

Analysis of free volumes and light transmission in hydrogel and silicone-hydrogel polymer contact lenses

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The free volume holes and light transmission of hydrogel and silicone-hydrogel polymer contact lenses were investigated. As the material, the Proclear family (omafilcon A) of hydrogel contact lenses and the Biofinity family (comfilcon A) of silicone-hydrogel contact lenses were used. Positron annihilation lifetime spectroscopy was used to characterize geometrical sizes and fractions of the free volume holes in the investigated samples. There was a clear difference in the size of free volume holes and the fractional free volume between silicone-hydrogel and hydrogel polymer contact lenses. These changes are shown by a thorough analysis of the long-lived component of lifetime of ortho-positronium. At the same time, UV-vis-NIR in the spectral range 200–1000 nm studies were performed on the same samples of contact lenses spectrometry.

Keywords: positron annihilation, UV-vis-NIR, polymers, contact lenses, free volume.

1. Introduction

There is an urgent need for the development of amorphous polymeric materials for biomedical application and thus the search for materials suitable for contact lenses fabrication is one of the examples in this context. The driving force of the evolution of materials used for contact lenses fabrication is the need to increase comfort and man's visual acuity, along with the improvement of the biocompatibility and the minimization of the impact of the material on the physiology of the cornea. Despite a significant progress in improving the properties of hydrogel and silicone-hydrogel material, the problem exists to a limited degree of oxygen available to the cornea and ocular use which results in various diseases such as damaged epithelium, papillary conjunctivitis, cataract, dry eyes at the end of the day, and more [1–4]. We used two types of contact lenses for our study: the Proclear family hydrogel contact lenses, and the Biofinity family silicone-hydrogel contact lenses.

Proclear lenses based on a hydrogel material omafilcon A, are made with the use of PC technology. Omafilcon A contains a polymer of 2-hydroxy-ethylmethacrylate and 2-methacryloyloxyethyl phosphorylcholine cross-linked with ethylene glycol dimethacrylate. The uniform PC (phosphorylcholine) coating on the surface of contact lens imitated the bipolar nature of the physiological film and increases bio- and hemo-compatibility. Water molecules also show a bipolar structure, hence many of them are loosely connected to the phosphorylcholine surface contained in contact lenses. As a result, water molecules bound to the surface of the PC inhibit the binding of other molecules, thereby reducing friction, which minimizes irritation to the eye. According to Cooper Vision, Proclear family lenses hold 98% of the water even after being used for 12 hours [5, 6].

Biofinity lenses contain comfilcon A as a silicone-hydrogel material and are made with the use of Aguaform technology. This fabrication method uses longer silicate chains, which translates into lower silicon content in the material of the contact lens. A smaller amount of silicone material makes the lens softer, more flexible, and more wet. Hydrogen bonding of water molecules forms naturally a water-loving contact lens, which keeps water in its interior, and minimizes drying. A smaller amount of silicone in the material is the reason why they exhibit a better oxygen permeability. Biofinity lenses also contain lots of water and are permeable to oxygen dosing [3, 4].

The search for new materials for advanced medical applications, called biomaterials, is now an interest for the large number of scientists: physicists, chemists, biologists, for whom a consistent interdisciplinary approach evolves. In fact, modern polymeric materials used for manufacturing contact lenses are hydrogel and silicone-hydrogel, and their chemical and biological properties must be biocompatible with the human organism [7, 8].

The positron annihilation lifetime spectroscopy (PALS) is a powerful tool for exploring open spaces at the atomic size level. It is one of the most sensitive and sophisticated tools for determining directly the average size of free volume and its relative concentration in polymeric materials [9].

2. Theory

2.1. Theory of positron annihilation

Positron annihilation results in the change in the whole mass of both particles and their kinetic energy into the energy of photons of electromagnetic radiation. Therefore, the study of photons generated in the process of annihilation, provides information on the state of an electron–positron pair. Annihilation of particles is possible only when conservation laws are satisfied, namely conservation of energy, momentum, angular momentum, charge, and parity. The annihilation of the antiparticle with the particle results in even (2γ) or odd (3γ) number of gamma quanta [10–12]. Besides the free annihilation, there also may exist electron–positron annihilation in bounded state. It occurs when an electron and a positron form a hydrogen-like atom called positronium (Ps).

High-energy positron annihilation is preceded by a thermalization phenomenon, which consists in the rapid loss of energy due to scattering of positrons and the excitation center. Thermalization is of a great importance when the positrons are created with the process of β^+ nuclei disintegration. Positron at the recent precipitation from 10 to 50 eV of its energy, goes in the same row and then the reaction can occur by positronium formation if one of the free electrons surrounding it has this same energy [13, 14].

Two states of positronium may be distinguished due to two different spin oscillations. One is called para-positronium (p-Ps) in which the positron and electron spins are anti-parallel. The other state, ortho-positronium (o-Ps), corresponds to parallel particle spins. In condensed matter, however, the positron in o-Ps predominantly annihilates during collisions with atoms or molecules with an electron other than its bound partner and possessing an opposite spin. In this process, which is referred to as “pick-off” annihilation, the o-Ps lifetime in polymers is reduced to a few nanoseconds. Ps cannot form in materials with high electron densities. The positronium formation probability and lifetime are extremely sensitive to electron density surrounding Ps. The o-Ps is localised in the space between and along polymer chains and at chain ends (free volume holes), and the lifetime gives indication on the mean radii of these holes [15, 16].

The existence of free volume holes – an areas of zero electron density – is necessary to positronium could survive in condensed medium without succumbing to extinction with an average lifetime by two 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 [17, 18].

In this paper, the relationship between the lifetime of ortho-positronium (o-Ps), and the size of free volume holes is described by the Tao–Eldrup model [17–19]. It can be assumed that positronium is located in a single spherical potential well. To simplify the calculations Tao proposed to replace the finite potential well by the infinite well with the value ΔR expanded. The parameter value ΔR should be chosen in such a way so that the probability of finding 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 τ_3 corresponds to a spherical space with a radius R of the free volume holes, according to the following equation [15, 20]:

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R_0 - \Delta R}{R_0} + \frac{1}{2\pi} \sin \left(2\pi \frac{R_0 - \Delta R}{R_0} \right) \right]^{-1} \quad (1)$$

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

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

The relative intensity of the longest component I_3 , is generally correlated to the density of the holes, which can be considered to be a kind of trapping centers for Ps. A semi-empirical relation may be used to determine the fractional 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 the long-lived component, C is an empirical parameter determined to be 0.0018 from the specific volume data [21].

2.2. Light transmission and absorbance

The harmful effects of UV radiation on the eyes and the need for adequate protection have been widely discussed in [22, 23]. Since eye protection is an important issue, additional tests were carried out using UV-vis-NIR spectroscopy. UV-vis-NIR spectroscopy is a technique, used for analytical purposes in the energy transition occurring in the molecules, caused by the absorption of electromagnetic radiation in the ultraviolet (200–400 nm), visible (400–800 nm) and near-infrared (800–1000 nm). When a light beam of radiation passes through the lens, then the outgoing radiation is attenuated with respect to the incident. Initial intensity of radiation is partially reflected or scattered, or partially absorbed, and only a portion passes through a lens [24]. The transmission is given by:

$$T_\lambda = \frac{S_\lambda}{R_\lambda} \times 100\% \quad (4)$$

where S_λ denotes transmitted light intensity for wavelength λ , and R_λ – reference light intensity for wavelength λ .

Light absorbance for each λ is calculated by

$$A_\lambda = -\log\left(\frac{S_\lambda}{R_\lambda}\right) \quad (5)$$

Including noise signal for each wavelength N_λ the Eqs. (4) and (5) can be rewritten as:

$$T_\lambda = \frac{S_\lambda - N_\lambda}{R_\lambda - N_\lambda} \times 100\% \quad (6)$$

$$A_\lambda = -\log\left(\frac{S_\lambda - N_\lambda}{R_\lambda - N_\lambda}\right) \quad (7)$$

The transmission and absorbance spectra presented in this papers were prepared with the use of Eqs. (6) and (7).

3. Experiment

In an attempt to compare the properties of hydrogel and silicone-hydrogel contact lenses, the positron annihilation lifetime spectroscopy (PALS) and UV-vis-NIR methods were used, simultaneously.

The studies were performed on new lenses which belong either to Proclear or Biofinity family. More detailed parameters are shown in Table 1.

As shown in previous publications [25–27], positron lifetime PALS measurements were performed at room temperature with a spectrometer ORTEC, based on a start–stop method [28]. Time resolution amounts to FWHM = 250 ps as monitored with a ^{60}Co source was used to record all PALS spectra. Each sample consists of 6 layers of contact lenses of a diameter of 10 mm and thickness of 1 mm. The sample, along with the source of positrons, which was the ^{22}Na sodium isotope with an activity 4×10^5 Bq, formed the so-called “sandwich” system. The measurements were carried out at room temperature. The examples of experimental PALS spectra of Proclear (omafilcon A) and Biofinity (comfilcon A) samples are shown in Fig. 1.

Table 1. Comparison of hydrogel contact lenses (Proclear) and silicone-hydrogel contact lenses (Biofinity).

Brand	Material	Water content	Oxygen permeability D_k
Proclear Multifocal Toric D	Omafilcon A (hydrogel)	59%	28
Proclear Multifocal Toric N	Omafilcon A (hydrogel)	59%	28
Biofinity Multifocal D	Comfilcon A (silicone-hydrogel)	48%	128
Biofinity Multifocal N	Comfilcon A (silicone-hydrogel)	48%	128

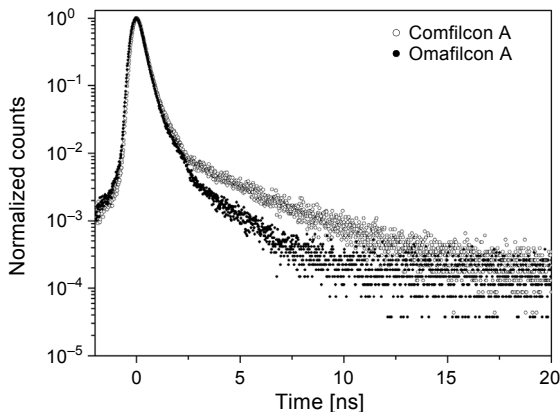


Fig. 1. The example of experimental PALS spectra of hydrogel (Proclear – omafilcon A) and silicone-hydrogel (Biofinity – comfilcon A) samples.

In order to gain a more complete picture of the phenomena, the spectrometric test UV-vis-NIR was used to study the second method. The test was performed with the use of Ocean Optics high-resolution HR4000CG-UV spectrometer with the spectral range from 200 to 1000 nm. A deuterium-tungsten-halogen covering the spectral range was used as the light source for testing the spectrometer. Lamp power was 3.8 W (deuterium lamp) and 1.2 W (tungsten halogen lamp). The examined contact lenses were brand new and their optical analysis was carried out when they were wet without buffered saline – the samples were rinsed in distilled water. The measurement was performed during the drying process, which resulted in significant changes in light transmission. Experimental setup is presented in Fig. 2.

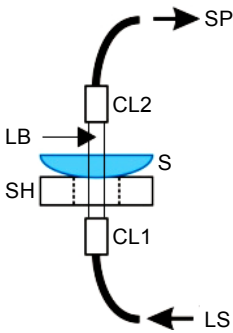


Fig. 2. UV-vis-NIR experimental setup. LS – light source, CL1 – collimating lenses 1, SH – sample holder, S – sample, LB – light beam, CL2 – collimating lenses 2, SP – spectrometer.

This type of measurement is useful for samples that do not focus or defocus light but can be used for contact lenses. It should be remembered that the contact lenses changed the direction of the transmitted light out of the collimating lens 2 (CL2) field of view. For this reason, the results are qualitative and show the general tendencies of changes of the light transmission. The final level of the light transmission was mainly related to the orientation of lenses in the sample holder (SH) after drying. In this work

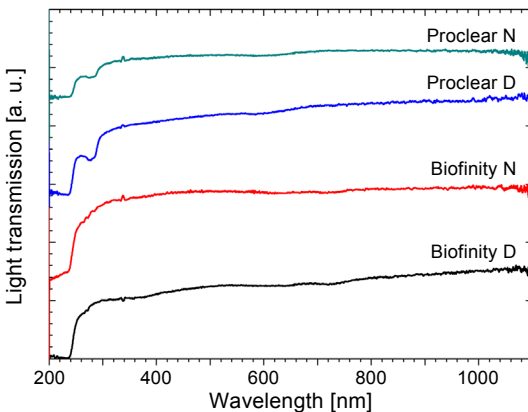


Fig. 3. UV-vis-NIR transmission spectra of the hydrogel (ProcLEAR – omafilcon A) and the silicone-hydrogel (Biofinity – comfilcon A) contact lenses.

we present the non-normalized transmission spectra of the dried lenses. Transmission spectra for the Biofinity and Proclear lenses family are shown in Fig. 3.

4. Results and discussion

Positron lifetime spectra were analyzed with the use of the LT computer program [29]. The obtained positron lifetime values revealed the existence of three components of τ_1 , τ_2 and τ_3 in the positron lifetime spectrum. For the analyses of PALS data the 3-component fitting procedure was used because in this case fit's variance χ^2 was near 1. The shortest lifetime component τ_1 is responsible for the annihilation of p-Ps (fixed to a value of 0.125 ns). The intermediate lifetime component $\tau_2 \sim 0.36$ ns is attributed to the free annihilation in the bulk material and positron trapping modes. As in the previous papers [27, 28, 30] on the subject, the attention was paid to the analysis of the long-lived component of the positron lifetime τ_3 . The values of positron lifetime of τ_3 o-Ps (the "pick-off" process) and their intensity I_3 , R hole radius R , the sizes of free volume V_f and the fractional of the free volume f_v are given in Table 2. The resulting errors are due to mathematical analysis. The fractional free volume f_v is proportional to $V_f \times I_3$, because C in Eq. (3) is constant.

Table 2. Calculated mean values of positron lifetime τ_3 , their intensity I_3 , the hole radius R , the sizes of the 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.]
Proclear Multifocal Toric D	1.853 ± 0.075	4.66 ± 0.17	0.271	83.33	388.32
Proclear Multifocal Toric N	1.893 ± 0.066	3.79 ± 0.26	0.275	87.08	330.03
Biofinity Multifocal D	3.210 ± 0.020	8.65 ± 0.15	0.377	224.35	1933.90
Biofinity Multifocal N	3.175 ± 0.024	7.56 ± 0.16	0.375	220.80	1669.25

Just as SZCZOTKA-FLYNN [31] compiled a chart of coefficient D_k/t and water content of the silicone-hydrogel lenses, in our work a set of average sizes of free volume V_f and the water contents of the samples for contact lenses is displayed in Fig. 4.

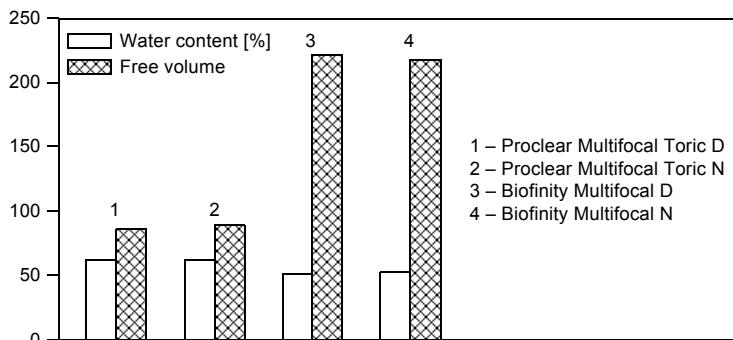


Fig. 4. The values of the average size of free volume V_f and the water content of the samples for contact lenses.

On the basis of the measurements, we can conclude that the size and the fraction of free volume are higher for silicone-hydrogel contact lenses. The high oxygen permeability coefficient for silicone hydrogel contact lenses can be also explained in terms of both higher free volume V_f and the fraction of free volume f_v for these contact lenses. From the physiological point of view, the oxygen permeability coefficient of the eye is the most important parameter characterizing contact lenses. The more oxygen can reach the eye, the more healthy the eye is. The lenses which permeable more oxygen to the cornea significantly reduce the risk of infection, and therefore are safer for the wearer and provide greater comfort.

The result of spectrometric measurements are presented in two figures. The first (Fig. 3) ones shows transmission spectra of examined lenses in full range of the spectrometers used. To improve the clarity, the respective transmission curves are arranged in a stack. In the visible region of electromagnetic radiation all of the examined lenses transmit the light perfectly. This high light transmission is maintained to the end of spectral range of spectrometer used (1100 nm – NIR region). Significant changes in transmission spectra for Proclear and Biofinity lenses are in UV range. Therefore this part of electromagnetic radiation was analyzed in particular. Figure 5 shows the absorbance spectra of the analyzed materials for range 200–400 nm. These spectra were calculated in Eq. (7). As shown, the Proclear lenses have a clear absorption peak in 270–280 nm. Moving in the direction of the visible light, the optical density of the examined lens reduces and are close to each other. This trend sustains up to 1100 nm wavelength what was previously shown in Fig. 3.

Changes in the value of the lifetime τ_3 and I_3 intensities are represented as changes in the size of free volume V_f and the fraction of free volume f_v . From Table 2 it can be found that the values of V_f in the tested contact lenses differ widely among the samples. This can be combined with the oxygen permeability, which for silicone hydrogel contact lenses is significantly higher. Taking into account the defined value

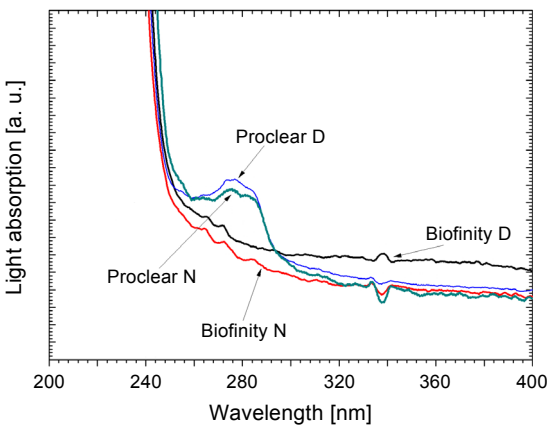


Fig. 5. UV absorption spectra for contact lenses.

of V_f (Eq. (2)) and f_v (Eq. (3)), we can conclude that the differences are responsible for the change in V_f free volume size, while the differences f_v are responsible for changes in the fraction of free volume. On the basis of the measurements, we can conclude that the size and the fraction of free volume are higher for silicone-hydrogel contact lenses. The high oxygen permeability coefficient for silicone-hydrogel contact lenses can also be higher due to the larger free volume V_f and the fraction of free volume f_v occurring in these lenses. From the point of view of the physiology, the oxygen permeability coefficient of the eye is the most important parameter characterizing the contact lens. The more oxygen reaches the eye, the healthier the eye is. Permeable contact lenses providing more oxygen to the cornea significantly reduce the risk of infection, are safer for the wearer and provide greater comfort. As for the parameters of the binary pattern positron annihilation studies, they showed that the differences between the lenses are too small to be able to extract a group of silicone-hydrogel and hydrogel contact lenses investigated. Division of the silicone-hydrogel group and the hydrogel is visible but when comparing medium-sized free volume V_f and the water content (%) for the samples of contact lenses (Fig. 4), silicone hydrogel contact lenses are characterized by a lower water content and have a much higher parameter V_f .

Both families of the lenses have perfect transmission in vis and NIR region. Significant differences can be observed in UV region which is presented in Fig. 3. The electromagnetic spectrum of ultraviolet radiation is subdivided to UVA (400–315 nm), UVB (315–280 nm) and UVC (280–100 nm). In UVA subregion, the absorptions are similar for both sample families. In UVC, we can see the absorption peaks beginning from 250 nm and rapidly rising in higher energy of the UV radiation. The difference occurs on the border between UVB and UVA radiation. Proclear lenses family has a wide absorption peak at 270–290 nm. It can be related to carbon $1s$ state and chemical bondings such as: O–C=O, N–C=O, C–O, C–N, C–Hx, C–C, C–Si [32], and the examples of the dependence on the difference between the absorption peak of hydrogel contact lens (omafilcon A) and silicone-hydrogel (comfilcon A) are shown in Fig. 5.

5. Conclusions

In this paper, we studied the structural changes of free volume holes in two different groups of contact lenses: hydrogel and silicone-hydrogel contact lenses, using the method of PALS (positron annihilation lifetime spectroscopy). The results of the measurements indicate that the formation of the free volume of the gaps takes place in all investigated contact lenses. However, the size of free volume holes V_f and the fraction of free volume present f_v for silicone-hydrogel contact lenses are larger than those in the hydrogel contact lenses. A complete understanding of the relation between oxygen permeability through the lenses and the free volume calls for more investigation.

From the study of UV-vis-NIR rises one main conclusion, namely that all of the investigated hydrogel and silicone-hydrogel contact lenses in a good way stop harmful ultraviolet radiation of 245 nm. The light transmission in vis and NIR region is high

and similar in the Biofinity and Proclear groups of contact lenses. The difference occurs on the border of UVB and UVA radiation and concerns carbon 1s state in the structure of the hydrogel contact lenses.

The PALS free volume spectroscopy and the UV-vis-NIR spectrometry carried out in parallel, indicate differences in the physical properties of the materials used for the production of contact lenses. The PALS experiment showed that the hydrogel contact lenses have almost three times smaller free volumes than the family of silicone-hydrogel contact lenses. For spectrometric investigations the clear differences are visible in UV region. In the visible region of the electromagnetic radiation the transmission is similar and imperceptible for a patient.

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