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# Positron annihilation study of the free volume changes in bifocal contact lenses

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**Positron lifetime spectroscopy has been applied to study free volume related properties of bifocal contact lenses. The measurements were made on new lenses and then after one, two, and three weeks wearing. The longest lifetime, obtained via three-component analyses of the spectra, was associated with the pick-off annihilation of *ortho*-positronium trapped in the free volume. After wearing of the lenses, changes in the *ortho*-positronium lifetimes and the relative intensity of the longest component were observed. The results are discussed on the basis of a free volume model.**

**Positron annihilation / Contact lenses / Positronium / Free volumes**

## Introduction

In recent years the study of amorphous polymers has become one of the most active fields in solid state research. The aim of this paper is to understand the changes induced by wearing of bifocal lenses, using positron annihilation lifetime spectroscopy (PALS).

The number of patients wearing soft contact lenses increases every year. Despite intensive improvements of the materials used to manufacture contact lenses there are still many problems caused by using lenses. Pathological changes of the cornea often occur in patients wearing contact lenses and are caused by polymeric materials used in the manufacture of contact lenses. The only materials ensuring visual acuity, comfort and safety are materials with biocompatible characteristics. Wearing the same contact lens for several weeks causes a risk of bacterial infection of the cornea, decreased comfort and disrupted vision, despite complying with specialists' recommendations. Moreover, the properties of polymeric materials of contact lenses used in patients are not well known. In order to produce contact lenses with required lubricity, optical parameters and ensuring the patients' comfort during wearing contact lenses for a long time, further research on physical features of polymeric materials used in the manufacture of contact lenses is required [1-4].

Positron annihilation is a useful technique to investigate material characteristics. Positrons injected in substances lose their energy through elastic collisions and finally annihilate with electrons through several processes. In the case of non-conductive molecular materials, in addition to the annihilation of the positron, formation and annihilation of positronium (Ps) take place. Ps is the bound state of the positron and electron having a radius comparable to that of the 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 state, ortho-positronium (o-Ps), corresponds to parallel particle spins.

In condensed matter, the positron in o-Ps predominantly annihilates, during a collision with atoms or molecules, with an electron other than its bound partner and possessing an opposite spin. This process, called pick-off annihilation, reduces the o-Ps lifetime in polymers to a few nanoseconds. Ps cannot form in materials with high electron densities. The formation probability and lifetime of the positronium are extremely sensitive to the electron density surrounding Ps. The o-Ps localises in the space between and along the polymer chains and at chain ends (free volume holes), and the lifetime gives an indication on the mean radii of these holes [5-8]. The original free volume theory for positron annihilation in molecular substances was proposed by Brandt, Berko and Walker [9]. The free volume was defined as the cell volume minus the excluded volume, which was based on Wigner-Seitz approximations.

The free volume model tells that Ps can only form in free spaces of the lattice having a size superior to some critical values. The electron pick-up depends on the overlap of the positron component of the Ps wave function with the lattice wave function. As the size of the free volume cavity increases, the local electron density surrounding the o-Ps decreases. Thus the o-Ps has a slower annihilation rate and longer lifetime. Tao and Eldrup *et al.* [10,11] derived an equation to correlate experimentally observed o-Ps lifetimes and free volume hole dimensions in polymers. They proposed a simple model in which the o-Ps particle resides in a spherical potential well, having an infinite potential barrier of radius $R_0$. It is assumed that an electron layer forming a thickness $\Delta R$ is present on the wall of the hole, the effective radius of which becomes $R = R_0 - \Delta R$, and that the lifetime of the o-Ps in the electron layer is the spin averaged Ps lifetime of 0.5 ns.

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 $\tau_3$ corresponds to a spherical space with a radius $R$ according to the following equation:

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

where $\Delta R = 0.166$ nm is the fitted empirical electron layer thickness. By fitting the above equation to the measured $\tau_3$ values, $R$ and the free volume size $V_f$, defined as:

$$V_\mathrm{f} = \frac{4}{3}\pi R^3 \quad (2)$$

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 trapping centres for Ps. A semi-empirical relation may be used to determine the fraction of free volume ($f_V$) in polymers as:

$$f_\mathrm{V} = \mathrm{C} V_\mathrm{f} I_3 \quad (3)$$

where $V_f$ is the free volume calculated from $\tau_3$, using Eq. 1 with a spherical approximation, and $I_3$ (in %) is the intensity of the long-lived component; C is an empirical parameter, which can be determined by calibrating with other physical parameters [6-8].

## Experimental

Modern technologies allow the manufacture of very good quality soft contact lenses thanks to a synthetic copy of the phosphorylcholine particle, which binds water within the lens, reduces its absorption and increases the patients' comfort. Normal metabolism in the eye structures under the contact lens can be achieved thanks to an increase in hydration and gas permeability of the lens, as well as to a decrease of its thickness. The modern contact lens has increased resistance to drying out, provides contact supply of oxygen in the eye during the day and ensures the patient's comfort when wearing the lens.

The purpose of this study was to undertake an estimation of physical features of polymeric materials used in the manufacture of contact lenses, employing the positron annihilation method (PALS). Bifocal contact lenses, worn every day by patients wearing lenses on a regular basis for many years, were used. The measurements were made on new contact lenses and then after one, two, and three weeks wearing. Mechanically damaged contact lenses were eliminated from the study. The lenses were made of galyfilcon A. The oxygen permeability was $86\times10^{-9}$ and the content of water in the lens was 47 %. The lenses had class 1 UV filter, a diameter of 17 mm and 0.7 mm thick [12].

The PALS measurements were performed at room temperature using a conventional fast-fast coincidence system with an ORTEC apparatus (block-scheme in Fig. 1). The time resolution of the system was 0.270 ps (full width at half maximum). Each specimen consisted of a system of layers, of total size of 10 mm diameter and 1 mm thick. A $^{22}$Na isotope positron source of $7.4\times10^5$ Bq activity was situated between two identical samples, forming a "sandwich" system. In general, each PALS spectrum recorded with a total number of $2\times10^6$ counts, which is high enough to obtain a good analysis, was measured five times to check its reproducibility. The lifetime spectra were analysed using the common microcomputer program LT designed by Kansy [13].

## Results and discussion

The positron lifetime spectra were analyzed using the LT computing program with a three-component model (Fig. 2 presents a typical curve of spectrum lifetime). Therefore, only three-component results are presented here. In polymers, the shortest-lived component is usually attributed to p-Ps annihilation. Therefore, during the fitting the shortest lifetime, $\tau_1$, was fixed at 125 ps (the p-Ps lifetime).

The intermediate lifetime ($\tau_2 \sim 0.36$ ns) is due to the annihilation of free positrons with electrons in the bulk material and positron trapping modes [8,14-16]. The results of the calculation of the mean values of positron lifetimes for the investigated samples showed the existence of a long-lived component in the positron annihilation lifetime spectra. According to the common interpretation we attribute the longest component, $\tau_3$, to the pick-off annihilation of o-Ps trapped by free volumes. In any given sample all the free volume holes are not of the same size. The LT results are averaged values, but the real long-lived annihilation events have some time-distribution around the averaged value. So, the concept of the average free volume size is used in practice.

As the o-Ps component is relevant to the free-volume properties, and it is markedly sensitive to the microstructure changes, in this paper we focus on $\tau_3$, and $I_3$. The variations of the o-Ps pick-off lifetime and

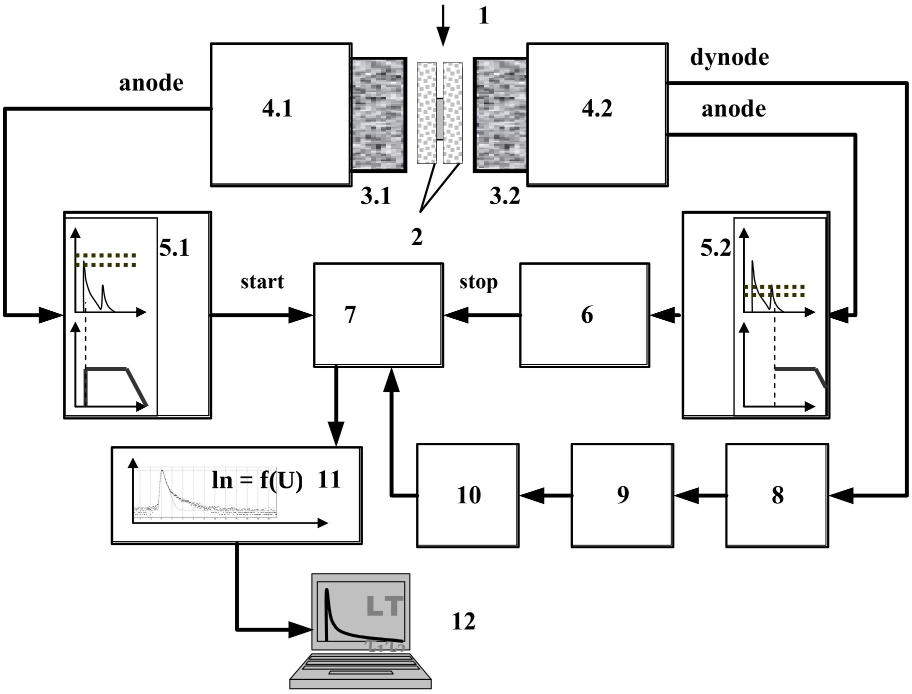


**Fig. 1** Block-scheme of a conventional sample-source "sandwich" arrangement for PALS measurements using an ORTEC apparatus:

| | |
|---|---|
| 1 – foil-covered $^{22}Na$ source, | 2 – two identical samples, |
| 3.1 and 3.2 – scintillators of $\gamma$-quanta, | 4.1 and 4.2 – photomultipliers, |
| 5.1 and 5.2 – constant fraction discriminators, | 6 – delay line, |
| 7 – time-pulse height converter, | 8 – preamplifier, |
| 9 – amplifier, | 10 – single channel analyzer, |
| 11 – multichannel analyzer, | 12 – personal computer |

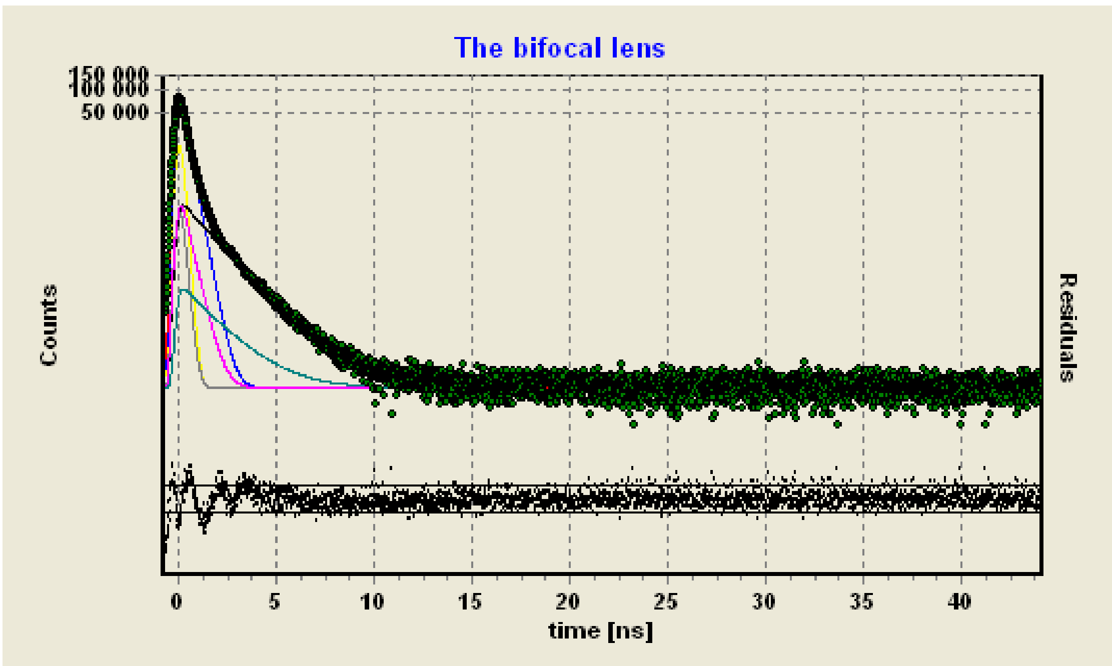


**Fig. 2** Typical curve of spectrum lifetime for the measured samples of bifocal lenses.

**Table 1** Mean values of the lifetime $\tau_3$, relative intensity $I_3$ of o-Ps, and radius $R$.

| Samples | $\tau_3$ [ns] | $I_3$ [%] | $R$ [nm] |
|---|---|---|---|
| Bifocal contact lens new – 0 | 1.664 ± 0.087 | 8.54 ± 0.09 | 0.25186 |
| Bifocal contact lens after one week wearing – 1 | 1.748 ± 0.09 | 11.275 ±0.105 | 0.26057 |
| Bifocal contact lens after two weeks wearing – 2 | 2.941 ± 0.098 | 13.44 ± 0.12 | 0.36518 |
| Bifocal contact lens after three weeks wearing – 3 | 1.652 ± 0.096 | 0.98 ± 0.10 | 0.25058 |

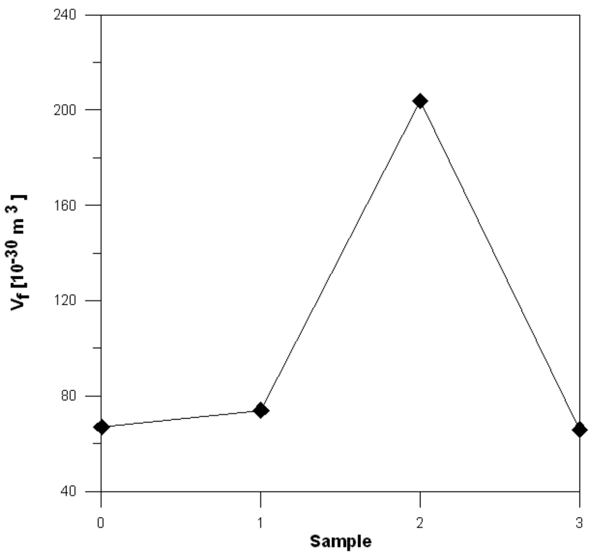


**Fig. 3** The average free volume size $V_f$ for the investigated samples of bifocal lenses.

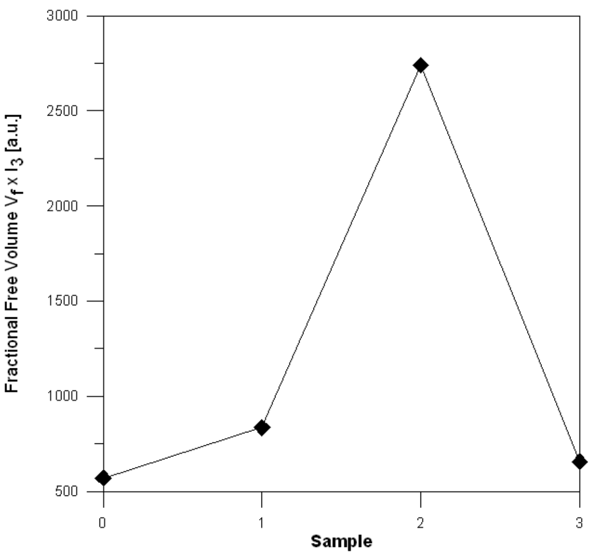


**Fig. 4** $V_f \times I_3 = f_v/C$ for the investigated samples of bifocal lenses.

its intensity and the radius $R$ for the investigated polymer bifocal contact lenses before and after wearing are presented in Table 1.

The values of the average free volume size $V_f$ and fractional free volume $V_f \times I_3 = f_v/C$ for the investigated samples are shown in Fig. 3 and in Fig. 4, respectively. The error bars are smaller than the symbols. The fractional free volume is proportional to $V_f \times I_3$ because C in Eq. 3 is constant.

Changes of $\tau_3$ and $I_3$ are transmitted to the free volume size $V_f$ and fractional free volume $V_f \times I_3$ (Fig. 3 and Fig. 4). From these figures it results that the free volume size $V_f$ grows significantly after two weeks wearing of the contact lenses. During the third week the value of $V_f$ falls. In the case of $V_f \times I_3$, the increase observed after one and two weeks of wearing is also followed by a decrease during the third week. From Eq. 2 and Eq. 3 we can see that changes of $V_f$ correspond to changes of the sizes of the free volumes, while changes of $V_f \times I_3$ correspond to changes of the amount of these free volumes. The presented measurements show that after two weeks wearing of the bifocal contact lenses both free volume parameters increase significantly and then decrease during the last week of wearing (third week).

The lifetime of the long-lived component $\tau_3$ and its intensity $I_3$ exhibit a significant increase of the relative intensity of o-Ps, which is a measure of the free volume hole density. This indicates that creation of additional free volume holes takes place in the samples of bifocal contact lenses. The largest creation of free volume holes, in size and quantity, occurs after two weeks of wearing the contact lenses. Changes of the free volumes are linked to mechanical changes inside the polymeric material used to produce the contact lenses. The largest tiring of the material takes place after two weeks of use. From the physical and medical point of view it is possible to suggest that the contact lenses should be worn for no longer than two weeks.

The results of our study suggest that further improvements of the materials used in contact lenses manufacture are necessary. Such improvements could facilitate the production of lenses that would minimize the risks related to their application and prolonged use.

## References

[1] I. Tranoudis, N. Efron, *Cont. Lens Anterior Eye* 27 (2004) 133-148.

[2] M. Guillon, C. Maissa, *Cont. Lens Anterior Eye* 28 (2005) 67-73.

[3] H. Pult, C. Purslow, M. Berry, P.J. Murphy, *Optom. Vision Sci*. 85 (2008) E924-E929.

[4] J.S. Wolffsohn, O.A. Hunt, A.K. Basra, *Cont. Lens Anterior Eye* 32 (2009) 37-42.

[5] Y.C. Jean, *NATO Advanced Research Workshop*, *Advances with Positron Spectroscopy of Solids and Surfaces*, Yarenna, Italy, July 16-17, 1993.
[6] R.A. Pethrick, *Prog. Polym. Sci.* 22 (1997) 1-6.
[7] M. Hyla, J. Filipecki, Z. Mandecki, R.I. Mervinskii, *J. Non-Cryst. Solids* 232-234 (1998) 446-449.
[8] M. Hyla, J. Filipecki, J. Swiatek, *J. Non-Cryst. Solids* 352 (2006) 2726-2730.
[9] W. Brandt, S. Berko, W.W. Walker, *Phys. Rev.* 120 (1960) 1289-1299.
[10] S.J. Tao, *J. Chem. Phys*. 6 (1972) 5499-5506.
[11] M. Eldrup, D. Lightbody, J.N. Sherwood, *Chem. Phys.* 63 (1981) 51-58.
[12] Y. Wu, N. Carnt, F. Stapleton, *Cont. Lens Anterior Eye* 12 (2010) 54-57.
[13] J. Kansy, *Nucl. Instr. Meth. Phys. Res. A* 374 (1996) 235-244.
[14] R. Krause-Rehberg, H.S. Leipner, *Positron Annihilation in Semiconductors*, Springer, Berlin, 1999.
[15] B. Bergersen, M.J. Stott, *Solid State Commun*. 7 (1969) 1203-1208.
[16] R. Krause-Rehberg, H.S. Leipner, *Appl. Phys. A* 64 (1997) 457-462.

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