ORIGINAL PAPERS

Polim. Med. 2015, **45**, 1, 31–35
ISSN 0370-0747

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Comparison of Occurrence of Free Volumes for Rigid Gas Permeable and Soft Contact Lenses

Porównanie występowania wolnych objętości w sztywnych gazo-przepuszczalnych i miękkich soczewkach kontaktowych

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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 the article

Abstract

Background. The polymeric materials: hydrogel, silicone – hydrogel and methacrylic acid are used in ophthalmology for the manufacture of contact lenses. It is important to research the structure of these materials, mainly the prevalence of free volumes.
Objectives. The study has been conducted in order to comparison the presence of free volume gaps in the structure of the polymer soft contact lenses: Etafilcon A (hydrogel), Narafilcon A (silicone-hydrogel) and the polymer rigid gas permeable (RGP) contact lens (Fluor-Silicon-Methacrylat-Copolymer). In addition, to demonstrate differences in the occurrence of free volumes between types of represented contact lenses.
Material and Methods. Three types of polymer contact lenses were used as materials: Etafilcon A, Narafilcon A and Fluor-Silicon-Methacrylat-Copolymer. The study was done by means of positron annihilation lifetime spectroscopy (PALS).
Results. As a result of the performed measurements, a graphical curve resulted which describes the relationship between the number of the annihilation acts in the time function. Significant changes were observed in the ortho-positronium long life component τ_3 and their intensities between the examined polymer contact lenses.
Conclusions. The conducted study using the Tao-Eldrup model indicates the presence of free volume holes in all research materials. There is a clear difference in the free volume sizes and their fractions between measured contact lenses are connected with oxygen permeability in these lenses. The results lead to the following connection: contact lenses of higher oxygen permeability coefficients and a water content of less, have more and larger free volumes than contact lenses of less oxygen permeability coefficient **(Polim. Med. 2015,45, 1, 31–35).**

Key words: positron annihilation, free volumes, biopolymers, contact lenses.

Streszczenie

Wprowadzenie. Materiały polimerowe hydrożelowe, silikonowo-hydrożelowe oraz metakrylowe w okulistyce są wykorzystywane do produkcji soczewek kontaktowych. Ważnym aspektem staje się badanie struktury tych materiałów, szczególnie dominowanie wolnych objętości.
Cel pracy. Badania zostały przeprowadzone w celu porównania występowania swobodnych objętości w strukturze wewnętrznej polimerowych miękkich soczewek kontaktowych Etafilcon A (hydrożelowa), Narafilcon A (silikonowo-hydrożelowa) i sztywnej gazo-przepuszczalnej soczewki kontaktowej Fluor-Silicon-Methacrylat-Copolymer. Wykazano różnice w występowaniu wolnych objętości miedzy typami badanych soczewek.
Materiał i metody. Trzy typy soczewek kontaktowych użyto jako materiał badawczy: Etafilcon A, Narafilcon A i Fluor-Silicon-Methacrylat-Copolymer. Badania struktury wewnętrznej próbek przeprowadzono z wykorzystaniem spektroskopii czasów życia anihilujących pozytonów (PALS).

Wyniki. W wyniku przeprowadzonych pomiarów uzyskano graficzne krzywe, które opisują zależność liczby aktów anihilacyjnych pozytonów w funkcji czasu. Wyraźne zmiany zaobserwowano dla długo żyjącej składowej czasu życia orto-pozytu τ_3 i jej natężeń między badanymi soczewkami kontaktowymi.
Wnioski. Przeprowadzone badania z wykorzystaniem modelu Tao Eldrupa wykazuje istnienie wolnych objętości we wszystkich badanych materiałach. Wyraźnie widać, że różnice w rozmiarach i frakcji występowania wolnych objętości mierzonych soczewek kontaktowych są powiązane ze współczynnikiem tlenoprzepuszczalności w tych soczewkach. Wyniki prowadzą do następującej zależności: soczewki kontaktowe o wyższych współczynnikach tlenoprzepuszczalności i mniejszej zawartości wody mają więcej i o większych rozmiarach wolne objętości niż soczewki kontaktowe o mniejszym współczynniku tlenoprzepuszczalności **(Polim. Med. 2015,45, 1, 31–35).**

Słowa kluczowe: soczewki kontaktowe, biopolimery, wolne objętości, anihilacja pozytonów.

There is an extraordinary need for the development of amorphous polymeric materials in biomedical application and the search for materials suitable for manufacturing contact lenses is one of the examples in this context. The driving force of the materials evolution which are used for manufacturing contact lenses is the need to increase comfort and human visual acuity, as well as to improve the biocompatibility and minimize the impact of the material on the cornea physiology. We used three types of contact lenses for our study: the first was a hydrogel soft contact lens, the second was a silicone hydrogel soft contact lens and the third was a copolymer hard contact lens.

The hydrogel soft contact lens based on the Etafilcon A polymer material is made with the use of PC technology (Phosphorylcholine) [1]. Etafilcon A contains polymer of 2-hydroxyethylmethacrylate and 2-methacryloyloxyethyl phosphorylcholine cross-linked with ethyleneglycol dimethacrylate. In these material, permanent tint is fixed by using colour additive Reactive Blue 4. A uniform coating PC larger coating the contact lenses surface bipolar nature the physiological membrane and increases the bio- and hemocompatible. Due to the fact that water molecules also have a bipolar structure, many of them are loosely linked to the surface of phosphorylcholine contained in contact lenses. The result is that water molecules bounded to the PC surface impeded the binding of other molecules, hence reducing friction, minimizing irritation to the eye [2–4].

The silicone-hydrogel soft contact lens based on the Narafilcon A polymer material is made with the use of the Aguaform technology. Longer silicate chains are used in this fabrication method, which results in lower content of silicon in the material of contact lens. Longer silicate chains are used in this fabrication method, which translates into a lesser silicon content in the material of the contact lens. Material containing less silicone increases the softness, flexibility and moistness of the lens. Hydrogen bonding of water molecules forms a naturally water-loving contact lens, which keeps water in its interior, thus minimizing drying. A smaller amount of silicone in the material that is the reason why they exhibit better oxygen permeability. The silicone-hydrogel lenses also contain lots of water molecules and are permeable to oxygen dosing [1–4].

The polymer RGP contact lens based on a Fluor-Silicon-Methacrylat-Copolymer is produced on the basis of silicone acrylate, fluorosilicone and fluoropolymers. These materials are distinguished by high gas permeability and wettability. They are used in all the eye visual impairments. RGP contact lenses are characterized by high strength, dimensional stability, good optical properties, resistance to surface contamination by microbes and sediments. Currently, these lenses are replaced by modern, comfortable soft contact lenses. However, there is a group of visual impairments, which cannot be corrected by using soft contact lenses (some forms of astigmatism, corneal structural defects, myopia and others). Computer precision of material processing allows to obtain contact lenses customized to the individual patient and his disease.

Free annihilation process is the collision of electron with its anti-particle, involving change of the entire mass of both particles and their kinetic energy into energy of photons. Therefore, the investigation of photons formed during annihilation process provides information on the state of electron-positron pair. Besides the free annihilation, it is possible to create a system consisting of an electron and positron, bound together into a hygrogen-like atom called positronium [5, 6].

Two states of positronium can be distinguished due to two different spin oscillations of the electron and the positron. One, with the anti-parallel spin is known as para-positronium (p-Ps), while the second, with the parallel spin is called ortho-positronium (o-Ps). However, in condensed matter, due to the longer lifetime, the o-Ps mainly annihilates in collision with atoms or molecules.

This process, which is referred to as the “ pick-off” annihilation, reduces the lifetime of orto-positronium o-Ps in polymer materials to a few nanoseconds. The o-Ps is localized in the space between and along polymer chains and at chain ends (free volume holes), and its lifetime indicates the mean radii of these holes [7–8]. Similarly, in our earlier our papers [9, 10], as well as in this paper, the relationship between the ortopositronium o-Ps lifetime, and the size of free volume holes are described by the Tao-Eldrup model [11, 12]. Theoretical deliberations on the model show that the τ_3 lifetime (responsible for positronium formation) is expressed as a function of the free volume R radius and is described by the formula [13, 14]:

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

where ΔR = 0.166 nm is the fitted empirical electron layer thickness. By fitting Eq. (1) with measured values of τ_3, the volume of the free volume holes V_f is a function of R and it is given by the following equation:

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

The relative intensity of the longest component I_3 is usually connected with holes density. This fact can be considered as some kind of trapping centers for positrons. To determine the fractional free volume (f_v) in polymers, one can use a semi-empirical relation:

$$f_v = CV_f I_3 \quad (3)$$

where: V_f – the free volume calculated from τ_3 by using Eg. (1) with a spherical approximation;
I_3 – intensity of the long-lived component;
C – empirically determined to be 0.0018 of the specific volume data [5].

Material and Methods

The study was carried out on originally packed lenses which belong to hydrogel, silicone-hydrogel and RGP family. More detailed parameters obtained from the manufacturer of contact lenses companies are shown in Table 1.

Positron annihilation lifetime PALS measurements were performed at room temperature with the use of an ORTEX spectrometer, [15, 16]. The spectrometer with a lifetime resolution of FWHM = 270 ps was monitored with a ^{60}Co source and used to record all PALS spectra. The specimen consisted of six parallel layers of contact lenses of 10 mm diameter and 1 mm thick. Samples were made of contact lenses, arranged into systems of six parallel layers. Such systems, subjected to pressure were dried out for several days. The presence of water and air can be neglected. The two stacks of specimens with the source of positron (^{22}Na isotope of an activity 4 × 10^5 Bq) and Kapton foli (at the thickness 6 μm), formed so-called "sandwich" system. Positron lifetime spectra were analysed using the LT computer program [17]. Typical examples of PALS spectra of the obtained soft (Etafilcon A, Narafilcon A) and GRP (Fluor-Silicon-Methacrylat-Copolymer) contact lens samples are shown in Fig. 1.

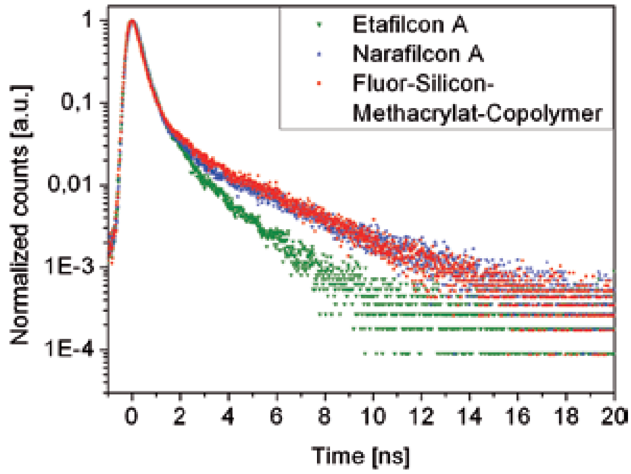

Fig. 1. Typical examples PALS spectra of samples Narafilcon A, Etafilcon A and Fluor-Silicon-Methacrylat-Copolymer (each PALS spectrum contained about 2 × 106 counts)

Results

The obtained positron lifetime values revealed the existence of three components of τ_1, τ_2 and τ_3 in the positron lifetime spectrum. Two shortest components representing the annihilation of parapositronium p-Ps (τ_1) (fits to a value of 0.125 ns) and the τ_2 component are typical for trapping of positrons [18, 19]. As in previous papers [10, 20] on the subject, the attention was paid to the analysis of the long-lived component of the positron lifetime τ_3 (the "pick-off" process). The values of positron lifetime of τ_3 ortopositronium o-Ps and their intensity I_3, R (hole radius), the sizes of free volume V_f and fractional of the free volume f_v are given in Table 2. The errors are the consequence of mathematical analysis. The number of measurements for each sample 1, 2 and 3 was n = 5. The error for the τ and I values was calculated by the program LT for n = 5 (standard deviation). While the error for the value of R, V_f and f_v was calculated as relative error (accuracy percentage).

Table 1. Comparison of soft, (hydrogel and silicone-hydrogel) and RGP (Fluor-Silicon-Methacrylat-Copolymer) contact lenses

Sample	Material	Water content (%)	Oxygen permeability: Dk (× 10^{-11})
Soft contact lens (Hydrogel) /1/	Etafilcon A	58	21.4
Soft contact lens (Silicone-Hydrogel) /2/	Narafilcon A	46	[1)]100
Rigid gas permeable contact lens (RGP) /3/	Fluor-Silicon-Methacrylat-Copolymer	≤ 1	[1)]100

[1)] Taking into account the edge effect and the border effect.

Table 2. Calculated mean values of positron lifetime τ_3, their intensity I_3, the hole radius R, the size of free volume V_f and fractional of the free volume f_v

Sample	τ_3 (ns)	I_3 (%)	R (nm)	V_f (10^{-30} m^3)	f_v (a.u.)
/1/	1.558 ± 0.041	20.02 ± 0.63	0.243 ± 0.007	60 ± 2	1201 ± 36
/2/	3.117 ± 0.062	20.14 ± 0.62	0.376 ± 0.011	223 ± 7	4491 ± 134
/3/	2.721 ± 0.053	25.87 ± 0.71	0.347 ± 0.010	174 ± 5	4501 ± 135

The fractional free volume f_v is proportional to $V_f \times I_3$, because C in Eq. (3) is a constant. From the Table 2 it results that the values of V_f and f_v in the examined contact lenses differ widely amid samples. Taking into account the defined value of V_f (Eq. (2)) and f_v (Eq. (3)), we can conclude that the differences V_f are responsible for the change in free volume sizes, while the differences in f_v are responsible for changes in the fraction of free volume. This can be combined with the oxygen permeability Dk, which is significantly higher for silicone hydrogel contact lenses. On the grounds of these measurements, it is possible to find out that the sizes and fractions of free volumes are higher for the silicon–hydrogel contact lens. For the RGP contact lens these values are slightly smaller, while the lowest values of V_f and f_v were obtained for hydrogel contact lenses.

Discussion

Changes in the value of the τ_3 life time and I_3 intensities are represented as changes in the size of free volume V_f and the fraction of free volume f_v (Table 2). From these figures it can be found that the values of V_f in the tested contact lenses differ widely amid samples. Taking into account the defined value of V_f (Eq. (2)) and f_v (Eq. (3)), we can conclude that the differences V_f are responsible for the change in free volume sizes, while the differences f_v are responsible for changes in the fraction of free volume. This can be combined with the oxygen permeability Dk, which is significantly higher for silicone hydrogel contact lenses. On the grounds of these measurements, it is possible to find out that the sizes and fractions of free volumes are higher for the silicon–hydrogel contact lenses, which is confirmed by the data provided by their manufacturer (Table 1 – values of Dk). The value of the size of free volume V_f for the RGP contact lens (Fluor-Silicon-Methacrylat Copolymer) is slightly lower than for the Narafilcon A soft contact lens, and significantly higher than for the Etafilcon A soft contact lens. However, the value of the fraction free volume f_v for the RGP contact lens (Fluor-Silicon-Methacrylate-Copolymer) is of the same order as the value for the soft silicone-hydrogel contact lens (Narafilcon A), and significantly higher than the one for the hydrogel contact lens (Etafilcon A).

Comparison of appearance of free volumes in three kinds of different contact lenses: soft (hydrogel; Etafilcon A), (silicone–hydrogel; Narafilcon A) and GRP (Fluor-Silicone-Methacrylat-Copolymer) by means of positron annihilation lifetime PALS spectroscopy were investigated in this paper. The measurements showed a close relation between free volume sizes V_f and fractions free volumes f_v in investigated contact lenses. Changes in the values of free volumes V_f and fraction free volumes f_v in the investigated soft and GRP contact lenses are related with the oxygen permeability Dk of these materials and water content (Table 1). The highest values of oxygen permeability Dk occurring for the RGP contact lens (Fluor-Silicon-Methacrylat-Copolymer) and the soft silicone-hydrogel (Narafilcon A) contact lens in contrast to value obtained for the hydrogel contact lens (Etafilcon A). Also PALS measurements showed that for these materials, the values of free volumes V_f and fraction free volumes f_v are significantly larger. For understanding of the above dependence, further investigation of the structure of soft and hard contact lenses are required.

References

[1] **Tranoudis I., Efron N.:** In-eye performance of soft contact lenses made from different materials. Cont. Lens Anterior Eye 2004, 27, 133–148.
[2] **Guillon M., Maissa C.:** Bulbar conjunctival staining in contact lens wearers and non lens wearers and its association with symptomatology. Cont. Lens Anterior Eye 2005, 28, 67–73.
[3] **Pult H., Purslow C., Berry M., Murphy P.J.:** Clinical tests for successful contact lens wear: relationship and predictive potential. Optom. Vis. Sci. 2008, 85, 924–929.
[4] **Wolffsohn J.S., Hunt O.A., Basra A.K.:** Simplified recording of soft contact lens fit. Cont. Lens Anterior Eye 2009, 32, 37–42.
[5] **Pathrick R.A.:** Positron annihilation – a probe for nanoscale voids and free volume. Prog. Polym. Sci. 1997, 22, 1–47.
[6] **Jean Y.C.:** NATO Advanced Research Workshop, Advances with Positron Spectroscopy of Surfaces. Italy, Yarenna 1993.
[7] **Eldrup M., Lighbody D., Sherwood J.N.:** Positron annihilation in polymers. Chem. Phys. 1981, 63, 51–62.
[8] **Brandt W., Berko S., Walker W.W.:** Positronium decay in molecular substances. Phys. Rev. 1960, 120, 1289–1295.

[9] **Kocela A., Filipecki J., Korzekwa P, Golis E.:** Investigation of the free volume changes in one day hydrogel and one day silicone hydrogel contact lenses by means of positron annihilation lifetime spectroscopy. Polim. Med. 2012, 42, 61–68.
[10] **Filipecki J., Kocela A., Korzekwa W.:** Study of Free Volumes of Polymer Hydrogel and Silicone-Hydrogel Contact Lenses by Means of the Positron Annihilation Lifetime Spectroscopy Method. Polim. Med. 2014, 44, 255–260.
[11] **Tao S.J.:** Positron annihilation in molecular substances. J. Chem. Phys. 1972, 56, 5499–510.
[12] **Eldrup M., Lighbody D., Sherwood J.N.:** Positron annihilation in polymers. Chem. Phys. 1981, 63, 51–62.
[13] **Liao Kuo-Sung, Chen Hongmin, Awad Somia, Yuan Jen-Pwu, Hung Wei-Song, Lee Kuier-Rarn, Lai Juin-Yih, Hu Chien--Chieh, Jean Y.C.:** Determination of Free-Volume Properties in Polymers Without Orthopositronium Components in Positron Annihilation Lifetime Spectroscopy. Macromolecules 2011, 44, 6818–6826.
[14] **Filipecki J., Kocela A., Korzekwa P., Miedzinski R., Filipecka K., Golis E., Korzekwa W.:** Structural study of polymer hydrogel contact lenses by means of positron annihilation lifetime spectroscopy and UV–vis–NIR methods. J. Mater. Sci. Mater. Med. 2013, 24, 1837–1842
[15] **Filipecki J., Golis E., Reben M., Filipecka K., Kocela A., Wasylak J.:** Positron life time spectroscopy as a method to study of the defect degree materials with disordered structure. Optoelectron. Adv. Mater. Rapid Communnication 2013, 7, 1029–1031.
[16] **Hyla M., Filipecki J., Shpotyuk O., Popescu M., Balitska V.:** Stoichiometric arsenic sulphoselenides as testing probes for positron trapping in chalcogenide glasses. J. Optoelectron. Adv. Mater. 2007, 9, 3177–3181.
[17] **Kansy J.:** Microcomputer program for analysis of positron annihilation lifetime spectra. Nucl. Instr. Meth. Phys. Res. A 1996, 374, 235–244.
[18] **Krause-Rehberg R., Leipner H.S.:** Positron Annihilation in Semiconductors. Defect Studies, Springer-Verlag, Berlin–Heidelberg–New York 1999.
[19] **Jean Y.C., David Van Horn J., Wei-Song H., Kuier-Rarn L.:** Perspective of Positron Annihilation Spectroscopy in Polymers. Macromolecules 2013, 46, 7133–7145.
[20] **Filipecki J., Sitarz M., Kocela A., Kotynia K., Jelen P., Filipecka K., Gaweda M.:** Studying functional properties of hydrogel and silicone-hydrogel contact lenses with PALS, MIR and Raman spectroscopy. Spectrochim. Acta A Mol. Biomol. Spectrosc. 2014, 131, 686–690.

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Conflict of Interest: None declared

Received: 20.03.2015
Revised: 03.04.2015
Accepted: 12.05.2015