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Investigation of the Degree of Disorder of the Structure of Polymer Soft Contact Lenses Using Positron Annihilation Lifetime Spectroscopy PALS

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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. Hydrogel and silicone-hydrogel polymeric materials are widely used in ophthalmology for the manufacture of contact lenses. An important aspect is the investigation of the structure of these materials.

Objectives. This study has been conducted in order to compare the degree of disorder and presence of free volumes in the internal structure of the polymeric soft contact lenses Omafilcon A (hydrogel) and Comfilcon A (silicone-hydrogel). Differences in the occurrence of trapping centers for positrons and free volumes between the types of investigated contact lenses have been demonstrated.

Material and Methods. Two types of polymeric contact lenses were used as materials: Omafilcon A (hydrogel) and Comfilcon A (silicone-hydrogel). The study was performed using positron annihilation lifetime spectroscopy (PALS).

Results. When the results of the measurements has been obtained, a graphical curve has created to describe the relationship of the number of annihilation acts in time. Significant changes were observed between the contact lenses investigated in positron trapping in macropores (based on a two-state model) and the presence of free volumes (based on the Tao-Eldrup model).

Conclusions. The use of the positron annihilation two-state model made it possible to demonstrate that a higher positron trapping rate in macropores occurs in the silicone-hydrogel contact lens. Additionally, calculations using the Tao-Eldrup model show the existence of free volumes in both types of materials. The size and fraction of free volumes is much larger in the silicone-hydrogel contact lens **(Polim. Med. 2016, 46, 1, 17–23)**.

Key words: free volumes, polymers, defects, contact lenses, positron annihilations.

A breakthrough in the development of contact lenses occurred in 1955 when Wichterle and Lim invented a hydrogel material – polyhydroxyethylmethacrylate (pHEMA). After their comprehensive study, development of the technological process and several years of testing on clinical material by Dreifus, hydrogel contact lenses are now widely used in biomedical and pharmaceutical applications [1]. After 1970, numerous foreign companies and research laboratories became interested in the production and technical processing of contact lenses. One result of the modernization and improvement of the production process was the development of the next series of soft contact lenses based on polymers and copolymers. In the eighties of the last century, disposable and systematic exchange soft contact lenses started to come into use. The advantage of hydrogels over other synthetic biomaterials is the relatively high degree of water content, softness and ductility, and properties similar to living tissue [2, 3]. Hydrogels are a homogeneous family of materials exhibiting a high degree of permeability to liquids and gases, which is important in normal tissue respiration and the metabolism of the cornea [4].

Positron annihilation lifetime spectroscopy (PALS) is a useful technique to study a variety of phenomena and materials on an atomic scale. Currently, it is a standard method used in the investigation of the behavior of vacancies, their aggregations or voids created in the material in various processes. PALS has been developed as a well-established tool for investigations of metals, semiconductors, polymers and porous materials.

Positrons penetrating the substances lose their energy through interactions with the material and are finally annihilated with electrons through several processes. In the case of polymeric materials, in addition to the annihilation of the positron, formation and annihilation of positronium (Ps) take place. Positronium is the bound state of a positron and electron having an atomic radius comparable to that of a hydrogen atom. It exists in two spin states.

One is called para-positronium (p-Ps), in which the positron and electron spins are anti-parallel. The other one, corresponding to parallel particle spins, is called ortho-positronium (o-Ps). However, in condensed matter, the o-Ps is predominantly annihilated, during a collision with atoms or molecules, with an electron other than its bound partner and possessing an opposite spin. This process is known as "pick-off" and reduces the o-Ps lifetime to a few nanoseconds. The formation probability and lifetime of positronium are very sensitive to the electron density surrounding Ps and it cannot form in high electron density materials. In the case of polymeric materials, the o-Ps localizes in the space between polymer chains and at chain ends (free volume holes), and the lifetime gives an indication of the mean radius of these holes [5–7].

The internal structure of the polymers used in the production of contact lenses may contain free volumes of different sizes. In these materials, the PALS method allows for the distinction of at least three lifetime components τ1, τ2 and τ3 and their intensities I1, I2 and I3 (I1 + I2 + I3 = 100%) from the spectrum. Component τ1 is responsible for free annihilation of positrons, annihilations with electrons at vacancy point defects and annihilation of para-positronium (p-Ps). Component τ2 is attributed to the annihilation of positrons with electrons in macropore defects. The value of third component, τ3, indicates of the presence of free volumes, in which ortho-positronium (o-Ps) is formed. Formation of o-Ps, and therefore the presence of free volumes, is typical for polymer contact lenses [8–10]. The relationship between the o-Ps lifetime and the size of a free volume is discerned using the Tao-Eldrup model [11, 12]. The assumption of this model is to locate positronium in a single spherical potential well. To simplify the calculations, the finite potential well was replaced by an infinite well expanded by the ΔR value. The value of the parameter ΔR should be chosen so that it does not change the value of the probability of finding positronium outside the sphere of radius R. With the Tao-Eldrup model, a very successful semi-empirical equation has been established relating the o-Ps lifetime to the size of the free volume in which it is annihilated, thus τ3 corresponds to a spherical space with a radius R, according to the following equation [11–14]:

$$\tau 3ns = 0.51 - RR + \Delta R + 12\pi \sin 2\pi RR + \Delta R - 1 \quad (1)$$

where ΔR = 0.166 nm is the fitted empirical electron layer thickness.

By combining the above equation with the measured τ3 values, the free volume size Vf is a function of R and it is given by the following equation:

$$Vf = 43\pi R3 \quad (2)$$

The relative intensity of the longest component, I3, is usually connected with the density of the free volume hole. This can be considered as a kind of trapping center for positrons. To determine the fractional free volume fv in polymers, one can use a semi-empirical relation:

$$fvC = VfI3 \quad (3)$$

where: Vf – the size of the free volume calculated from τ3 by using equation (1), above, with a spherical approximation; I3 – intensity of component τ3 expressed in [%]; C – constant, empirically determined to be 0.0018 [15].

In order to analyze components τ1 and τ2 and their intensities I1 and I2, a so-called two-state model is used [16, 17]. Following this model, the numerical parameters of positron trapping (mean τ_{av} and defect-free bulk τ_b positron lifetimes, and positron trapping rate in defects κ_d) can be calculated in accordance with the established formulas below:

$$\tau_{av} = \tau 1I1 + \tau 2I2I1 + I2 \quad (4)$$

$$\tau_b = I1 + I2I1\tau 1 + I2\tau 2 \quad (5)$$

$$\kappa d = I2I11\tau b - 1\tau 2 \quad (6)$$

In addition, the difference τ2 – τb can be calculated as an indicator of the size of extended defects which trap positrons in terms of the equivalent number of monovacancies, whereas the τ2τb ratio is ascribed to the nature of these defects [16, 17].

The purpose of this study was to undertake an estimation of the degree of disorder of the polymeric materials used in the manufacture of contact lenses, employing positron annihilation lifetime spectroscopy PALS. In our study, two different types of contact lenses were used – a hydrogel (Omafilcon A) and silicone-hydrogel (Comfilcon A). In order to describe the relationship between the lifetime of ortho-positronium (o-Ps), the size of free volumes and fractional free volumes, the Tao-Eldrup model was used. Moreover, the parameters of a trapping model were determined.

Material and Methods

The study was performed on brand-new, commercially-available hydrogel Proclear and silicone-hydrogel Biofinity contact lenses manufactured by Cooper Vision. Mechanically damaged contact lenses were eliminated from the study. More detailed parameters of the contact lenses investigated are listed in Table 1.

Table 1. Properties of the contact lens material evaluated in this study

USAN	Omafilcon A	Comfilcon A
Proprietary name	PROCLEAR	BIOFINITY
Water content (%)	62	48
Oxygen permeability ($\times 10^{-11}$), Dk	28	128
Oxygen transmissibility ($\times 10^{-9}$), Dk/t	42	116
Principal monomers	HEMA, PC, EGDMA	NVP, VMA, IBM, TAIC, M3U, FM0411M, HOB

HEMA – 2-hydroxyethyl methacrylate; PC – phosphorylcholine; EGDMA – ethylene glycol dimethacrylate; NVP – *N*-vinyl pyrrolidone; VMA – *N*-vinyl-*N*-methylacetamide; IBM – isobornyl methacrylate; TAIC – 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione; M3U – bis(methacryloyloxyethyl iminocarboxy ethyloxypropyl)-poly(dimethylsiloxane)-poly(trifluoropropylmethylsiloxane)-poly[methoxy-poly(ethyleneglycol] propylmethylsiloxane); FM0411M – methacryloyloxyethyl iminocarboxyethyloxypropyl-poly(dimethylsiloxy)-butyldimethylsilane; HOB – 2-hydroxybutyl methacrylate.

Contact lenses belong to the Proclear family are based on the hydrogel material Omafilcon A. Omafilcon A is composed of 2-hydroxyethyl methacrylate (HEMA) and 2-methacryloyloxyethyl phosphorylcholine (MPC) polymers crosslinked with ethylene glycol dimethacrylate (EGDMA). Proclear lenses are made with PC technology – technology using phosphorylcholine, a unique material which resembles naturally occurring substances in human cell membranes. These molecules naturally attract and surround themselves with water, providing hydration and comfort even after 12 hours of wear. By allowing the lens to form hydrogen bonds with water, this technology causes the water molecules to actually become a part of the lens, creating a natural resistance to dryness [18, 19].

Biofinity contact lenses are made of the silicone-hydrogel material Comfilcon A and are made using Aquaform Technology. This fabrication method uses longer silicate chains, which translates into a lesser silicon content in the material of the lens. "The molecular structure of Aquaform Technology lens material provides not only uniform wettability, creating a smooth lens surface, but also natural wettability. The lenses can come with artificial coatings and wetting agents that dissipate over time. The silicone macromers in Aquaform Technology lenses lock water into the lens, keeping them moist even after periods of extended wear. Moreover, the material in Aquaform technology lenses has high oxygen transmissibility for increased breathability, to keep eyes healthy" [18].

The chemical structures of the principal monomers used in the production of Omafilcon A and Comfilcon A are shown in the Figures 1 and 2, respectively.

The PALS measurements were performed at room temperature using an ORTEC spectrometer, based on a "start-stop" method [20, 21]. The spectrometer, with a lifetime resolution of FWHM = 270 ps, was monitored with a ^{60}Co source and was used to record all PALS spectra. The samples, along with the source of positrons (^{22}Na isotope of an activity of 4×10^5 Bq) and Kapton foil (thickness of 8 μm), formed a so-called "sandwich" system. The positron lifetime spectra were analyzed using the LT_9 computer program designed by Kansy [22]. The obtained results of the calculations are presented in the form of mean values and standard deviation.

Results

The positron lifetime spectra obtained for the samples investigated are shown in the Figure 3. The results of the calculations of mean positron lifetime values for the materials investigated revealed the existence of three components, τ1, τ2 and τ3, with the intensities I1, I2 and I3, respectively. In our previous studies [19, 23], we have

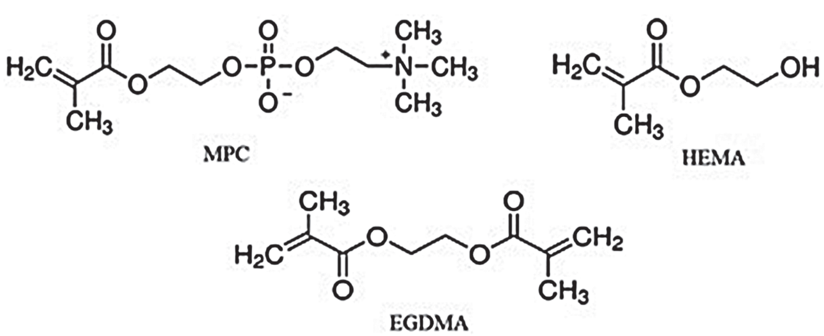

Fig. 1. Chemical structures of principal monomers of Omafilcon A

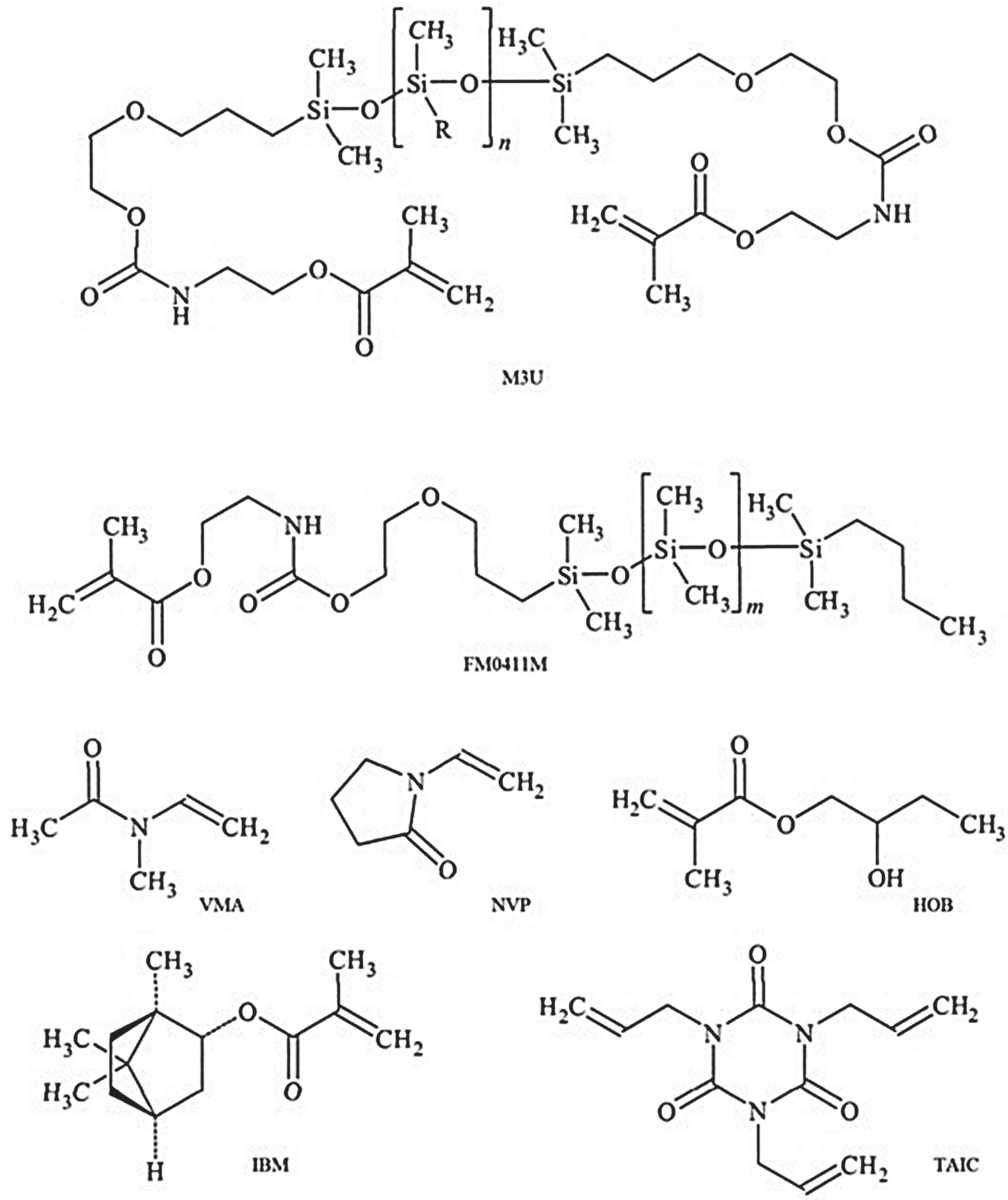

Fig. 2. Chemical structures of principal monomers of Comfilcon A

isolated and calculated the values of long-living components τ3 and their intensity I3 for hydrogel contact lenses belong to the Proclear family (Omafilcon A) and silicone-hydrogel lenses belong to the Biofinity family (Comfilcon A). The measurements conducted allowed us to estimate the size Vf and amount fv of free volumes. Additionally, in this paper we analyze components τ1 and τ2 and their intensities I1 and I2 by using a positron annihilation two-state model. The mean positron lifetime values and their intensities are collected in Table 2. The accuracy of the calculations are the result of mathematical analysis.

According to the common interpretation, the long-lived component τ3 is associated with the formation of o-Ps and is a measurement of the density distribution

Table 2. Mean positron lifetime values τ1, τ2 and τ3 and their intensities I1, I2 and I3

Sample	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)
Omafilcon A	0.212 ± 0.006	59.98 ± 0.93	0.474 ± 0.019	32.88 ± 0.64	1.814 ± 0.031	7.14 ± 0.38
Comfilcon A	0.164 ± 0.007	77.04 ± 0.85	0.602 ± 0.022	16.20 ± 0.89	3.249 ± 0.104	6.76 ± 0.14

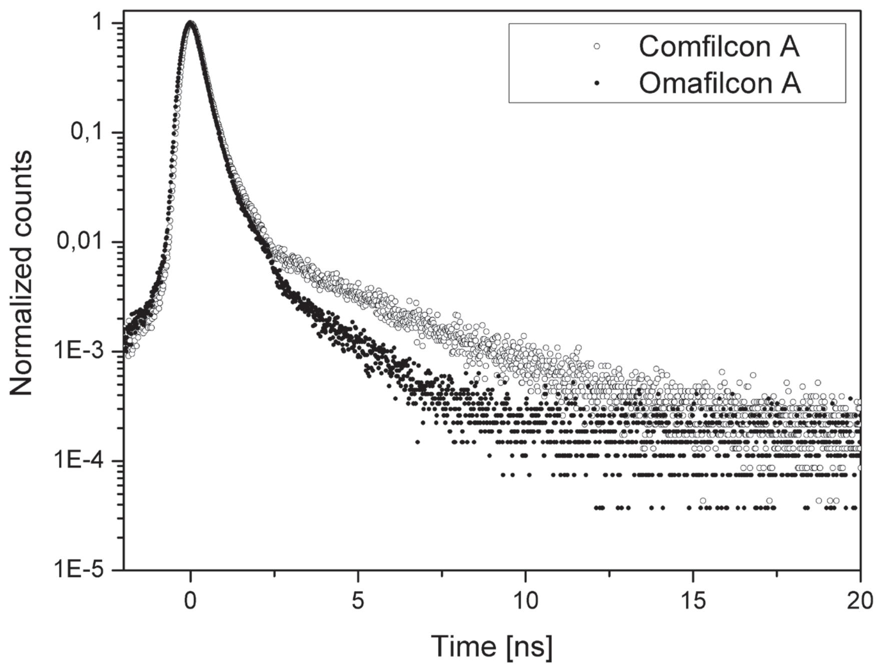

Fig. 3. Positron lifetime spectra for the investigated contact lenses

of the formation of free volumes. Changes in the values of lifetimes τ3 and their intensities I3 are represented as changes in the free volumes Vf and the amount of free volumes fv. Table 3 shows the values of the average parameters of free volumes R, Vf and fvC, calculated from equations (1) – (3). Free volume holes are formed in both types of contact lenses investigated. The values of Vf and fvC were, respectively, 2.8-fold and 2.7-fold higher in the Comfilcon A sample than in the Omafilcon A sample. The size of free volume Vf as well as the value of fractional free volume fvC for the silicone-hydrogel lenses are larger (about 35% and 37%, respectively) than in the case of the hydrogel lenses. It may be worth noting that the oxygen permeability of the silicone-hydrogel lens is also much higher, 4.6-fold.

The parameters of the two-state positron trapping model calculated using formulas (4) – (6) are showed in Table 4. An increase of the mean positron lifetime τ_{av} for the hydrogel contact lens indicates an increased concentration of positron traps. The bulk non-trapped positron lifetime τ_b indicates the distribution of electron density at the sites where the positron annihilation occurs. The positron trapping rate κ_d is about 17% higher for the hydrogel contact lens, which reflects a much greater concentration of defects and capture centers of positrons. This is also confirmed by the pronounced increase (32.88%) in the intensity of the I2 component for the samples. This relationship indicates an increased amount of positron trapping in defects (macropores). The parameter τ2-τ_b shows that the average sizes of the defects in which positron trapping occurs is 2-fold higher for the silicone-hydrogel contact lens. Both types of contact lenses are characterized by different defects. Also, the τ2τ_b ratio is different for both type of contact lenses (1.8-fold higher in the Comfilcon A sample) suggesting differences in the nature of the defects. The positions of positron captures have a different nature depending on the type of material.

Table 3. Calculated parameters of free volumes: R, Vf and fv/C

Sample	R [nm]	V_f [10^{-30}m^3]	f_v/C [a.u.]
Omafilcon A	0.2672 ± 0.0021	79.86 ± 2.23	570 ± 5
Comfilcon A	0.3792 ± 0.0034	228.28 ± 4.83	1543 ± 14

Table 4. Parameters of two-state positron trapping model

Sample	Parameters of trapping model				
	τ_{av} [ns]	τ_b [ns]	κ_d [ns^{-1}]	$\tau_2-\tau_b$ [ns]	τ_2/τ_b [ns]
Omafilcon A	0.305 ± 0.003	0.264 ± 0.002	0.923 ± 0.005	0.210 ± 0.001	1.798 ± 0.089
Comfilcon A	0.240 ± 0.002	0.188 ± 0.001	0.771 ± 0.004	0.414 ± 0.004	3.207 ± 0.160

Discussion

Unequal electron density in the material of hydrogel and silicone-hydrogel contact lenses, in particular the difference between defect-free and empty regions, is a source of measurable positron lifetimes (every disorder is reflected in the time spectrum). In free volumes, where electron density is lower due to the repulsive potential of electrons, the positron lifetime is extended.

The positron lifetime measurements conducted for the materials investigated revealed a lower degree of disorder for the hydrogel contact lens (Omafilcon A). This is related to the sizes of macropores and free volumes. In Omafilcon A, macropores and free volumes are much more filled with water, hence the average size of defects in which annihilation occurs is smaller than for Comfilcon A.

The geometry and nature of the defects which trap positrons in the contact lenses investigated are completely different due to the technology used in the production process and the type of material. In the silicone-hydrogel contact lens, the concentration of volume defects and trapping centers is increased. Thus, the average size of defects in which annihilation occurs is larger in the silicone-hydrogel contact lens. Therefore, the hydrogel contact lens exhibits a more regular and compact structure.

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