THE INFLUENCE OF MECHANICAL DAMAGING ON POSITRONS LIFETIME IN ULTRA-HIGH-MOLECULAR POLYETHYLENE

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The influence of damaging of the ultra-high-molecular polyethylene (PE-UHMW) Chirulen®1120, which is applied, among others, to produce hip endoprostheses, on spectra of positrons lifetime in this material was investigated. Polyethylene samples were damaged by: impact, rolling friction and collisions with metal balls in a planetary mill. Changes in the parameters of positrons lifetime spectra related to annihilation of ortho-positronium (o-Ps) were analyzed in dependence on the mechanical energy passed to the sample. On the basis of the Eldrup–Tao model, changes in the radii of voids in which a positronium is formed and annihilated, as well as changes in the degree of filling up the space atoms in the examined polymer were determined.

Keywords: *polyethylene, positronium, damaging, positrons lifetime.*

For many years new Polyethylene (PE) has been one of the polymers that is the most frequently used in practice. Its physical properties, and especially the mechanical and thermal ones, depend, among others, on the manner of its production and, therefore, it is an object of continuous researches concerning its morphology, structure and relaxation behavior [1–5].

PE is obtained in a high-pressure process, in the presence of initiators of radical polymerization or in a low-pressure process in which metal-organic catalysts of coordinating polymerization take part. Macro-molecules of PE which is formed in the high-pressure process, due to the considerable participation in them of the long branching side chains, which makes the dense packing difficult, are characterized by a low density (the so-called LDPE). On the other hand, the PE obtained in the low-pressure synthesis contains few short branchings, being a polymer of nearly linear structure thanks to which it possesses a higher density. It is labeled HDPE (High Density PE).

In the recent decade, PE of a very big mol mass, one exceeding 1000 kg/mol, and of the linear structure of its macro-molecules has been produced. It is labeled as PE-UHMW (Ultra High Molecular Weight Polyethylene). It is characterized by a good chemical and mechanical resistance, physiological indifference, good biological tolerance and by a relatively low production cost. For these reasons it is used in medicine on a broad scale to make surgical endoprostheses [5]. During the insertion in the patient and also while being exploited, the endoprosthesis is exposed to strong and cyclical mechanical stresses which can affect the duration and comfort of its usage. So far, in order to investigate destructions of PE-UHWM caused by mechanical factors macroscopic methods have been used mainly for researches. They consist in determining changes in, for instance, elasticity, hardness, friction coefficient, without penetrating in the microscopic changes occurring in the material.

Since 1996 [6] research in the mechanisms of formation and kinetics of defects in polymers has made use of the phenomenon of positrons annihilation, in particular the technique of measurement of positrons lifetime. The condition which allows applying

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this technique is the fact that part of the positrons which penetrate into the polymer sample can form positronium in it and the latter can come in two forms: ortho (o-Ps) and para (p-Ps). The positronium annihilating from the o-Ps state is characterized by the lifetime of 1–2 ns in the pick-off process. The time depends on, among others, the size and shape of free atoms of the polymer space.

Annihilation of positrons in PE has been investigated by many authors [7–18]. In the first works, the experimentally obtained spectra of positrons lifetime were distributed into two components, still the interpretation of the results turned out to be easier using de-convolution of spectra into three components, of which one was characterized by a long lifetime of the nanoseconds order. Some researchers [8, 10, 13] noticed the occurrence of one more long-lived component of the spectrum, also connected with the formation of o-Ps. An interpretation of the obtained values of positrons lifetime is difficult, for the reason that, generally speaking, the examined polymers had partially amorphous and crystalline structures. The crystalline phase of PE contains different forms of the polymer macro-chains ordering from lamellar and non-lamellar macro-crystals, in which the whole macro-particles are built in the crystalline structure through different forms of crystallites, where only fragments of macro-chains compose an ordered form. As Dlubek [10] and Dębowska [11] proved, the value of the long-lived component of the positrons lifetime spectrum in the crystalline state is lower than in the amorphous phase. For HDPE polymers, the long-lived component takes, generally, a lower value than that for LDPE polymers. Furthermore, the value of the long-lived component of this spectrum depends on a great number of physical factors such as temperature, time of initial annealing, pressure, illumination of samples with visible light while taking measurements, as well as cyclically changing strains.

At first the annihilation techniques were applied to investigations of equilibrium defects, and then of non-equilibrium ones in solids, assuming that the defects are distributed evenly over the whole volume of the material. Making use of the sources emitting mono-energetic positrons of regulated energy allowed examining the defect states in the top layer of solids. This in the most interesting question because the top layer can have completely different physical properties than the layers of material, which are deep inside the samples. The top layer of solids is often plastically deformed. The thickness of this layer depends, among others, on the way of mechanical interacting with the external layers.

The results of research by Dryzek, Pietrzak et al. [19–22] indicate, however, that application of the positron sources of a continuous energetistic spectrum of positrons can be used to investigate properties of the top layers of solids.

The primary mechanical and physiochemical properties of polyethylene of which an endoprosthesis is built can undergo considerable destructive changes both in the process of its installation and as a result of mechanical strains that change cyclically over a long period during movements. Therefore, it is indispensable to determine the changes occurring in the material of polyethylene under the influence of various factors leading to such a destruction.

We presented the results of research of positrons annihilation in PE-UHMW Chirulen®1120 polyethylene [23]. We proved there that after damaging caused by an impact, the parameters of o-Ps component of the positrons lifetime spectrum undergo changes. We also found that when the deformation caused by an impact is of the plastic character, the lifetime of the positronium and the intensity of the component corresponding to this channel of annihilation are subject to far clearer changes than after an elastic deformation. The value of the changes depends on the density of surface energy passed to the sample over a time unit. We come to deal with an impact-related action on PE-UHMW applied in an endoprosthesis mainly during its installation in the patient's body, whereas, while it is in use, we often deal with damaging the polyethylene material through rolling friction, as well as the joint stroke action and rolling friction.

This work presents the results of research on changes in positrons lifetime in the top layer of PE-UHMW Chirulen®1120 induced by defects formed in this layer by repetitive bombarding of the samples with metal balls in a planetary mill and by rolling friction.

Despite the fact that the results of the investigation of the influence of the stroke-based damaging were partially presented in [23], in this paper we are going to make references to them since it is only jointly that they can yield a certain picture of PE-UHMW Chirulen®1120 degradation in an endoprosthesis during its installation and usage. The stroke-based action described in [23] is connected with transferring mechanical energy in the direction perpendicular to the surface, while damaging which follows during rolling friction consists in passing energy in the direction parallel to the surface (Fig. 1). In turn, damaging in a planetary mill is connected with both a stroke and friction (Fig. 2). As it follows from a good amount of researches, the parameters of o-Ps component of positrons lifetime spectrum can be connected with the sizes of natural volumes that are free from atoms and with the degree of filling-up the space in the material with atoms [24–27].

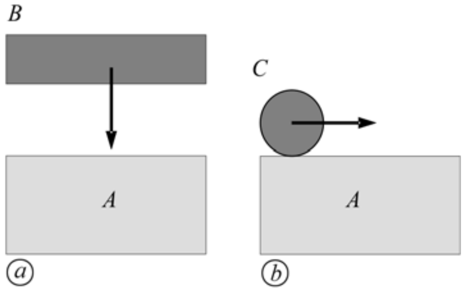


Fig. 1.

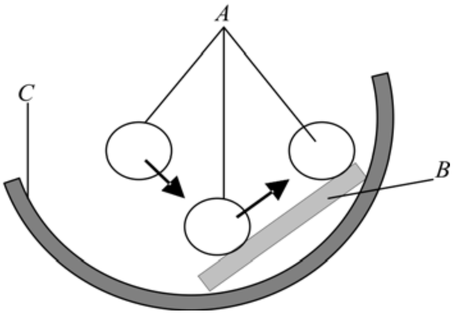


Fig. 2.

Fig. 1. Scheme of mechanical action on polyethylene during damaging: *a* – by an impact; *b* – by rolling friction (*A* – polyethylene sample; *B* – steel element acting on the sample; *C* – steel cylinder).

Fig. 2. Scheme of mechanical action on polyethylene during damaging in a planetary mill: *A* – steel balls; *B* – polyethylene sample; *C* – container.

One of the goals of the present work was also to determine to what degree the radii of voids in which positronium annihilates depend on the manner of passing energy to the sample and its value. We hope that the obtained information can prove to be useful in the technology of new types of this polymer to equip it with even better physiochemical properties.

Experimental part. The samples used in the research were 3 mm thick discs, with the diameters of 10 mm (for impact-and slide-based investigations in the mill) and 21 mm (for the tribological investigations), respectively. The samples were cut out of large blocks of material at temperatures not exceeding 100°C. On having been cut out, they were being annealed for 5 h at 60°C, under lowered pressure, and slowly cooled down to room temperature. Then, the surfaces of the samples were cleaned for a few hours in an ultrasonic cleaner, also at 60°C. For the thus prepared samples, before damaging them, positrons lifetime were measured. The source of 22 Na positrons was placed between two identical samples. Thanks to that, positrons penetrated into the area of the surface layer and the majority of them annihilated there. The samples were damaged after the measurement and their positrons lifetime spectra were measured again.

The stroke-slide damaging of the samples took place in Pulversisete 7 planetary mill manufactured by Fritsch. On the bearing plate of the mill there was a container in which there were placed two samples and 8 steel balls with the masses of 8 g or 16 g, respectively, and the diameters of 6.3 mm and 7.9 mm, respectively. The bearing plate of the mill and the container were rotating in the opposite directions. While the plate and the container were rotating, the balls in it crashed against and then rolled over the sample, altering partially its surface structure. The time of damaging always amounted to 10 min. The used frequencies ω of the mill rotating were 400 and 1066.5 min^{-1}.

The tribological damaging of the samples (through rolling friction) took place at a specially constructed device (Fig. 3). A steel cylinder rolled 10 times over the samples placed in special recessions, at the speed of 1.1 and 1.31 cm/s, respectively. The applied parameters of stress N on the sample were 22.1 and 46.2 MPa, which corresponded to a relative decrease in the thickness by 3.33 and 6.66%.

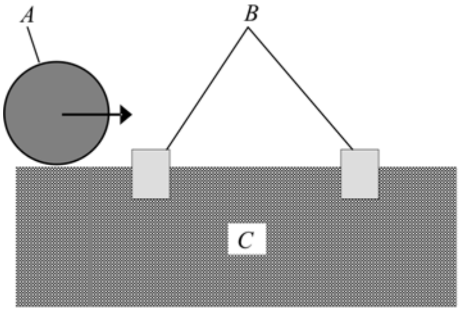


Fig. 3. Scheme for damaging samples during rolling friction: *A* – steel cylinder; *B* – polyethylene samples; *C* – steel plate with recesses for samples.

The description of damaging of the samples by a stroke and the manner of determining the duration of a collision are included in [23].

The lifetime spectra were measured by means of a fast-fast spectroscope with the resolution of 220 ps. The source of positrons was placed between two samples of the same degree of damaging. The experimentally measured spectra of positrons lifetime always exceeded 106 impulses. The de-convolution of the spectra into discreet components was made with the use of Lifetime 9 program [28]. The spectra were analyzed by accepting that they were composed of: one component, two free components, three free components, four components, of which one had an assumed value of 125 ps.

In order to interpret the results, distributions were chosen for which the index of experimental data adjustment to a selected annihilation model (χ^2) was the closest to one and the scatter of points on the so-called error strip did not display systematic changes. The obtained results indicate that the best adjustment is always obtained with the distribution of spectra into two free components, still the component of a greater value of positrons lifetime took on values exceeding 2.1 ns. That testified to the formation of o-Ps in the investigated samples.

Results of the measurements and their interpretation. The majority of researchers investigating positrons annihilation in polyethylene have managed to resolve the experimentally obtained spectra of positrons lifetime into three and even four components, of which, at least, one component has the lifetime of the nanoseconds order. Perhaps the reason why it has not been possible to distinguish, in the spectrum, two components of the picoseconds order was the insufficient temporal dissolution ability of the spectrometer used, and the determined short-lived component of the spectrum is a composition of two components of the similar lifetime values. The physical interpretation of the changes in this component is difficult and not unambiguous. Therefore, further in the work, we will discuss the changes in the clearly distinguished long-lived component of the spectrum, interpreted as a result of the creation and annihilation of o-Ps in the pick-off process.

It seemed natural to us to accept the assumption that the annihilation parameters of this long-lived component of the spectrum (positrons lifetime τ_2 and intensity of the component I_2) depend on energy (falling to a unit of deactivated surface) passed to the sample over a unit of time. That is why we will discuss the changes in the values of lifetime τ_2 of positrons which annihilate in the pick-off process induced by different factors: rolling friction, damaging in a planetary mill and a stroke in dependence on the energy passed.

For samples damaged by a stroke in the direction perpendicular to the surface. The energy passed to the sample was calculated as the difference in the potential energies of the Charper hammer before and after a stroke. A half of the measured time of the stroke was accepted to be the time of compression action during the stroke.

For samples damaged by friction. Work done during the rolling friction of the metal cylinder against the sample was accepted to be the energy passed to the sample.

Work W done against the forces of friction T during rolling along path d equals:

$$W = T \cdot d\,, \tag{1}$$

Whereas, the force of friction is equal:

$$T = \mu \cdot N\,, \tag{2}$$

where μ is rolling friction coefficient; N is force of pressure exerted by the cylinder on the sample during rolling.

The initial calculations pointed to the fact that the stresses applied in the experiment resulted in elastic deformations in the sample. Thus:

$$N = S \cdot E \cdot \frac{\Delta l}{l}\,, \tag{3}$$

where S is area of cross-section of the sample; $\Delta l/l$ is relative decrease in the thickness of the sample; E is Young's modulus. Since the cylinder was rolling along path d with constant velocity υ, hence $t = d/\upsilon$. Substituting dependences (2) and (3) in Eq. (1), we will finally notice that during one rolling of the cylinder over the sample the following energy will be passed to the sample within a time unit:

$$\varepsilon = \frac{W}{S \cdot t} = \mu \cdot E \cdot \upsilon \cdot \frac{\Delta l}{l}\,, \tag{4}$$

On the other hand, after the n-th (n = 10) rolling, the sample will receive the energy:

$$\varepsilon = n \cdot \mu \cdot E \cdot \upsilon \cdot \frac{\Delta l}{l}\,, \tag{5}$$

For further calculations we accept that $\mu = 0.007$, $E = 750$ MPa. The values υ and Δl are included in Section 2.

For samples damaged in a planetary mill. It was proved [29] that in the process of interaction between the balls and the sample there is the passed energy W which equals as follows:

$$W = A \cdot m \cdot \omega^2 \cdot r^3, \tag{6}$$

where m is mass of the balls; ω is frequency of rotating of the mill wheel; r is diameter of the balls; A is constant, dependent on the type of material, number of balls and number of strokes of the balls against the sample.

For further calculations we accept that the mean time of interaction between the balls and the sample equals the mean time of interacting during a stroke, which amounts to $1.02 \cdot 10^{-3}$ s. Knowing the sizes and masses of the balls, it is possible to determine the value $\varepsilon = \frac{W}{S \cdot t}$.

Fig. 4 shows the dependence of lifetime τ_2 on the energy passed to a unit surface over a unit of time. It can be seen that for all the ways of damaging time τ_2 rises approximately in a logarithmic manner along with a rise in the energy passed to the sample during damaging.

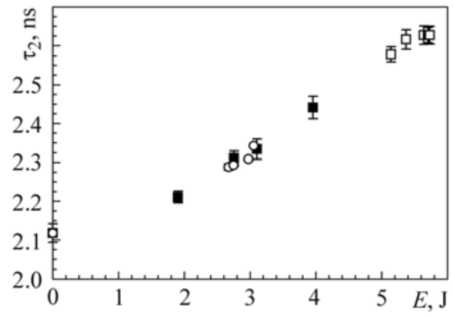


Fig. 4.

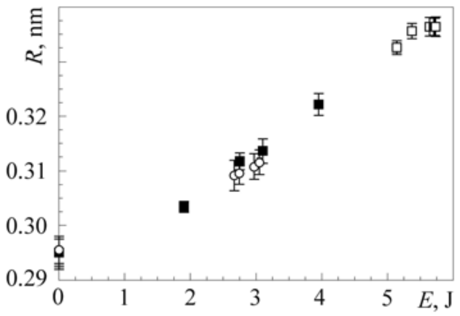


Fig. 5.

Fig. 4. Dependence of the o-Ps component of lifetime, τ_2, of the spectrum of positrons lifetime in PE Chirulen®1120 on the energy passed to the sample during damaging: by rolling friction (○); in a planetary mill (■); by an impact (□).

Fig. 5. Dependence of the value of the radii of spherical voids in which positronium forms on the energy passed to the sample during damaging: by rolling friction (○); in a planetary mill (■); by an impact (□).

In compliance with Eldrup's [24] and Tao's [25] models, o-Ps component of the spectrum of positrons lifetime in polymers, liquids and porous materials is connected with the mean radius of free volume, in which positronium is formed. For the voids of spherical symmetry and radius R, the relation takes on the form:

$$\tau_2 = \lambda_0\left[1-\frac{R}{R+\Delta R}+(2\pi)^{-1}\sin\frac{2\pi R}{R+\Delta R}\right]^{-1}, \qquad (7)$$

where ΔR is a constant parameter determined experimentally. In this work, we accepted that $\Delta R = 0.1656$. The dependence of the values of radii R, calculated with the use of (7) on the energy passed to the sample, is presented in Fig. 5. As it is visible, the values of the radii of empty space, in which o-Ps annihilates, increase very clearly together with the amount of the energy passed, and their values change from 44% to 14% in relation to the voids in non-defected PE Chirulen®1120, in dependence on the manner of damaging.

The energy absorbed by the polymer initiates cracking of the bonds of both C–H and C–C. As a result the hydrogenous radicals, as well as alkyl radicals of the first and the second order are formed. They are characterized by (especially the hydrogenous radicals) a high motility. Their transfer within the matrix causes the occurrence of voids of spherical symmetry in which positronium is formed. As it can be seen, the radii of these voids depend on the size of the energy passed to the sample, still their concentration, determined by intensity I_2 of the long-lived component of the spectrum of positrons lifetime depends also on the way of passing energy to the sample.

Fig. 6 presents the dependence of I_2 on the energy passed to the sample in a unit of time. For the manners of damaging described in this paper the intensity I_2 decreases along with the amount of the transferred energy; however, the drop in the intensity is the fastest for damaging of samples during rolling friction and the slowest – during damaging in a planetary mill. The character of the dependences of the radii of the voids in which positronium is formed and the concentration of these voids on energy suggests that looser spaces in the PE Chirulen®1120 sample are formed probably as a result of associations existing still before damaging of voids of a smaller radii. It can also be thought that the passing energy in the direction parallel to the surface of the sample favours loosening of close-to-surface layers of defected samples.

Measurements of the spectra of positrons lifetime in systems in which positronium is formed allow determining the parameter called a relative free volume, which is significant from the point of view of medical applications of the examined polymer. The parameter is defined in the following way:

$$F = \frac{(V_t - V_0)}{V_0}, \tag{8}$$

where V_t is the total macroscopic volume of the examined sample; V_0 is a sum of the volumes occupied by all the atoms of the sample.

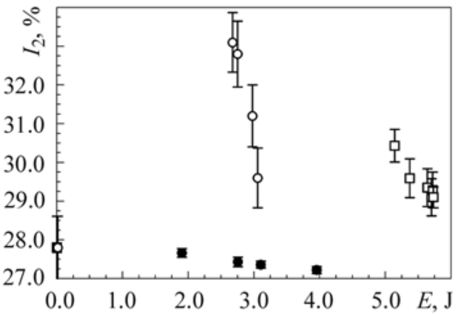
Wang [26] and also Kobayashi [27] proposed a half-empirical dependence to determine the value of this parameter on the basis of parameters of the positrons lifetime spectra:

$$F = A \cdot \frac{4}{3}\pi R^3 \cdot I_2, \tag{9}$$

where A is a normalizing constant, equaling, approximately, unity (at room temperature); R is the radius of a spherical void calculated from the Eldrup–Tao formula.

Fig. 7 presents the dependence of the relative free volume calculated from Eq. (9) on the surface density of mechanical energy passed to the investigated samples over a unit of time. As it can be seen, for damaging during rolling friction and a stroke the relative free volume in the close-to-surface layers of this polymer decreases along with the rise in the energy passed, whereas it increases during damaging in a planetary mill.

The mechanism of these changes is not yet fully understood and will make a subject of further research.



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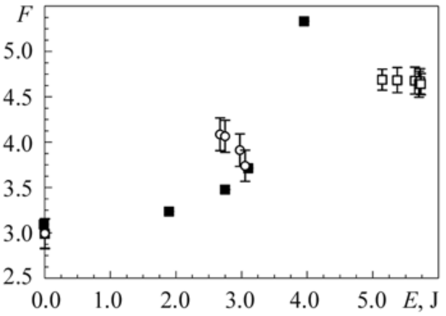

Fig. 7.

Fig. 6. Dependence of intensity, I_2, of the o-Ps component of the spectrum of positrons lifetime in PE Chirulen®1120 on the energy passed to the sample during damaging: by rolling friction (○); in a planetary mill (■); by an impact (□).

Fig. 7. Dependence of relative free volume, F, in PE Chirulen®1120 on the energy passed to the sample during damaging: by rolling friction (○); in a planetary mill (■); by an impact (□).

CONCLUSIONS

The conducted research shows that regarding PE Chirulen®1120 there occur conditions for positronium to form; during mechanical damaging, the radii of voids of spherical symmetry increase along with a rise in energy passed to the sample, independent of the manner of damaging; concentration of voids decreases along with a rise in energy passed to the sample, still the rate of the changes in the concentration depends on the manner of damaging; damaging of PE Chirulen®1120 samples in a planetary mill causes expansion of relative free volumes, while damaging by friction and impact decreases this parameter together with the amount of mechanical energy passed during the damaging.

РЕЗЮМЕ. Досліджували вплив пошкоджень ультрависокомолекулярного поліетилену марки Chirulen®1120, який застосовують для виготовлення тазостегнових ендопротезів, на час існування позитронів в цьому матеріалі після опромінення. Зразки поліетилену пошкоджували в лабораторних умовах методами удару, вальцювання та тертя, а також шляхом зіткнення з металевими кульками у планетарному млині. Зміни часу існування орто-позитронів аналізували залежно від механічної енергії, отриманої зразком, а зміни радіусів порожнин, в яких утворюються та анігілюються позитрони, визначали, застосовуючи модель Елдрупа–Тао.

РЕЗЮМЕ. Исследовали влияние повреждений ультравысокомолекулярного полиэтилена марки Chirulen®1120, который применяют для изготовления тазобедренных эндопротезов, на время существования позитронов в этом материале после облучения. Образцы полиэтилена были повреждены в лабораторных условиях методами удара, прокатывания и трения, а также путем столкновения с металлическими шариками в планетарной мельнице. Изменения времени существования орто-позитронов анализировали в зависимости от механической энергии, полученной образцом, а изменения радиусов полостей, в которых образуются и аннигилируются позитроны, определяли с применением модели Елдрупа–Тао.

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