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Ageing Phenomenon in Acrylic Polymer Dental Materials Detected by Means of Positron Annihilation Lifetime Spectroscopy

Zjawisko starzenia się w akrylowych materiałach dentystycznych mierzone za pomocą spektroskopii czasów życia pozytonów

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A – research concept and design; **B** – collection and/or assembly of data; **C** – data analysis and interpretation; **D** – writing the article; **E** – critical revision of the article; **F** – final approval of article

Abstract

Background. Polymer materials based on acrylic monomers are commonly used in dentistry. It is important to research the structure of dental filling materials towards the material ageing.
Objectives. The study has been conducted in order to determine the presence of free volume gaps in the structure of polymer materials.
Material and Methods. Brand new, acrylic polymer based samples of dental Dipol materials were used as a research material. The study was conducted by means of the positron annihilation lifetime spectroscopy (PALS).
Results. As a result of the conducted measurements, curves describing numbers of counts of the acts of annihilation in the time function were obtained. The conducted studies revealed the existence of four components τ1, τ2, τ3 and τ4. The τ3 and τ4 components are attributed to the pick-off annihilation of o-Ps orthopositronium trapping by free volume gaps and provide information about geometrical parameters of the volumes. LT 9 computer program was used to calculate components. Free volume holes were determined from empirical relationship between the radius of free volume and the long lifetime components.
Conclusions. Conducted studies indicate the presence of free volume holes in the research materials. It has been noted that a new long lifetime component is assigned to a new kind of free volumes that exist in the structure of material related to the material ageing **(Polim. Med. 2014, 44, 1, 21–28)**.

Key words: acrylic polymers, dental materials, positron annihilation, free volumes.

Streszczenie

Wprowadzenie. Materiały polimerowe oparte na monomerach akrylowych są powszechnie stosowane w stomatologii. Ważnym aspektem staje się badanie struktury wewnętrznej dentystycznych materiałów wypełnieniowych w kierunku ich starzenia się.
Cel pracy. Badania zostały przeprowadzone w celu wykazania występowania swobodnych objętości w strukturze wewnętrznej materiałów polimerowych.
Materiały i metody. Nowe próbki o nazwie Dipol, oparte na polimerach akrylowych, zostały zastosowane jako materiał badawczy. Badania struktury wewnętrznej próbek były przeprowadzone z użyciem spektroskopii czasów życia pozytonów (PALS).
Wyniki. W wyniku przeprowadzonych pomiarów uzyskano krzywe opisujące ilość zliczeń aktów anihilacji par pozyton–elektron w materiale w funkcji czasu. Badania wykazały istnienie w widmie czasów życia pozytonów czterech składowych

τ1, τ2, τ3 i τ4. Składowe τ3 i τ4, dające informacje o geometrycznych parametrach wolnych przestrzeni, są związane ze zjawiskiem anihilacji w wyniku procesu pick-off ortopozytu (o-PS) zlokalizowanego w swobodnych objętościach. W celu rozkładu widma czasów życia pozytonów zastosowano program komputerowy LT9. Następnie wymiary swobodnych objętości zostały obliczone z użyciem empirycznej zależności między promieniem swobodnej objętości a czasem długo żyjącej składowej widma.

Wnioski. Przeprowadzone badania wskazują na istnienie w badanym materiale swobodnych objętości. Zauważono również, że długo żyjącą składową można przyporządkować istnieniu nowych centrów anihilacji w materiale związanych z procesem jego starzenia się **(Polim. Med. 2014, 44, 1, 21–28)**.

Słowa kluczowe: polimery akrylowe, materiały dentystyczne, anihilacja pozytonów, swobodne objętości.

With the beginning of the third Millennium, the modern Materials Science Engineering has faced new challenges, which determine the economical sustainability and the quality of life of the modern human society [1]. Such spheres of people's activity as energy and living environment, life safety and security, mobility and transportation, information and communication, medicine and health care have become most important ones, where successes in the development of new materials play a pivotal role, the latter being decisive in the view of the future socio-economic human prosperity. That is why new materials for advanced medical application – biomaterials – are currently in a sphere of interests for a great number of scientists, from pure materials-science theoreticians-physicists-chemists to technologists-designers-engineers and consumer-end-users (incl. biologists), converging interdisciplinary approach evolved materials structural organization from angstrom/nano-/sub-nano- to micro-meso-macro scale levels [2]. In fact, modern biomaterials used in the majority of eventual medical applications are typically used as biologically-adaptive implants, which, when it comes to their chemical origin, are polymeric and, from the point of view of their environmental response in a human body, are biological Undoubtedly, all breakthrough resolutions in the medical sphere have been achieved due to successes in biopolymers [3, 4].

Polymers are materials composed of large molecules (macromolecules) by repeating certain structural units. These units are typically connected by covalent chemical bonds, which make them similar to network glasses [5]. The term polymer covers a large, diverse group of molecules, including substances from proteins to high-strength Kevlar fibers. The repetition of monomers occurs during polymerization, in which many molecules link to each other. Because polymers are distinguished by constituent monomers, polymer chains are often not of equal length [6].

Attractive forces between polymer chains play an important role in polymer properties. Because chains are so long, these inter-chain forces are amplified far beyond attractions between molecules. Also, longer chains are more amorphous (randomly oriented). These stronger forces typically result in high tensile strength and melting points. Polymeric systems require controlled mixing/compounding, the stabilization of the achieved dispersion, orientation of the dispersed phase, and the optimization of interactions in the finished product. Appropriate properties of polymeric materials are very important in various medical applications, including dentistry. Polymers based on acrylic monomers are mainly used in dentistry [4]. Dental filling Dipol is the example of the use of acrylic polymers [7]. Most commonly utilized dental materials are composite materials, containing resins based on Bisphenol A-Glycidyl Methacrylate, referred as Bis-GMA. This type of resin has large viscosity; hence it is difficult to mix inorganic phase into the matrix. Tri-ethylene glycol dimethacrylate (TEGMA) is commonly used to control the viscosity of the unmixed resin. Structure formulas of Bis-GMA and TEGMA are presented in Fig. 1.

Free positron annihilation is a process involving the change of the entire mass of both particles and of their kinetic energy into the photon energy of electromagnetic radiation. This is why studying photons formed in the process of annihilation provides information about the condition of the annihilating electron positron pair. Apart from free annihilation, there is also the bounded state annihilation when a positron forms with an electron a hydrogen-like atom called a Ps positronium. The high energy positron annihilation in the matter is preceded by the phenomenon of thermalization, which involves the quick loss of positron energy due to scattering and excitation of the medium and thermalization. When losing the last 10–50 eV of its energy, a positron covers the distance of the same order and then there may occur the reaction of positronium formation with one of the liberated electrons accompanying, as it were, the positron. Due to different placement of spins, we can distinguish 2 different types of positronium: parapositronium p-Ps of anti-parallel placement of spins (the 2g annihilation) and ortho-positronium o-Ps of parallel placement of spins (the 3g annihilation). Physical properties of a positronium change as a result of its interaction with the surrounding medium. One of the observed phenomena is the shortening of three-photon orthopositronium mean annihilation lifetime, which is also called o-Ps annihilation. The basic annihilation process is the "pick-off" annihilation. It involves the ability of the positron, which is the part of orthopositronium, to perform two-photon

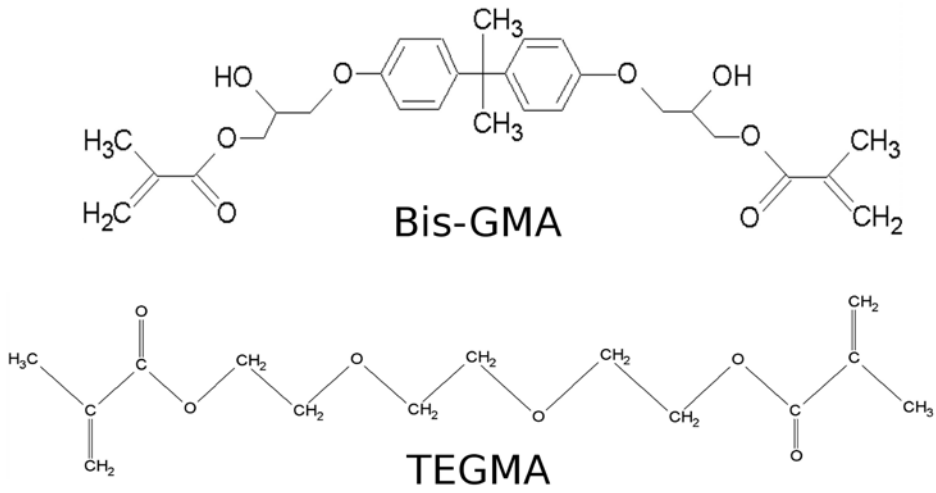

Fig. 1. Structural formula of Bis-GMA and TEGMA

Ryc. 1. Wzory strukturalne Bis-GMA i TEGMA

annihilation with one of the atoms that can be found in the surroundings of the positronium. The existence of free volume holes, an area of zero electron-density, is necessary so that the positronium can survive in condensed medium without succumbing to extinction with an average life span by 2 orders of magnitude faster than in a vacuum. Local free volume holes occur due to irregular molecular packing in the materials. Structural changes are combined with changes in the free volume [8].

In this paper, the relationship between the lifetime of orto-positronium o-Ps, and the size of free volume holes is described by the Tao–Eldrup model [9, 10]. It assumes that the positronium is located in a single spherical potential well. In order to simplify calculation, the replacement of the finite potential trough by an infinite potential trough, restricted by the ΔR parameter. The value of the ΔR parameter should be chosen in such a way so that the probability of finding the positronium outside the sphere of radius R remains unchanged. Furthermore, a very successful semi-empirical equation has been established, relating the o-Ps lifetime to the size of the free volume hole in which it annihilates, thus τ3 corresponds to a spherical space with a radius R of the free volume holes, according to the following equation:

$$\tau = 0.5\left[1-\frac{R_0-\Delta R}{R_0}+\frac{1}{2\pi}\sin\left(2\pi\frac{R_0-\Delta R}{R_0}\right)\right]^{-1} \quad (1)$$

where ΔR = 0.166 nm is the fitted empirical electron layer thickness. By fitting the above equation with the measured τ3 values, the Vf volume of free volume holes is the following function of R:

$$V_f = \frac{4}{3}\pi R^3 \quad (2)$$

The relative intensity of the longest component I3, is generally correlated to the density of the holes, which can be considered as a kind of trapping centres for Ps. A semi-empirical relation may be used to determine the fractional free volume (f v) in polymers as:

$$f_V = CV_fI_3 \quad (3)$$

where:
Vf – is the free volume calculated from τ3, using Eq. (1) with a spherical approximation,
I3 – (in %) is the intensity of long-lived component,
C – is empirically determined to be 0.0018 from the specific volume data [11].

In this paper, the authors described the influence of ageing effect on the polymer dental material. Changes of structural parameters were obtained by means of the positron annihilation lifetime spectroscopy (PALS) and further discussed in this work. Figure 2 shows the essence of conducted studies. There is presented a summary of research containing main points of work, such as measurement, obtained data in the form of spectra and calculations by means Tao-Eldrup theory. More details about the measurement method are described in the experimental section.

Material and Methods

The aim of this study was to determine free volume holes dimensions in acrylic dental materials Dipol using the positron annihilation lifetime spectroscopy (PALS). Three samples, characterized by a different time of polymerization process, were subjected to the research. Samples were prepared by the Department of Pediatric Dentistry at Lviv National Medical University. Research material consists of acrylic matrix, based on

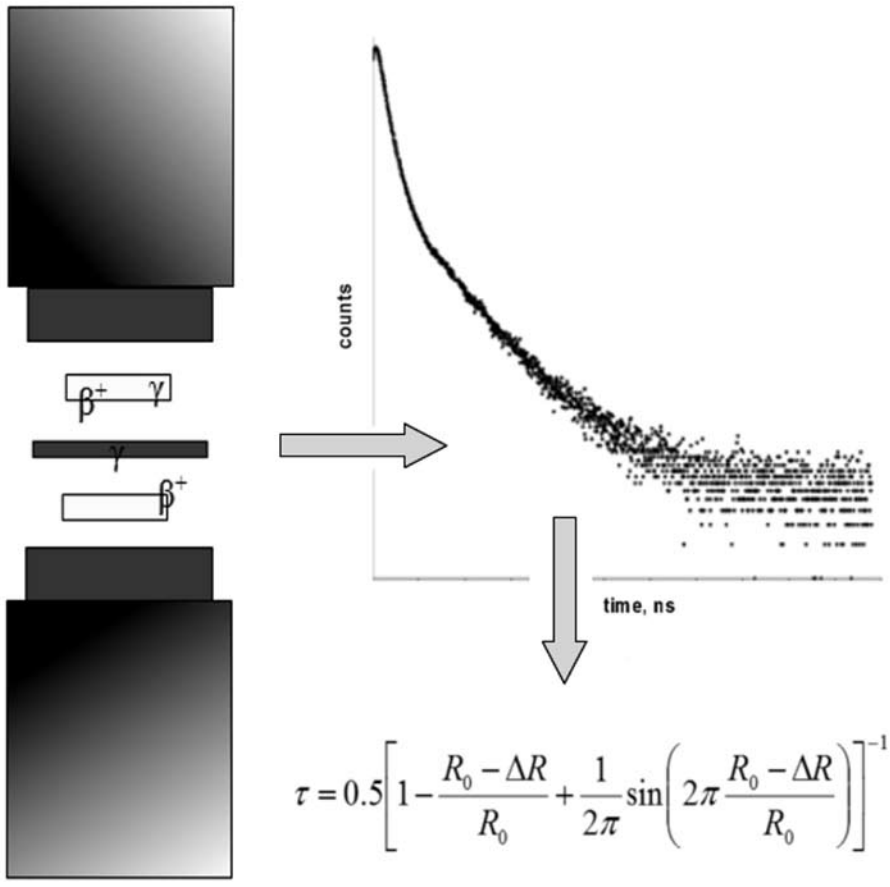

Fig. 2. Essence of conducted studies showing: measurements, received data and calculations on them

Ryc. 2. Rysunek poglądowy ukazujący istotę przeprowadzanych badań obejmujący proces pomiarowy, uzyskanie danych i przeprowadzenie obliczeń

Bis-GMA with TEGMA, modified by sub-micro particles of silica and fluoride. Furthermore samples contain a radiation-activated initiator. Acrylate materials were affected by photoexposure to light with the wavelength up to 450 nm. The 1st sample was polymerized to 5 s photoexposure, the 2nd sample to 20 s photoexposure and the 3rd sample to 60 s photoexposure [7]. The time of 20 s is considered as the time of the optimal curing recommended by the manufacturer. Samples were formed from discs of about 5 mm in diameter and about 1–2 mm of thickness.

An apparatus manufactured by ORTEC, based on „start-stop" mode, was used to determine the positron lifetime. The block scheme of the apparatus is shown in Fig. 3. The system can measure the time between the birth of a positron in a source and the death of the positron in the material by using 2 measuring lines. The Na-22 isotope with 4 × 105 Bq activity was used as a source of positrons. The time resolution of the system was obtained by using Co-60 isotope and equaled FWHM = 260 ps. During the measurement, the source located between 2 samples formed a so-called „sandwich" system. Measurements were performed twice at the same samples, at first in 2011 and then, for the second time, in 2013. Before measurements in 2013, samples were stored in a dry and dark place at room temperature.

Results

As a result of measurements, a curve of the number of counts of annihilation acts was obtained as a function of time. The spectrum was separated into components by using LT9 computer program [12]. Attempts were made to achieve 4 components. Results of the 2011 measurements gave only 3 components, whereas later measurements showed the existence of 4 components into the spectrum. Among the received components, the shortest lifetime component attributed to p-Ps annihilation was equal to 0.125 ns. The intermediate component indicates trapping of positrons and their free annihilation in the material. Fixed value of short lifetime

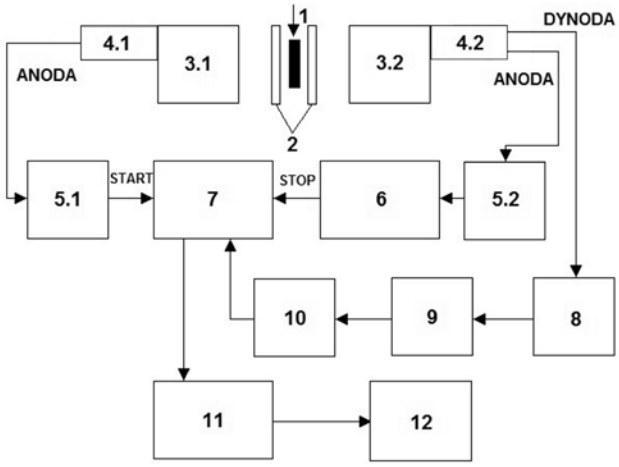

Fig. 3. Block diagram of positron lifetime spectrometer 1 – positron source (^{22}Na); 2 – two identical parallel fiat sample; 3.1.3.2 – sciiitillators; 4.1.4.2 – photomultiplier (RCA8575); 5.1.5.2 – constant fraction discriminator (ORTEC473A); 6 – delay linę (ORTEC 425A); 7 – converter tiine to amplitudę (ORTEC 467); 8 – preamplifier (ORTEC 113); 9 – amplifier (ORTEC 471); 10 – single channel analyzer amplitudę (ORTEC 455); 11 – multichannel analyzer (TUKAN 8K); 12 – PC computer

Ryc. 3. Schemat blokowy spektrometru czasów życia pozytonów: 1 – źródło pozytonów (^{22}Na); 2 – dwie identyczne równoległe płaskie próbki; 3.1.3.2 – scyntylatory; 4.1.4.2 – fotopowielacze (RCA8575); 5.1.5.2 – stałofrakcyjne dyskryminatory (ORTEC473A); 6 – linia opóźniająca (ORTEC 425A); 7 – konwerter czas amplituda (ORTEC 467); 8 – przedwzmacniacz (ORTEC 113); 9 – wzmacniacz (ORTEC 471); 10 – jednokanałowy analizator amplitudy (ORTEC 455); 11 – analizator wielokanałowy (TUKAN 8K); 12 – PC komputer

component allowed obtaining intermediate component values which are in accordance with theoretical values. The long lifetime components relate to the annihilation of o-Ps in the gaps of the research material. The radiuses of gaps, their volumes and the fraction of free volumes were determined by using equations (1), (2), (3). Similarly to the earlier publications [13–15], dealt with the analysis was the third component of the positron lifetime τ3 and their intensities, concerning free volumes. Also, existence of τ4 component was explained. Results of the 2011 measurements are collected in Table 1 and presented in charts in Fig. 4, 5, where volumes and the fraction of free volumes for individual samples are shown. The 2013 results are shown in Tables 2, 3 and in charts in Figs. 6–9.

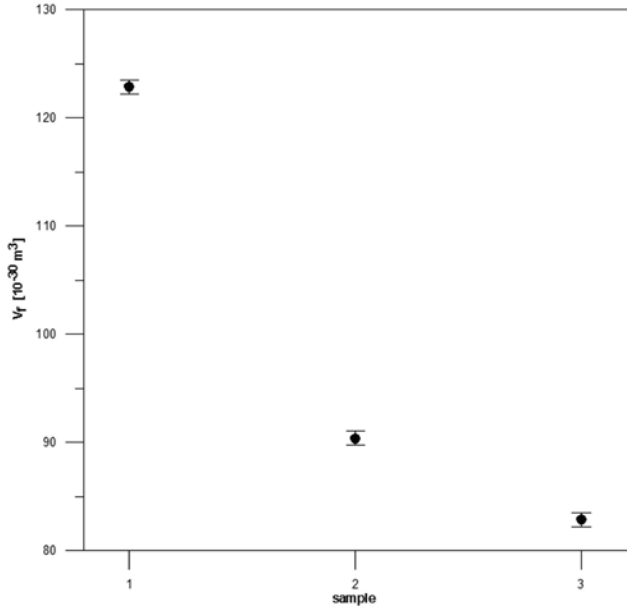

Fig. 4. The average free volume size for: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s. The 2011 measurements

Ryc. 4. Średnie wymiary wolnych objętości dla: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s; pomiary z 2011 r.

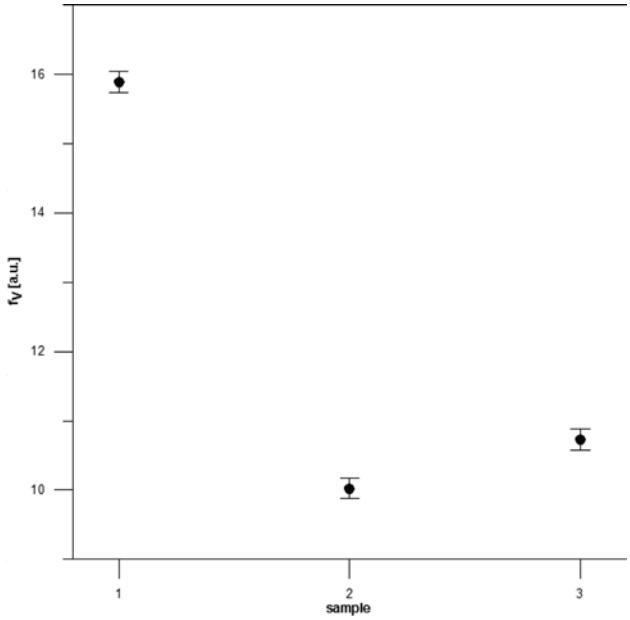

Fig. 5. The values of fractional free volume for: (1) Dipol 5s, (2) Dipol 20s and (3) Dipol 60s. The 2011 measurements

Ryc. 5. Wartości ułamka całkowitej objętości materiału zajętej przez swobodne objętości dla: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s; pomiary z 2011 r.

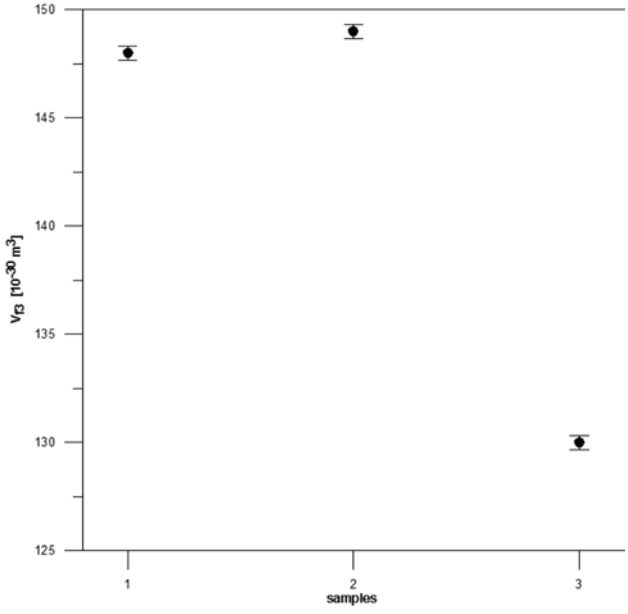

Fig. 6. The average free volume size for: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s. Results received for the τ3 component. The measurements were performed in 2013

Ryc. 6. Średnie wymiary wolnych objętości dla: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s; wyniki uzyskane dla składowej τ3; pomiary przeprowadzone w 2013 r.

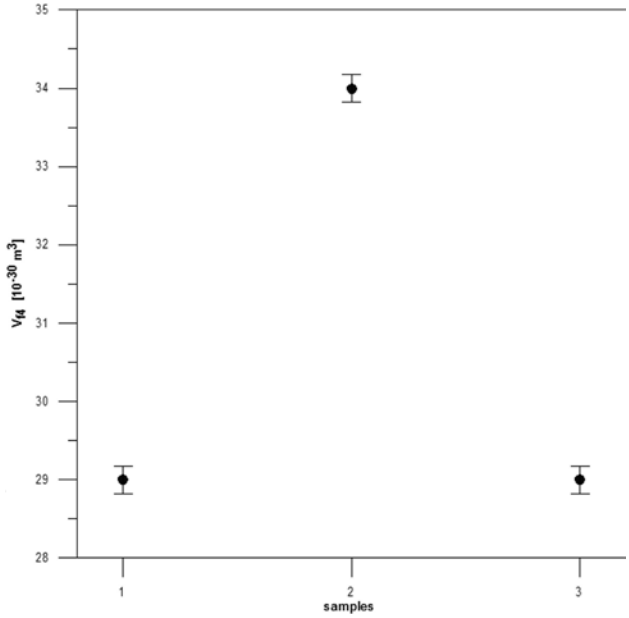

Fig. 8. The average free volume size for: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s. Results received for the τ4 component. The measurements were performed in 2013

Ryc. 8. Średnie wymiary wolnych objętości dla: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s; wyniki uzyskane dla składowej τ4; pomiary przeprowadzone w 2013 r.

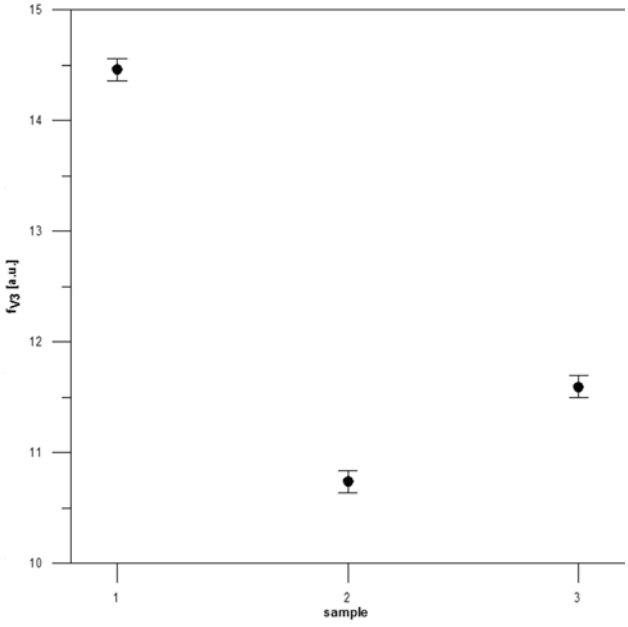

Fig. 7. The values of fractional free volume for: (1) Dipol 5s, (2) Dipol 20s and (3) Dipol 60s. Results received for τ3 component. The measurements were performed in 2013

Ryc. 7. Wartości ułamka całkowitej objętości materiału zajętej przez swobodne objętości dla: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s; wyniki uzyskane dla składowej τ3, pomiary przeprowadzone w 2013 r.

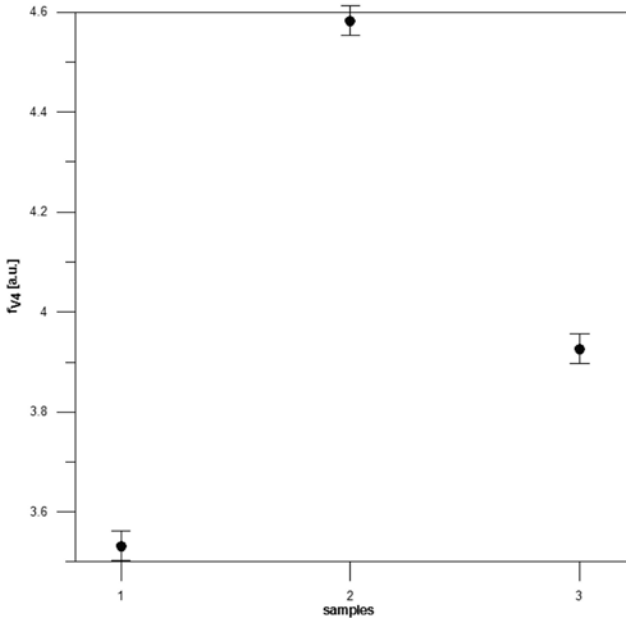

Fig. 9. The values of fractional free volume for: (1) Dipol 5s, (2) Dipol 20s and (3) Dipol 60s. Results received for τ4 component. The measurements were performed in 2013

Ryc. 9. Wartości ułamka całkowitej objętości materiału zajętej przez swobodne objętości dla: (1) Dipol 5s, (2) Dipol 20s, (3) Dipol 60s; wyniki uzyskane dla składowej τ4; pomiary przeprowadzone w 2013 r.

Table 1. Average values of the τ_2 and τ_3 components in the 2011 measurements

Tabela 1. Uśrednione wartości składowych τ2 i τ3 uzyskane z pomiarów w 2011 r.

Sample	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	R_3 [nm]	V_f [10^{-30} m]	f_V [a.u.]
Dipol 5s	0.381 ± 0.006	62.55 ± 0.82	2.226 ± 0.054	12.93 ± 0.59	0.3084	123	1,6
Dipol 20s	0.349 ± 0.005	88.3 ± 0.92	1.900 ± 0.054	11.09 ± 0.59	0.2784	90	1,0
Dipol 60s	0.353 ± 0.006	73.97 ± 0.88	1.816 ± 0.054	12.94 ± 0.59	0.2705	83	1,1

Table 2. Average values of the τ_2 and τ_3 components in the 2013 measurements

Tabela 2. Uśrednione wartości składowych τ2 i τ3 uzyskane z pomiarów w 2013 r.

Sample	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	R_3 [nm]	V_{f3} [10^{-30} m]	f_{V3} [a.u.]
Dipol 5s	0.347 ± 0.005	67.79 ± 0.82	2.470 ± 0.068	9.77 ± 0.64	0.3282	148	1,45
Dipol 20s	0.336 ± 0.005	66.70 ± 0.72	2.485 ± 0.068	7.21 ± 0.64	0.3290	149	1,07
Dipol 60s	0.340 ± 0.006	68.23 ± 0.85	2.300 ± 0.068	8.92 ± 0.64	0.3143	130	1,16

Table 3. Average values of the components τ_4 in the 2013 measurements

Tabela 3. Uśrednione wartości składowej τ4 uzyskane z pomiarów w 2013 r.

Sample	τ_4 [ns]	I_4 [%]	R_4 [nm]	V_{f4} [10^{-30} m]	f_{V4} [a.u.]
Dipol 5s	1.150 ± 0.058	12.18 ± 0.57	0.1908	29	0.35
Dipol 20s	1.224 ± 0.058	13.48 ± 0.57	0.2007	34	0.46
Dipol 60s	1.145 ± 0.058	13.54 ± 0.57	0.1908	29	0.39

Discussion

The data presented in the Tables show that 2 years after first measurements of the 4th component, which corresponds to the new type of free volume holes, appeared in the spectra. Since the 4th component (the order of 1 ns) is 2 times shorter than the 3rd component (the order of 2 ns), so it can be concluded that gaps corresponding to the shorter long lifetime component are smaller. This, in turn, leads to the conclusion that the stored material undergoes the process of aging. This can be explained by degradation of bigger free volumes due to the attractive van der Waals forces between the medium molecules which exert the pressure on the gaps. Since the intensities of fourth component are larger than expected, therefore the new component may be contain a contribution of other acts of annihilation like trapping of positrons by broken chains of the polymer matrix. This effect should be investigated further. Moreover, it can be seen that the time of the polymerization process affects dimensions of free volume holes. As shown in Fig. 4, the longer the material is subjected to a polymerization process; the sizes of the free volume holes are smaller. Similarly, the time of the polymerization process affects fractional of free volume holes. After 2 years, the relationship between the time of cross-linking and sizes of gaps in the material changes. Sizes of free volume holes for Dipol material, whose time of exposure equals 20s, increased in comparison with earlier measurements, as shown in Fig. 6. As for the other samples, it is still visible that longer time of exposure causes the decrease in gap sizes in the material. Fractional of free volume holes corresponds to τ3 component and has a similar relationship with time of polymerization as in earlier measurements, which can be seen in Fig. 7. Sizes of free volume holes calculated for new τ4 component show that for all samples dimensions of gaps are smaller than for the τ3 component. As shown in Fig. 8, sizes of free volume holes for Dipol 5s and Dipol 60s samples are close, whereas those for the Dipol 20s sample are greater than the other. Fractional of free volume holes in this case is less than for the τ3 component, which can be seen in Fig. 9. Fractional of free volume holes for the Dipol 20s sample is greater than for other samples, which also can be seen in the figures specified above. Since obtained results indicate that ageing effect in materials stored at room temperature and a dry place occurs, whereas structure of research materials is hygroscopic and hydrolytic [7], this implies the ability to carry out research in conditions similar to those prevailing in the oral cavity.

The studies conducted by means of positron annihilation lifetime spectroscopy (PALS) have shown the existence of free volume holes in Dipol polymer materials. The research, repeated after 2 years, showed increased values of the free volume holes, which correspond to τ3 component and the emergence of free volume holes relates to the degradation of primary holes and/or the rising of new centers of positrons trapping, which corresponds to τ4 component. It may be inferred that the new kind of free volume holes is associated with the aging process of the stored materials. From clinical point of view, these processes may influence the mechanical properties of filling material. This may result in lower compressive strength and fatigue limit of composite material as well as the appearance of micro cracks inside the material. Furthermore, the influence of time of the polymerization process on the sizes of free volume holes in the material was noted.

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