gasket was rotated during the irradiation process for two reasons. Firstly, to achieve a homogeneous activated area on the sealing edge over the whole circumference of the gasket and secondly, to avoid high energy density and material heating in a small spot area. The total ^{7}Be activity after activation was approximately 80 kBq to achieve a high signal-to-noise ratio during the envisaged wear measurement. Figure 3 shows a picture of the gasket six days after irradiation in good condition with no visible damage of the material.

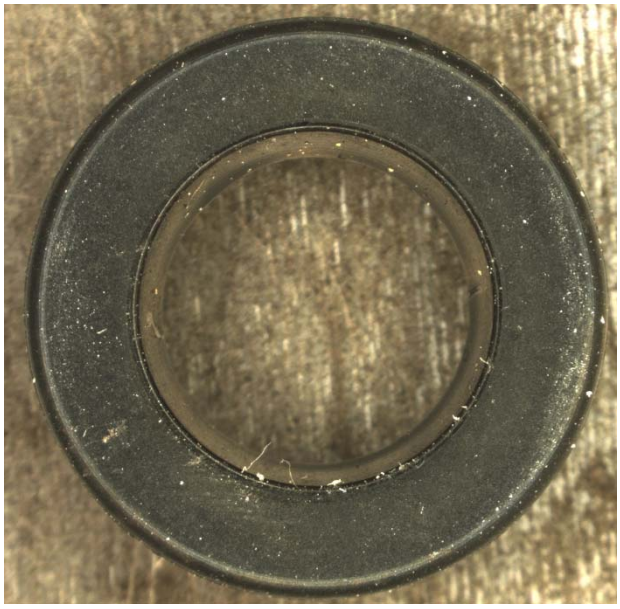

Figure 3. Gasket activated with 50 nA beam current and 80 kBq ^{7}Be activity six days after activation

However, three weeks after the activation, when the gasket was prepared for the wear test, it showed severe material damage in the form of cracks. The cracks can be observed in the detailed picture (Fig. 4), which were not observable at the inspection six days after the TLA irradiation.

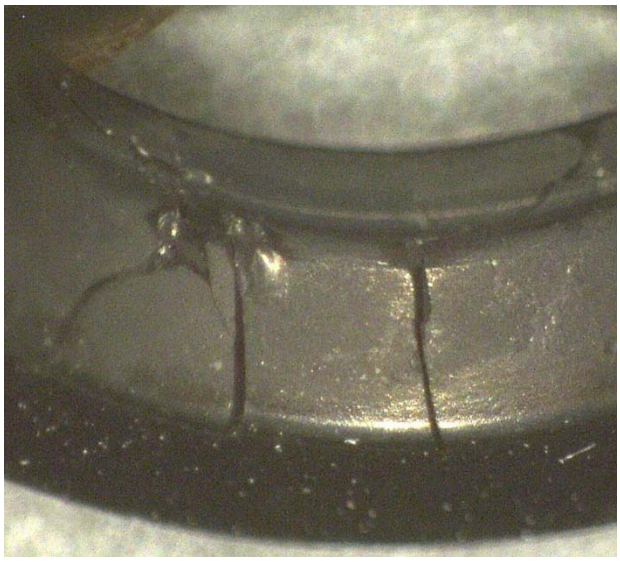

Figure 4. Gasket from Figure 3 about three weeks after activation (detailed picture of cracks in the material)

As the EPDM gasket 6 days after the activation showed no damages but 3 weeks after the activation showed several cracks, it can be assumed that embrittlement occurred in the elastomer matrix. As mentioned in the introduction, chain scissioning and crosslinking are the two most important chemical reactions leading to changes in the structure and the mechanical and physical properties [8]. Chain scissioning breaks chemical bonds along the polymer chain, leading to the shortening of macromolecular chain length and molecular weight, while crosslinking creates internal networks and increases the molecular weight [39,40]. Although crosslinking is predominant in an oxygen-free environment, crosslinking does not necessarily occur for oxygen-containing atmospheres during and after TLA. Furthermore, such chemical reactions are hard to predict if ambient conditions, such as the concentration of specific gas types or gas temperature, are difficult to control.

However, although the degradation of the EPDM occurred with a certain time delay, it seems evident that the aging is triggered through TLA-induced irradiation. Since irradiation and storage of the activated sample did not take place in an oxygen-free environment, the material probably suffered from oxidation and post-irradiation oxidation effects. Therefore, based on the available technical options, it is a complex task to adapt the entire activation process in such a way that no material degradation occurs. Therefore, the TLA technique can hardly be applied to EPDM and probably similar materials without damaging the specimen. As the EPDM gasket was damaged, it was not considered for further tribometer tests.

2.3 DLC activation – Results and discussion

Figure 5 shows the calculated depth profile for a DLC coating with approximately 2.3 µm thickness and an approximate composition of 90 % C and 10 % H in mass percentage. No other elements are included in the coating. The illustrated depth profile is valid for a sample with a ^{7}Be activity of 100 kBq, while for other sample activities, the values change proportionally. In the white section on the left side, the red solid line is the depth profile curve in the DLC coating, which is also covered by the blue horizontal line representing the approximation with a constant specific activity. It can be seen that this approximation is a solid approach for the DLC coating with such thickness. In the grey area, the dashed red line refers to a hypothetical depth profile trend, if the DLC coating were up to 45 µm thick. The depth, until the profile could be estimated as being constant in such a case, is indicated by the vertical line. However, in our case of the 2.3 µm thin coating, the ^{3}He particles, that are penetrating (5 – 12 hours at 500 nA and 15° beam angle) deeper than the coating thickness, do actually result in activating the bulk material as well. Measurements with an HPGe detector immediately after activation showed 7.96 kBq of ^{7}Be, while other isotopes which were produced originate from the bulk. The depth profile and activities of the bulk are not discussed in this work but provide the possibility for detecting wear of the bulk material as well [15].

Zellhofer et al. [15] investigated the impact of irradiation with the identical TLA procedure and the same DLC material and geometry on the material's key properties. DLC layer was measured for modulus of elasticity and hardness by nanoindentation (load: 10 mN; penetration depth: 120 – 150 nm). The activated surface (modulus of elasticity: 175 ± 14 GPa, hardness: 20 ± 3 GPa) showed no significant changes compared to the non-activated surface (modulus of elasticity: 172 ± 12 GPa, hardness: 19 ± 3 GPa). A comprehensive surface analysis (for example

transmission electron microscopy and nanoindentation) also did not reveal any structural or material changes caused by the TLA irradiation [15].

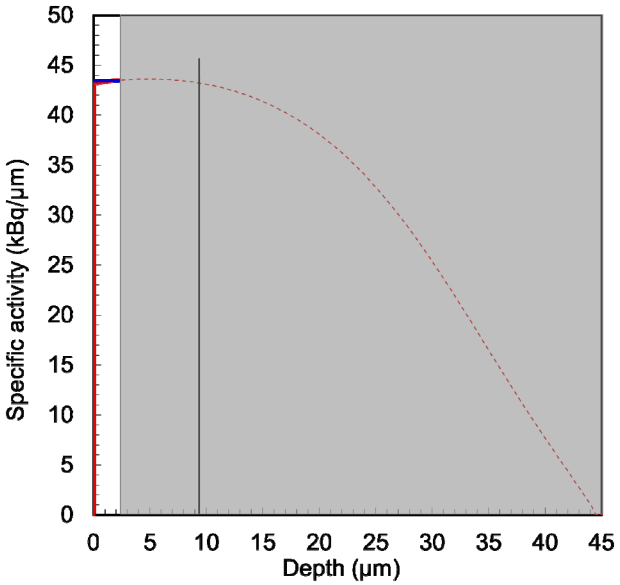

Figure 5. Theoretical depth profile of ^{7}Be in DLC coating (red dashed line); blue line in white area shows the real profile of the 2.3 µm thick coating

2.4 PEEK activation – Results and discussion

The journal bearing shell sample is composed of a PEEK layer on a steel substrate. The PEEK layer consists mainly of pure PEEK but with the insertion of other materials namely 10 ± 1 wt. % graphite, 10 ± 1 wt. % carbon fibre, 10 ± 1 wt. % zinc sulfide and 10 ± 1 wt. % titanium oxide for mechanical/ tribological purposes. The sample was irradiated by the ^{3}He beam with 460 nA beam current for approximately 16 hours. The angle between the beam and the irradiated surface area was set to 15°. For the overall material composition of the PEEK layer, the depth profile of ^{7}Be was calculated as shown by the red solid line, while ^{48}V (green line) is a result of the nuclear reaction between the Ti and ^{3}He particles (Fig. 6). The depth profile is normalised to a sample activity of 100 kBq. For ^{7}Be the blue horizontal line indicates a constant specific activity value as a practical approximation of the red curve in a range until the vertical line. This means that a wear signal is proportional to this constant specific activity with good approximation within this constant depth profile. The activation of the journal bearing shell resulted in 602 kBq of ^{7}Be and 20.4 kBq of ^{48}V. Other isotopes which are produced in the substrate are not discussed further.

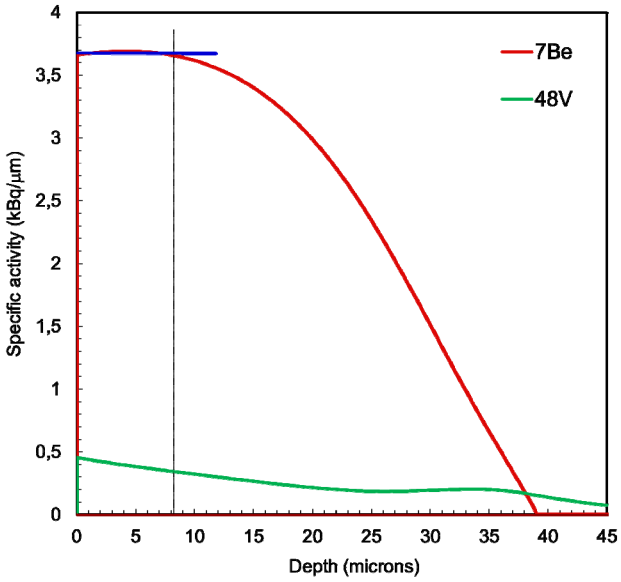

Figure 6. Depth profile for PEEK reinforced with graphite, carbon fibre, zinc sulphide and titanium oxide

Table 1 shows the measurements of the modulus of elasticity and the hardness values for non-activated and activated surface regions of the PEEK samples, which were obtained by nanoindentation (load of 1 mN and a penetration depth of 235 – 250 nm for the activated surface and 310 – 320 nm for the non-activated surface). Both quantities are higher for the activated zones indicating changes in the material due to irradiation. Nevertheless, no geometrical changes, such as raised and lowered regions, could be observed on the irradiated surfaces.

Table 1. Modulus of elasticity and hardness of non-activated and activated PEEK surface regions

Surface	Modulus of elasticity, GPa	Hardness, GPa
Non-activated	8.2 ± 0.8	0.37 ± 0.04
Activated	10.7 ± 1.6	0.43 ± 0.07

According to the changes of modulus of elasticity and hardness for the PEEK sample, an influence on absolute wear rates for this material cannot be excluded, but a relative comparison between the results of, for example, different load levels is permissible.

3. Tribometry

3.1 Tribological testing with RIC method and wear measurement with confocal microscopy

For application of the TLA method with ^{7}Be tracer radioisotopes, PEEK and DLC samples were activated

and tested in specific tribometers connected to a lubricant circuit with a pump and the RIC [1] wear measurement device. A schematic of the setup is illustrated in Figure 7, which shows the activated area and tribometric application for the DLC plate samples. For these samples, a UMT TriboLab (Bruker) tribometer with a linear reciprocating movement was used. The tests with the PEEK journal bearing shell sample were performed on a journal bearing tribometer Sinterlagerprüfgerät – SLPG (SKF; OENORM M 8124:2009). The set-up of the test equipment, especially the lubricant circuit, was similar, also refer to [15].

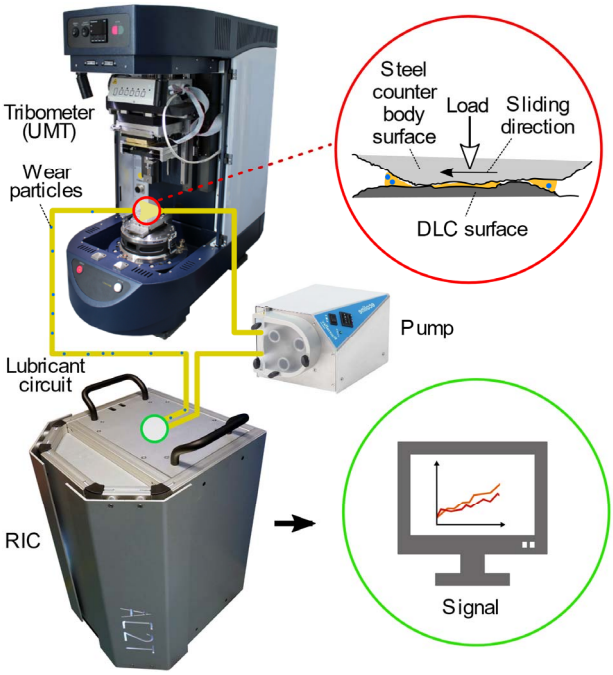

Figure 7. RIC measurement circuit with particle flow from the tribological contact situation to the RIC detector

The tribometers were adapted with tribological chambers, where the cooling/lubricating liquid was used to remove the worn particles from the contact surface and transport them to the RIC measuring device detecting the gamma radiation. The RIC mainly consists of a NaI(Tl) well detector with lead shielding and a suitable glass vial, which is connected through a closed lubricant circuit with the enclosed tribological contact zone. The vial fits into the well and serves as a measuring volume for the lubricant carrying the wear particles. The activity $A(t)$ of the worn particles is measured continuously in the well detector. From the planning of the TLA, the activity distribution in depth of the activated component is known and by determining an irradiated area, the activity concentration ρ in Bq/µm^3 can be defined for a specific total activity. It can be assumed that ρ is a scalar within a limited depth of the component (see Figs. 5 and 6). Wear volume is then calculated as

$$w_V = \frac{A(t)}{\rho}. \quad (1)$$

Wear depth results are then calculated by dividing $w_V(t)$ with the worn area within the activated area of the component.

With this setup the wear can be measured continuously, determining running-in wear, steady-state wear and total wear depth at the end of the wear process. For the RIC method, possible deposition of particles in the lubricant circuit, as well as adhesion of worn material to the counteracting sample have to be taken into account for correcting the total wear volume by post measurements, as described by Lee [12]. Therefore, the counter-body, the sample holder and the tubes of the lubricant circuit are measured with respect to a signal from the tracer isotope.

For investigating DLC coatings, the DLC plate samples were tested against 100Cr6 steel ball counterparts with 10 mm diameter in a UMT TriboLab unit. Figure 8 shows the concept of irradiation of the DLC plate and the tribocontact between the DLC plate and the ball counter-body during tribometer testing. On the UMT TriboLab, the lower sample is moved in a reciprocating motion with a special sample holder while the upper body is pressed downwards with the adjusted normal force. The bulk material is indicated with grey colour and the DLC coating with black. The red colour depicts the activated zone, which extends further than the thickness of the DLC coating into the bulk. As discussed, the activity depth profile can be assumed to be constant within the thin coating. The right part of the figure shows the alignment of the irradiation beam angle towards the DLC plate.

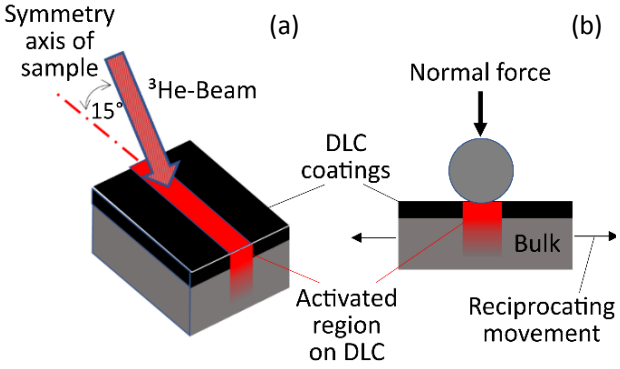

Figure 8. Test on DLC plate: (a) schematic representation of the irradiation beam angle and (b) tribological contact situation with the activation zone

Tests were conducted with a normal force of 60 N (corresponding to an initial pressure of 1704 MPa) and diesel lubrication at room temperature (RT) and 80 N (corresponding to an initial pressure of 1875 MPa) at RT and at 100 °C. The stroke was set to 4 mm with an oscillating frequency of 25 Hz, resulting in a sliding distance of about 6120 m for each measurement.

The investigated PEEK-coated sample had a journal bearing shell shape, which is usually subject to a sliding contact caused by rotational motion. Therefore, an SLPG tribometer with rotating motion was chosen, with a 10 mm X90CrMoV18 steel shaft mounted on the axis and rotating as a counter-body against the fixed PEEK journal bearing shell (Fig. 9).

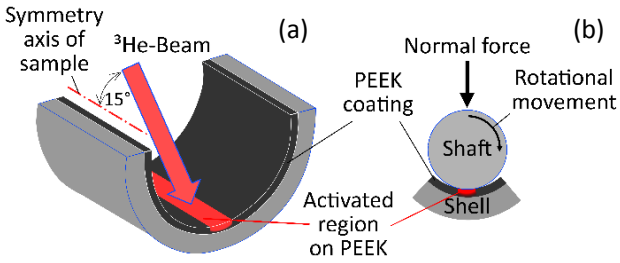

Figure 9. Tests on PEEK journal bearing shell: (a) schematic representation of the irradiation beam angle and (b) tribological contact situation with activation zone

Tests with a rotating shaft against the journal bearing shell were carried out at RT at three different normal loads (20, 30 and 40 N, resulting in different contact pressures of 26, 33 and 37 MPa, respectively) and therefore different tribological stress between the wearing parts. The tribocontact was diesel-lubricated, a ramp program consisting of repeated velocity ramps from 0 to 0.08 m/s and back to 0 m/s (with a ramp duration of one minute per ramp). Each wear measurement lasted 60 min, resulting in a sliding distance of about 290 m for each measurement.

Complementary to the RIC, the wear depth was also determined by an optical chromatic confocal profiler JR25 (Nanovea), with a lateral resolution of 1.3 µm and vertical resolution of 5.7 nm, after the end of the test run. Profiles were measured across the wear scar perpendicular to the sliding direction and the average depth of such a wear scar was calculated. Grooves and scratches lead to some uncertainties in evaluating the wear depth. Thus, there are some methodical differences between optical and isotope-based wear measurements, which need to be considered especially in the low micrometre or even submicrometer regime.

3.2 DLC tribometry – Results and discussion

The results of the RIC wear measurements for the DLC experiments are illustrated in Figure 10a. Each data point is obtained by averaging the wear signal over a period of 30 min. A significant difference can be seen between experiments at room temperature compared to the experiment with samples and lubricant heated to 100 °C. The wear progress of the test at 100 °C shows an exponential-like growth at the end of the wear progress. Exponential (or divergent) wear growth often indicates unstable or the beginning of severe wear that can lead to specimen failure. The tests carried out at room temperature show a constant wear rate (linear increase), indicating a "mild" wear compared to the experiment performed at 100 °C.

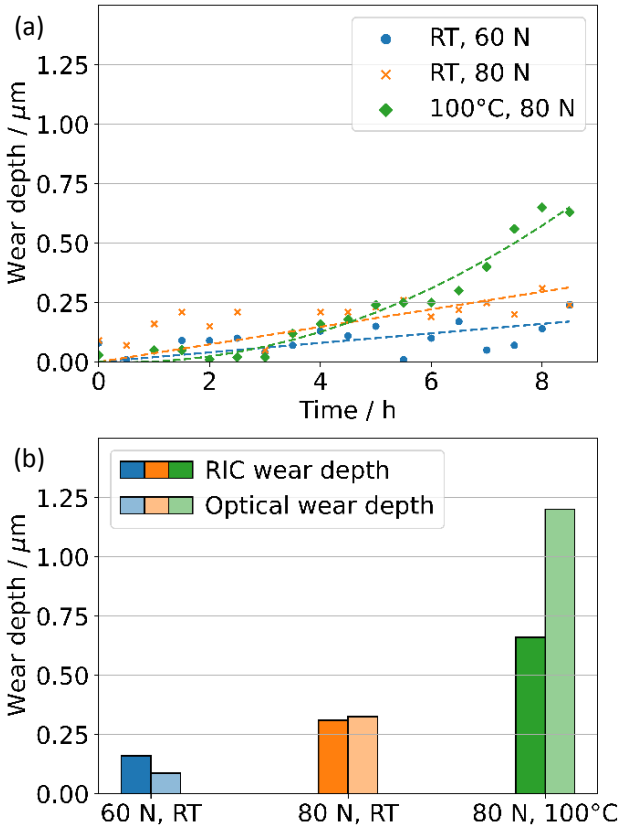

Figure 10. Results of: (a) continuous DLC wear data of RIC with variation of temperature and load and (b) wear depths at the end of measurements measured by RIC (opaque bars) and optical measurements by confocal microscopy (translucent bars)

The RIC and optical wear depths are compared in Figure 10b and show similar trends as a function of the testing parameters. The RIC wear depths in this graph are determined from the endpoints of the fit functions in Figure 10a. For the DLC experiments, no signals from particle depositions on the counter-body or in the lubricant circuit were detected and therefore no corrections to the

wear depth had to be made. Optically measured wear depths are shown in Figure 11.

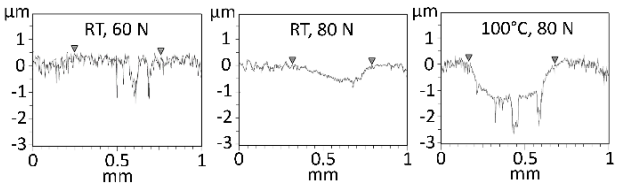

Figure 11. Cross-section of the wear tracks from the optical measurements of the three different tests on the DLC sample with the marked wear track widths

Considering these fundamental differences between the two measurement methods, the RIC and optical wear measurements are in good accordance. Compared to the optical method, the RIC method is additionally applicable for continuous monitoring and enables the differentiation of wear behaviour for different tribological conditions like different load and temperature, as well as for time-dependent wear phases such as running-in and steady-state wear.

Although the RIC method utilises the comparatively high count rate of radioactive decay, some uncertainties need to be considered. The continuous wear signal (data points) depends on several factors such as radioactive statistics and possible deposition of wear particles in the circuit. The former is a result of the absolute wear volume, the activity concentration in the measured material and the duration over which a single data point is averaged. However, despite the low activity of a single sample below the exempt quantities for radiation given by law, a wear resolution in the submicrometre range can be achieved.

3.3 PEEK tribometry – Results and discussion

Figure 12 illustrates the results for the PEEK journal bearing shell. Figure 12a shows the wear curves (wear depth over time) for the three normal loads. One data point represents the average value of 30 s measuring time. The noise/fluctuations of the wear curve are typical for the statistics of radioactive decay and can be considered negligible with respect to the measured wear depths. Consequently, it can be concluded, that the activity concentration in the PEEK material near the surface was suitable for wear measurement with good quality for the chosen measurement set-up (for example, lubricant volume, background noise, etc.). The total wear depth at the end of the test runs increased with increasing normal load, being 1.1, 1.9 and 2.5 µm for 20, 30 and 40 N, respectively.

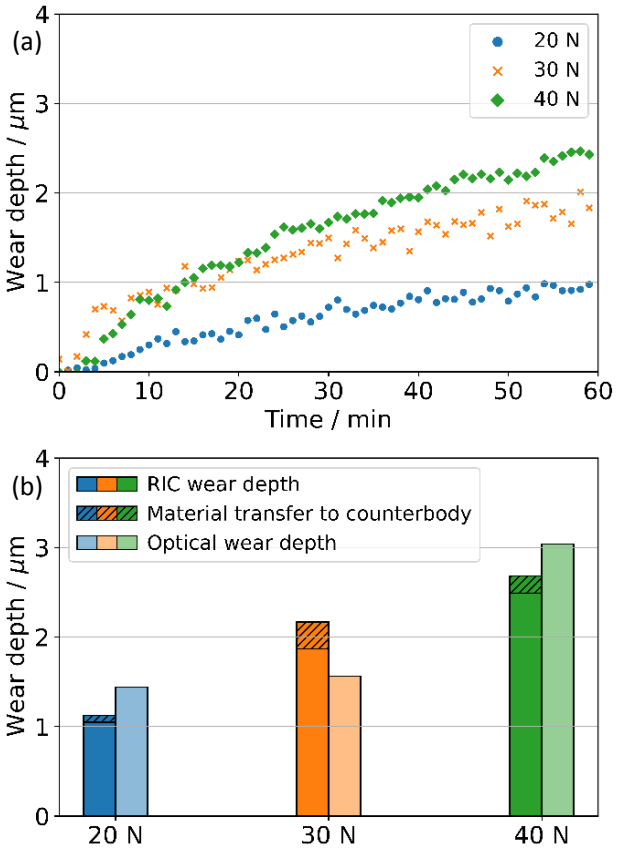

Figure 12. Results of: (a) continuous PEEK wear data of RIC for 20, 30 and 40 N load and (b) wear depths at the end of measurements measured by RIC (opaque bars from the continuous measurement and hatched bar from complementary counter-body measurements) and optical measurements by confocal microscopy (translucent bars)

Figure 12b presents the test results with different loading conditions measured by RIC and the confocal microscopy (cross-section of the different tests, see Fig. 13). For the RIC measurements the signals deposited on the counter-body and in the lubricant circuit were added to the end value of the online measurement. The RIC and optical wear depths show good agreement. Small deviations can arise from the different measuring principles and uncertainties in the exact determination of the wear track area.

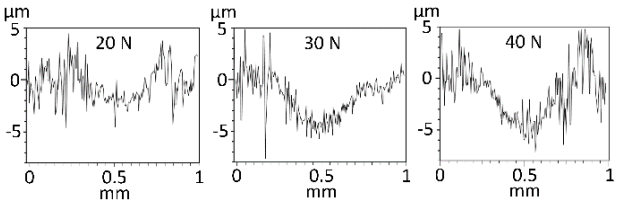

Figure 13. Cross-section of the wear tracks from the optical measurements of the three different tests performed on the PEEK sample

However, given the fact that the modulus of elasticity and hardness were slightly altered on the activated surface compared to the non-activated surface, it is advisable to only conduct comparative tribological testing (e.g. variation of loads) with the activation parameter chosen for this test. Lowering the beam current might lead to a better result in terms of PEEK material alteration.

4. Conclusion

The irradiation and experimental application of the irradiated samples for wear testing led to the following conclusions.

The activation of carbon-based materials by using the reaction $^{nat}C(^{3}He,x)^{7}Be$ leads to a sufficient amount/activity of ^{7}Be for the purpose of wear measurement even for a total activity of the specimen below the exempt quantities for radiation given by law.

Certain types of elastomers, such as EPDM, are significantly affected by TLA, resulting in either immediate degradation of the material due to a too-high irradiation beam current or to a mid/long-term alteration of the material properties, such as by embrittlement.

On the other hand, PEEK has proved to be applicable with TLA for wear measurement tasks, although marginal material changes have been observable. PEEK can be used for specific wear measurement tasks (e.g. relative comparison of wear for different loads) as well. However, to optimise the activation process for PEEK, we recommend even lower beam currents than the applied 460 nA.

TLA enables wear measurement with high resolution in the range of a few nanometres, also for carbon-based materials. Due to the good accordance between optical wear measurement results and wear measurement using the ^{7}Be isotopes, it can be concluded that the used cross-sections for the reaction $^{12}C(^{3}He,x)^{7}Be$ provided by the TLA tool are reasonable and reliable for industrial applications as well as for fundamental research of wear behaviour.

Acknowledgement

The work of the authors A. Hofer, M. Zellhofer, T. Wopelka and M. Jech was funded by the Austrian COMET Program (project K2 InTribology2, No. 906860) and carried out at the "Excellence Centre of Tribology" (AC2T research GmbH). The work of the authors F. Ditrói and S. Takács was partly supported by Project No. NKTA-42, which has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021 funding scheme. This work was also partly supported (F. Ditrói) by IAEA RER Project 1020 and by IAEA CRP F22069.

References

[1] M. Jech, C. Lenauer, Radionuclide methods, in P.J. Blau (Ed.), ASM Handbook, Volume 18: Friction, Lubrication, and Wear Technology, ASM International, Metals Park, 2017, pp. 1045-1055.

[2] F. Ditrói, S. Takács, F. Tárkányi, M. Reichel, M. Scherge, A. Gervé, Thin layer activation of large areas for wear study, Wear, Vol. 261, No. 11-12, 2006, pp. 1397-1400, DOI: 10.1016/j.wear.2006.03.049

[3] T. Wopelka, U. Cihak-Bayr, C. Lenauer, F. Ditrói, S. Takács, J. Sequard-Base, M. Jech, Wear of different material pairings for the cylinder liner – piston ring contact, Industrial Lubrication and Tribology, Vol. 70, No. 4, 2018, pp. 687-699, DOI: 10.1108/ILT-07-2017-0218

[4] E. Corniani, M. Jech, T. Wopelka, F. Ditroi, F. Franek, A. Pauschitz, High-resolution wear analysis of a ball-on-disc contact using low-activity radioactive isotopes, Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science, Vol. 226, No. 2, 2012, pp. 319-326, DOI: 10.1177/0954406211424865

[5] F. Ditrói, S. Takács, F. Tárkányi, I. Mahunka, Study of the $^{nat}C(^{3}He,2\alpha)^{7}Be$ and $^{9}Be(^{3}He,\alpha n)^{7}Be$ nuclear reactions and their applications for wear measurements, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, Vol. 103, No. 4, 1995, pp. 412-414, DOI: 10.1016/0168-583X(95)00660-5

[6] A. Ashfaq, M.-C. Clochard, X. Coqueret, C. Dispenza, M.S. Driscoll, P. Ulański, M. Al-Sheikhly, Polymerization reactions and modifications of polymers by ionizing radiation, Polymers, Vol. 12, No. 12, 2020, Paper 2877, DOI: 10.3390/polym12122877

[7] M. Tavlet, S. Ilie, Behaviour of organic materials in radiation environment, in Proceedings in the Fifth European Conference on Radiation and its Effects on Components and Systems (RADECS 99), 13-17.09.1999, Fontevraud, France, pp. 210-215, DOI: 10.1109/RADECS.1999.858582

[8] J.G. Drobny, Radiation-resistant polymers and their applications, Ionizing Radiation and Polymers, William Andrew, Oxford, 2013, pp. 213-224, DOI: 10.1016/B978-1-4557-7881-2.00007-9

[9] K. Wündrich, A review of radiation resistance for plastic and elastomeric materials, Radiation Physics and Chemistry (1977), Vol. 24, No. 5-6, 1984, pp. 503-510, DOI: 10.1016/0146-5724(84)90185-7

[10] G. Spadaro, S. Alessi, C. Dispenza, Ionizing radiation-induced crosslinking and degradation of polymers, in Y. Sun, A.G. Chmielewski (Eds.), Applications of Ionizing Radiation in Materials Processing, Institute of Nuclear Chemistry and Technology, Warsaw, 2017, pp. 167-182.

[11] J. Davenas, I. Stevenson, N. Celette, G. Vigier, L. David, Influence of the molecular modifications on the properties of EPDM elastomers under irradiation, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, Vol. 208, 2003, pp. 461-465, DOI: 10.1016/S0168-583X(03)00635-9

[12] G. Lee, Radiation resistance of elastomers, IEEE Transactions on Nuclear Science, Vol. 32, No. 5, 1985, pp. 3806-3808, DOI: 10.1109/TNS.1985.4334510

[13] H. Domininghaus, Kunststoffe [Plastics], Springer, Heidelberg, 2012, DOI: 10.1007/978-3-642-16173-5 [in German].

[14] D.G. McCulloch, D.R. McKenzie, S. Prawer, A.R. Merchant, E.G. Gerstner, R. Kalish, Ion beam modification of tetrahedral amorphous carbon: The effect of irradiation temperature, Diamond and Related Materials, Vol. 6, No. 11, 1997, pp. 1622-1628, DOI: 10.1016/S0925-9635(97)00033-2

[15] M. Zellhofer, M. Jech, E. Badisch, F. Ditrói, A. Kübler, P.H. Mayrhofer, Evaluation of wear measurement with radioactive isotopes for DLC coatings affected by abrasive particles, Tribology Letters, Vol. 70, 2022, Paper 55, DOI: 10.1007/s11249-022-01587-2

[16] G. Zheng, M. Zhu, C. Liu, Q. Xiao, Q. Wang, Progress in ionizing radiation resistance modification of polymer materials, Journal of Physics: Conference Series, Vol. 2109, 2021, Paper 012021, DOI: 10.1088/1742-6596/2109/1/012021

[17] J. Fontaine, Towards the use of diamond-like carbon solid lubricant coatings in vacuum and space environments, Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, Vol. 222, No. 8, 2008, pp. 1015-1029, DOI: 10.1243/13506501JET323

[18] A. Vanhulsel, F. Velasco, R. Jacobs, L. Eersels, D. Havermans, E.W. Roberts, I. Sherrington, M.J. Anderson, L. Gaillard, DLC solid lubricant coatings on ball bearings for space applications, Tribology International, Vol. 40, No. 7, 2007, pp. 1186-1194, DOI: 10.1016/j.triboint.2006.12.005

[19] B. Shi, Y. Wu, Y. Liu, L. Wang, J. Gao, H. Hei, K. Zheng, S. Yu, A review on diamond-like carbon-based films for space tribology, Materials Science and Technology, Vol. 38, No. 15, 2022, pp. 1151-1167, DOI: 10.1080/02670836.2022.2074124

[20] C. Donnet, J. Fontaine, T. Le Mogne, M. Belin, C. Héau, J.P. Terrat, F. Vaux, G. Pont, Diamond-like carbon-based functionally gradient coatings for space tribology, Surface and Coatings Technology, Vol. 120-121, 1999, pp. 548-554, DOI: 10.1016/S0257-8972(99)00432-6

[21] A. Choleridis, S. Sao-Joao, J. Ben-Mohamed, D. Chern, V. Barnier, G. Kermouche, C. Heau, M.-A. Leroy, J. Fontaine, S. Descartes, C. Donnet, H. Klöcker, Experimental study of wear-induced delamination for DLC coated automotive components, Surface and Coatings Technology, Vol. 352, 2018, pp. 549-560, DOI: 10.1016/j.surfcoat.2018.08.048

[22] I.S. Vinoth, S. Detwal, V. Umasankar, A. Sarma, Tribological studies of automotive piston ring by diamond-like carbon coating, Vol. 13, No. 1, Tribology – Materials, Surfaces & Interfaces, Vol. 13, No. 1, 2019, pp. 31-38, DOI: 10.1080/17515831.2019.1569852

[23] R. Hauert, An overview on the tribological behavior of diamond-like carbon in technical and medical applications, Tribology International, Vol. 37, No. 11-12, 2004, pp. 991-1003, DOI: 10.1016/j.triboint.2004.07.017

[24] İ. Ucun, K. Aslantas, F. Bedir, The performance of DLC-coated and uncoated ultra-fine carbide tools in micromilling of Inconel 718, Precision Engineering, Vol. 41, 2015, pp. 135-144, DOI: 10.1016/j.precisioneng.2015.01.002

[25] S. Grigoriev, M. Volosova, S. Fyodorov, M. Lyakhovetskiy, A. Seleznev, DLC-coating application to improve the durability of ceramic tools, Journal of Materials Engineering and Performance, Vol. 28, No. 7, 2019, pp. 4415-4426, DOI: 10.1007/s11665-019-04149-1

[26] Y. Ren, L. Zhang, G. Xie, Z. Li, H. Chen, H. Gong, W. Xu, D. Guo, J. Luo, A review on tribology of polymer composite coatings, Friction, Vol. 9, No. 3, 2021, pp. 429-470, DOI: 10.1007/s40544-020-0446-4

[27] N.A.M. Tahir, M.F.B. Abdollah, N. Tamaldin, H. Amiruddin, M.R.B.M. Zin, A brief review on the wear mechanisms and interfaces of carbon based materials, Composite Interfaces, Vol. 25, No. 5-7, 2018, pp. 491-513, DOI: 10.1080/09276440.2018.1380472

[28] Z. Zhang, X. Jia, F. Guo, Y. Wang, Effect of vulcanization on the tribological behavior and sealing performance of EPDM seals: Experimentation and simulation, Tribology International, Vol. 164, 2021, Paper 107219, DOI: 10.1016/j.triboint.2021.107219

[29] A. Mukhopadhyay, Friction and wear characteristics of indegenous 'EPDM' rubber under dry sliding condition, Asian Review of Mechanical Engineering, Vol. 3, No. 2, 2014, pp. 19-25, DOI: 10.51983/arme-2014.3.2.2382

[30] D. Massocchi, G. Riboni, N. Lecis, S. Chatterton, P. Pennacchi, Tribological characterization of polyether ether ketone (PEEK) polymers produced by additive manufacturing for hydrodynamic bearing application, Lubricants, Vol. 9, No. 11, 2021, Paper 112, DOI: 10.3390/lubricants9110112

[31] J. Zhu, F. Xie, R.S. Dwyer-Joyce, PEEK composites as self-lubricating bush materials for articulating revolute pin joints, Polymers, Vol. 12, No. 3, 2020, Paper 665, DOI: 10.3390/polym12030665

[32] S. Arevalo, C. Arthurs, M.I. Echeverria Molina, L. Pruitt, A. Roy, An overview of the tribological and mechanical properties of PEEK and CFR-PEEK for use in total joint replacements, Journal of the Mechanical Behavior of Biomedical Materials, Vol. 145, 2023, Paper 105974, DOI: 10.1016/j.jmbbm.2023.105974

[33] P.M. Racolta, Nuclear methods for tribology, Applied Radiation and Isotopes, Vol. 46, No. 6-7, 1995, pp. 663-672, DOI: 10.1016/0969-8043(95)00131-X

[34] M Scherge, K Pöhlmann, A Gervé, Wear measurement using radionuclide-technique (RNT), Wear, Vol. 254, No. 9, 2003, pp. 801-817, DOI: 10.1016/S0043-1648(03)00230-8

[35] B.N. Limata, L. Gialanella, A. Di Leva, N. De Cesare, A. D'Onofrio, G. Gyurky, C. Rolfs, M. Romano, D. Rogalla, C. Rossi, M. Russo, E. Somorjai, F. Terrasi, ^{7}Be radioactive beam production at CIRCE and its utilization in basic and applied physics, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, Vol. 266, No. 10, 2008, pp. 2117-2121, DOI: 10.1016/j.nimb.2008.02.083

[36] M. Hoffmann, K. Abbas, T. Sauvage, G. Blondiaux, L. Vincent, M.F. Stroosnijder, ^{7}Be recoil implantation for ultra-thin-layer-activation of medical grade polyethylene: Effect on wear resistance, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, Vol. 183, No. 3-4, 2001, pp. 419-424, DOI: 10.1016/S0168-583X(01)00721-2

[37] Thin layer activation (TLA) technique for wear measurement, available at: https://www-nds.iaea.org/tla, accessed: 10.07.2023.

[38] Experimental nuclear reaction data (EXFOR), available at: https://www-nds.iaea.org/exfor/exfor.htm, accessed: 10.07.2023.

[39] M. Ferry, Y. Ngono-Ravache, C. Aymes-Chodur, M.C. Clochard, X. Coqueret, L. Cortella, E. Pellizzi, S. Rouif, S. Esnouf, Ionizing radiation effects in polymers, in Reference Module in Materials Science and Materials Engineering, Elsevier, Amsterdam, 2016, DOI: 10.1016/B978-0-12-803581-8.02095-6

[40] J.H. O'Donnel, Radiation chemistry of polymers, in E. Reichmanis, J.H. O'Donnell (Eds.), The Effects of Radiation on High-Technology Polymers, American Chemical Society, Washington, 1989, pp. 1-13, DOI: 10.1021/bk-1989-0381.ch001