Structural study of polymer hydrogel contact lenses by means of positron annihilation lifetime spectroscopy and UV–vis–NIR methods

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Abstract A study has been conducted in order to determine presence of free volume gaps in the structure of structure of polymer hydrogel contact lenses made in phosphoryl choline technology and of the degree of defect of its structure. The study was made by means of positron annihilation lifetime spectroscopy. As a result of the conducted measurements, curves were obtained, which described numbers of counts of the acts of annihilation in the time function. The conducted studies revealed existence of three components τ_1, τ_2 and τ_3. The τ_3 component is attributed to the pick-off annihilation of o-Ps orthopositronium trapping by free volume gaps and provides information about geometrical parameters of the volumes. At the same time, the UV–vis–NIR spectrometry examination was conducted on the same samples in the spectral range 200–1,000 nm.

1 Introduction

Search for new materials for advanced medical applications, the so called biomaterials, is at present within the range of interest of a large number of scientists: physicists, chemists, biologists, for whom the coincident interdisciplinary approach evolves. Hydrogel materials are modern polymer materials used for making contact lenses, and their chemical and biological properties must be biocompatible with human organism [1–4].

The objective of the work is making an assessment of physical properties of the polymer material used for making contact lenses by using the positron annihilation lifetime spectroscopy (PALS) method and UV–vis–NIR spectroscopy. In spite of constant improvement of the materials used for making contact lenses, many patients keep suffering from pathological changes in their cornea. There is a need for conducting new studies on properties of polymer materials used for making contact lenses, so as to provide patients with good moistening and appropriate optical parameters, as well as comfort by ensuring their long time use.

Proclear family of contact lenses made by means of the PC technology contain Omafilcon A. The PC technology is based on the assumption that the external layer of the red blood cell membrane is hemocompatible, whereas the internal layer is thrombogenic. The internal, thrombogenic surface has negatively charged phospholipids, while the outer surface is made of closely arranged positively and negatively charges phospholipids, which are, consequently, electrically neutral. 80 % of the external surface of the erythrocyte cell membrane contains phosphoryl-choline, whereas the remaining part is composed of other phospholipids. The smooth PC coating on the surface of contact lenses imitated the bipolar nature of the physiological film and increases bio- and hemo-compatibility. Water molecules also have bipolar structure and this is why many of them are loosely bound on the surface of phosphoryl-choline contained in the contact lenses. Consequently, water molecules bound on the PC surface inhibit binding other molecules and thus reduce the friction factor, which

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minimize irritation of an eyeball. CooperVision informs that the Proclear family lenses maintain 98 % of water even after 12-h-use. PC covered lenses inhibit formation of bio-film on the surface of the contact lenses. Very little deposit and few bacteria accumulate on the surface (Fig. 1). The biofilm contains diverse microorganisms and extracellular matrix, therefore, it is considered to be as a permanent reservoir of bacteria contributing to development of inflammation of eyeballs.

Free positron annihilation is a process involving change of the entire mass of both particles and of their kinetic energy into 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 P_s positronium. The high energy positron annihilation in the matter is preceded by the phenomenon of thermalization, which involves 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 a 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 two different types of positronium: para-positronium p-P_s of anti-parallel placement of spins (the 2γ annihilation) and ortho-positronium o-P_s of parallel placement of spins (the 3γ annihilation). Physical properties of positronium change due to its interaction with the surrounding medium. One of the observed phenomena is shortening of three-photon orthopositronium mean annihilation lifetime, which is also called o-P_s annihilation [5, 6]. The basic annihilation process is the "pick-off" annihilation. It involves the ability of the positron, which is part of orthopositronium, to perform two-photon annihilation with one of the atoms that can be found in the surroundings of

the positronium [7, 8]. The existence of free volume—an area of zero electron density is necessary for the positronium to survive in a condensed medium without being quenched with a mean lifetime shorter by two orders of magnitude. Local free volumes occur in materials due to irregular molecular packing. In this paper, the Tao–Eldrup model was used to describe the relations between the o-Ps orthopositronium lifetime and the size of a free volume. The model has fully accomplished its task and it has been used for years to calculate the dimensions of free volumes in polymer materials by numerous research centers throughout the world. It assumes that a positronium is trapped within a spherical free volume, is capable of spontaneous annihilation with emission of three γ quanta, or as a result of the pick off process into two γ quanta [9–12].

2 Experiment

Modern technologies make it possible to produce lenses of better and better parameters that allow using them by children and adolescents by solving problems of dry eyes and tissue reactions to anoxia that occur in hydrogel lenses. They provide possibility for safe use in the case of ageing eyes [13, 14]. The aim of this paper is making an attempt at comparative analysis between individual hydrogel lenses of the Proclear family by means of PALS and UV–vis–NIR spectroscopy. Table 1 shows the family of Proclear contact lenses used in the study.

As described in the preceding paper, measurements of PALS positron lifetimes were taken in room temperature with ORTEC spectrometer, based on the "start–stop" principle. The temporary peak resolution of the measuring system was FWHM = 270 ps. Each sample was formed by 8 layers of contact lenses of 10 mm diameter and 1.2 mm thickness. The examined sample, together with the positron source, which was Na^{22} sodium isotope of 4×10^5 Bq activity, formed a "sandwich" type system.

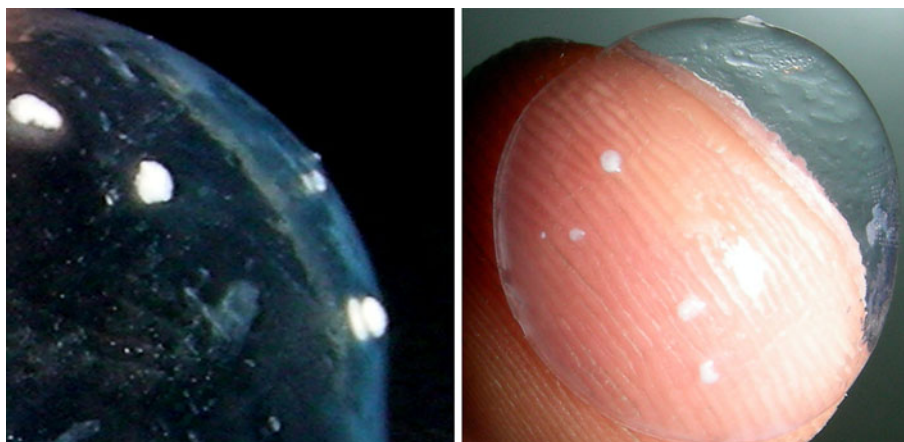**Fig. 1** Contact lens with a visible reservoir of bacteria

Table 1 Family Proclear contact lenses used in the study

Sample	Brand	Oxygen permeability: DK/t	Water content (%)	Material Omafilcon A (%)
1	Proclear asphere	28	60	40
2	Proclear sphere	42	62	38
3	Proclear ep	16	60	40
4	Proclear multifocal toric D	42	59	41
5	Proclear multifocal toric N	42	59	41

Fig. 2 The spectrum of positron lifetime in a contact lens sample

Harmful effect of UV radiation to eses and the necessity to use appropriate protection have been discussed for years. Protecting eyes from solar radiation is very important, and this is why additional UV–vis–NIR spectroscopy has been carried out. The UV–vis–NIR spectroscopy is an instrumental technique in which energetic transitions taking place in molecules is used. The transitions are caused by absorption of the electromagnetic radiation in the UV range (200–400 nm), visible range (400–800 nm) or near-infrared range (800–1,000 nm). The technique consists in quantitative measurement of absorption, emission or reflection of light [15].

Tao and Eldrup et al. [10, 11] developed the model in 1972 for free volumes in polymers. They pondered over a simple model in which the P_s atom is located in a finite, spherical potential trough. In order to simplify calculation, replacement of the finite potential trough by an infinite potential trough, extended by the ΔR value. It is necessary for reconstruction of the values of probability of finding o-P_s outside the potential trough of finite depth and radius R. Successive theoretical deliberations showed that τ_3 o-P_s lifetime expressed as a function of radius R free volume is expressed by the formula:

$$\tau_3 \, (ns) = 0.5 \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + \Delta R} \right) \right]^{-1} \quad (1)$$

where $\Delta R = 0.166$ nm is the fitted empirical electron layer thickness. By fitting the above equation with the measured τ_3 values, R and free volume size V_f as:

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

can be evaluated. The relative intensity of the longest component I_3, 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 fraction of free volume (f_v) in polymers as:

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

where: V_f—is the free volume calculated from τ_3, using Eq. (1) with a spherical approximation, I_3—(in %) is the
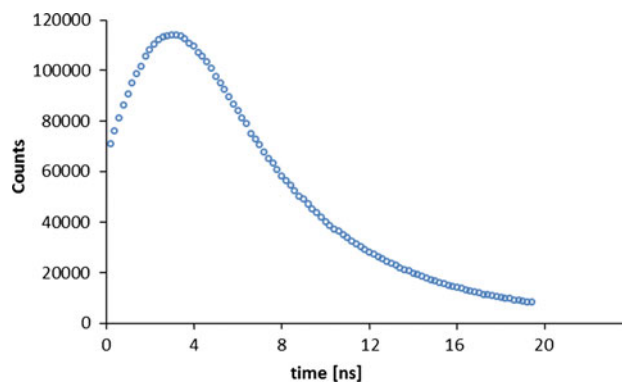
intensity of long-lived component, C—is empirically determined to be 0.0018 from the specific volume data [5].

In the further part of the study, a two-state model of positron annihilation was proposed for the analysis of PALS spectra. In this model, a positron annihilates from the free state and from one state localized in a defect, without the detrapping process. After calculating, with the use of the LT program, the major annihilation parameters—mean positron lifetimes τ_1, τ_2 and their intensities, we can also calculate [16]:

Mean positron lifetime τ_{av} illustrating defectiveness of the dominant medium in the examined lenses;

$$\tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2} \quad (4)$$

Mean positron lifetime in an unidentified structure τ_b;

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}} \quad (5)$$

Capture speed of positrons by traps (defects) κ_d;

$$\kappa_d = \frac{I_2}{I_1} \left(\frac{1}{\tau_b} - \frac{1}{\tau_2} \right) \quad (6)$$

$\tau_2 - \tau_b$—the magnitude connected with means size of defects in which annihilation occurs, τ_2/τ_b—illustrating the type of volume defects.

A model experimental curve of the spectrum of positron lifetime in a contact lens sample is shown in Fig. 2.

The UV–vis–NIR spectrometric testing was carried out with an OceanOptics high-resolution HR 4000CG-UV–NIR spectrometer in the spectrum range 200–1,000 nm. A deuterium–tungsten-halogen lamp, covering the spectrum range of the spectrometer used in the study was used as a source of light. The power of the source of light was 3.8 W (deuterium lamp) and 1.2 W (tungsten-halogen lamp). The transmission spectra for the examined contact lenses are shown in Fig. 3. The graph shows that the examined lenses stop ultraviolet radiation.
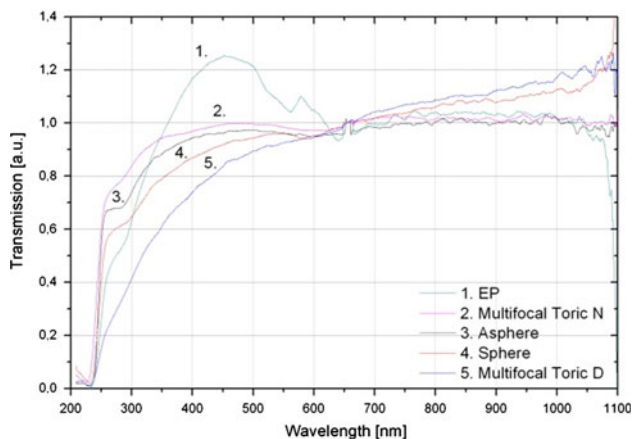
Fig. 3 UV–vis–NIR transmission spectra for the examined contact lenses

Table 3 Mean positron lifetime values τ_3, their intensity I_3 and sizes of free volumes

Sample	τ_3 (ns)	I_3 (%)	R (nm)	V_f (10^{-30} m^3)	f_v (a.u.)
1 asphere	1.800	5.75	0.265	77.92	448.04
2 sphere	1.803	5.80	0.266	78.80	457.04
3 ep	1.822	7.07	0.268	80.59	569.77
4 multifocal toric D	1.853	4.66	0.271	83.33	388.32
5 multifocal toric N	1.893	3.79	0.275	87.08	330.03

3 Results and discussion

Positron lifetime spectra were analysed with the LT computer program [17]. Results of calculation of values of mean lifetimes of positrons in the examined samples revealed existence of three components, τ_1, τ_2 and τ_3, in the positron lifetime spectra. In our earlier publications on the topic we concentrated on analyzing only τ_3, the third component of positron lifetimes [18]. This time we additionally analyse the components τ_1 and τ_2, which concern the two-state model of positron annihilation. Mean positron lifetime values τ_1, τ_2, τ_3 and their intensities are shown in Table 2.

The obtained errors are the result of mathematical analysis. Positron lifetime values τ_3 o-P$_s$ (the "pick-off" process) and their intensity I_3, as well as the dimensions of free volumes R are displayed in Table 3.

The free volumes dimensions V_f and the fraction of free volumes $V_f \times I_3 = f_v/C$ for all the examined samples are displayed in Figs. 4 and 5 respectively.

The fraction of free volume f_v is proportional to $V_f \times I_3$, because C in the Eq. (4) is constant. There are values of τ_1 and τ_2 positron lifetimes and their intensities, as well as the determined parameters of positron capture for the examined samples of contact lenses presented in Table 4.
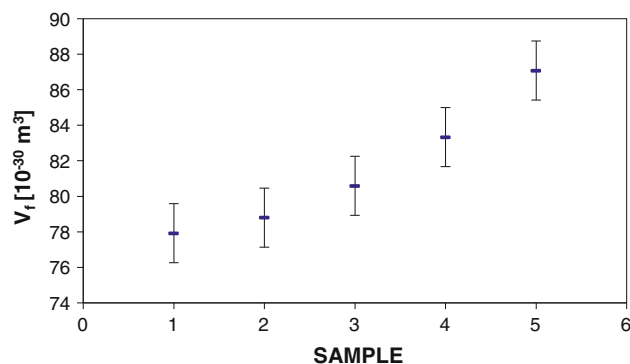

Fig. 4 The average size of free volume V_f for samples of contact lenses: *1* proclear asphere, *2* proclear sphere, *3* proclear ep, *4* proclear multifocal toric D, *5* proclear multifocal toric N
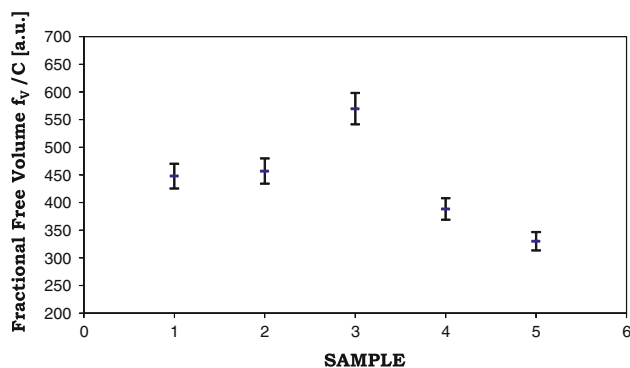

Fig. 5 The fractional of free volume f_v/C for samples of contact lenses: *1* proclear asphere, *2* proclear sphere, *3* proclear ep; *4* proclear multifocal toric D, *5* proclear multifocal toric N

Table 2 Mean positron lifetime values τ_1, τ_2, τ_3 and their intensities

Sample	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)
1 asphere	0.207 ± 0.006	76.03 ± 1.56	0.580 ± 0.034	18.23 ± 1.60	1.800 ± 0.180	5.75 ± 0.35
2 sphere	0.180 ± 0.006	63.06 ± 0.97	0.476 ± 0.010	31.12 ± 0.97	1.803 ± 0.024	5.80 ± 0.19
3 ep	0.211 ± 0.007	68.05 ± 1.45	0.533 ± 0.022	24.90 ± 1.53	1.822 ± 0.028	7.07 ± 0.30
4 multifocal toric D	0.230 ± 0.005	71.34 ± 1.34	0.517 ± 0.054	24.01 ± 1.43	1.853 ± 0.075	4.66 ± 0.17
5 multifocal toric N	0.235 ± 0.005	76.17 ± 1.43	0.564 ± 0.089	20.07 ± 1.47	1.893 ± 0.066	3.79 ± 0.26

Table 4 Calculated values of positron lifetime and positron capture of the examined samples of contact lenses

Sample	Fitting parameters						Parameters of positron capture				
	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	τ_{av} (ns)	τ_b (ns)	κ_d (ns^{-1})	$\tau_2-\tau_b$ (ns)	τ_2/τ_b (ns)
1	0.207	76.03	0.580	18.23	1.800	5.75	0.279	0.236	0.603	0.344	2.458
2	0.180	63.06	0.476	31.12	1.803	5.80	0.278	0.226	1.146	0.250	2.106
3	0.211	68.05	0.533	24.90	1.822	7.07	0.297	0.252	0.766	0.281	2.115
4	0.230	71.34	0.517	24.01	1.853	4.66	0.302	0.267	0.610	0.250	1.936
5	0.235	76.17	0.564	20.07	1.893	3.79	0.304	0.268	0.515	0.296	2.104

Changes of τ_3 life time values and their intensities I_3 are presented as changes of free volumes V_f and numbers of free volumes f_v (Figs. 4, 5). It results from Fig. 4 that each sample is characterized by a different V_f value. As for the f_v parameter, responsible for changes of free volume numbers occurring in the examined contact lenses, there are certain similarities. There are values close to f_v in the Asphere and Sphere lenses, another pair are the Multifocal Toric D and Multifocal Toric N lenses. The EP lens, on the other hand, is distinguished by an indirect value for both V_f and f_v parameters. It is possible to look for connections with the optical properties of the contact lens. According to CooperVision, the lens is "something in between" ordinary lenses for correcting far-sightedness and multifocal lenses, and it is generally used to correct presbyopia in young people.

When analyzing results of the study (Table 4), it is noticeable that there is a relation between the percentage of Omafilcon content and τ_1 responsible for free annihilation of positrons and the annihilation with electrons of point defects of vacancy type. Two contact lenses, Multifocal Toric D and Multifocal Toric N stand out as having the highest τ_1 values and the highest Omafilcon content (41 %). The same relation can also be found for the mean positron lifetime τ_{av} reflecting defectiveness of the medium for the same contact lenses. Apart from that the lenses Multifocal Toric D and Multifocal Toric N also stand out because of highest values of τ_b. Analysing subsequent parameters of positron capture, one can observe that the highest speed of positron capture by the κ_d traps (defects) is demonstrated by the Sphere lens, whereas the lowest speed is demonstrated by the Multifocal Toric N lens. The parameter $\tau_2-\tau_1$, i.e. mean defect sizes is the highest for the Asphere lens and the lowest for the Sphere and Multifocal Toric D lenses. Differences for the τ_2/τ_1 parameter can be observed, which is evidence of geometric variability for individual contact lenses.

4 Conclusions

This paper deals with a study on determining occurrence of free volume vacancies in the structure of polymer hydrogel contact lenses made by means of PC technology by CooperVision and on the degree of defectiveness of the structure by means of the PALS method.

As a result of the conducted studies and calculations of positron lifetime spectra values of three τ components (τ_1 short-lived, τ_2 average-lived, and long-lived τ_3 o-P$_S$) and their intensities I have been obtained. The results of these measurements show that formation of free volume vacancies takes place in all contact lenses of the Proclear family. In spite of the fact that all the examined contact lenses are made of the same polymer material (Omafilcon), the designated parameters vary. The calculated values of dimensions of V_f free volumes and the fraction of f_v free volumes show that the highest values of V_f occur in Multifocal Toric D and Multifocal Toric N lenses, and at the same time the lowest f_v values are observed for the same contact lenses.

As for the positron capture parameters (the degree of defectiveness of the structure), Multifocal Toric D and Multifocal Toric N contact lenses show the highest defectiveness of the medium, but at the same time a low speed of defecting positrons. However, the same type of positron trapping forms in all cases, and the differences in results confirm structural changes in contact lenses resulting from their technological modification.

There arises one basic conclusion from the UV–vis–NIR study, which indicates that all the examined contact lenses from the CooperVision Proclear family stop harmful ultraviolet radiation.

References

1. Tranoudis I, Efron N. In-eye performance of soft contact lenses made from different materials. Cont Lens Anterior Eye. 2004;27:133–48.

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 PJ. Clinical tests for successful contact lens wear: relationship and predictive potential. Optom Vis Sci. 2008;85:924–9.

4. Wolffsohn JS, Hunt OA, Basra AK. Simplified recording of soft contact lens fit. Cont Lens Anterior Eye. 2009;32:37–42.

5. Pathrick RA. Positron annihilation—a probe for nanoscale voids and free volume. Prog Polymer Sci. 1997;22:1–47.

6. Jean YC, NATO Advanced Research Workshop. Advances with positron spectroscopy of surfaces. Italy: Yarenna; 1993.

7. Shao-Jie W, Yin-Hua X, Zhong-Xun T, De-Chong T. Section J29: Positron annihilation study of structural relaxation and crystallization of amorphous alloys. In: Jain PC, Singru RM, Gopinathan KP, editors. Positron annihilation. Singapore: World Scientific Publishing Co. Pte. Ltd; 1985. p 924–927

8. Dryzek J. Wstęp do spektroskopii anihilacji pozytonów w ciele stałym (Introduction to positron annihilation spectroscopy in solids). Krakow: Jagiellonian University; 1997.

9. Brandt W, Berko S, Walker WW. Positronium decay in molecular substances. Phys Rev. 1960;120:1289–95.

10. Tao SJ. Positron annihilation in molecular substances. J Chem Phys. 1972;56:5499.

11. Eldrup M, Lighbody D, Sherwood JN. Positron annihilation in polymers. Chem Phys. 1981;63:51–62.

12. Kuo-Sung L, Hongmin C, Sornia A, Jen-Pwu Y, Wei-Song H, Kuier-Rarn L, Juin-Yih Lai M, Chien-Chieh H, Jean YC. Determination of free-volume properties in polymers without orthopositronium components in positron annihilation lifetime spectroscopy. Macromolecules. 2011;44:6818–26.

13. Rydz M. Nowe kierunki w korekcji wzroku silikonowo hydrożelowymi soczewkami kontaktowymi (New trends in silicone hydrogel vision correction contact lenses). Contactology and optics eyepiece; 2004. p. 1.

14. Holden B. Przedłużone noszenie—przeszłość, teraźniejszość i przyszłość (Prolonged wearing—past, present and future). Contactology and optics eyepiece; 2002. p. 1.

15. Nowicka-Jankowska T, Wieteska E, Gorczyńska K, Michalik A. Spektrofotometria UV/VIS (UV/VIS spectrophotometry). Warsaw: PWN; 1988.

16. Klym H, Ingram A, Shpotyuk O, Filipecki J, Hadzaman I. Extended positron-trapping defects in insulating MgAl2O4 spinel-type ceramics. Phys Stat Sol. 2007;4(3):715–8.

17. Kansy J. Microcomputer program for analysis of positron annihilation lifetime spectra. Nucl Instr Meth Phys Res A. 1996;374:235–44.

18. 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. Polym Med. 2012;42(1):61–8.