

Modification influence on the structural parameters of polymer ophthalmic materials

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Studies on polymer materials used in ophthalmological surgery as intraocular implants are presented in this paper. The material under investigation were brand new lenses provided by Alcon. The first lens, model SA60AT, was the basis structure, whereas the other one, model SN60AT, was a structure with an added modification in the form of a blue light chromophore. Results obtained with the use of the positron annihilation lifetime spectroscopy, as well as UV-vis-NIR methods, showed that the structure modified by the chromophore becomes more packed, while the results obtained by means of the UV-vis-NIR methods showed that the modification restricts the blue light transmission.

Keywords: intraocular lenses (IOLs), positron annihilation, UV-vis-NIR, polymers, biomaterials.

1. Introduction

Functional materials are materials that have closely defined functions, appropriate for a specific functional use. Manufacturing of these types of materials is aimed, at present, at manufacturing specific applications, which makes appropriate chemical and physical modification of their internal structures very important. Among the obtained functional materials, the most distinctive are those having electric, magnetic and optical properties used among other things in such branches of industry as electronics, telecommunication, nuclear or medical industries [1–3].

Medicine is a peculiar field to use functional materials, where specifically modified biomaterials are used as implants for replacement and taking over the functions of patients' natural tissues. Naturally, the materials used in this type of applications must first of all be characterized by good biocompatibility with the biological environment of the living organism. As living organisms are built mainly on the basis of high-mo-

lecular organic compounds, in many cases biomaterials are manufactured with the use of materials similar in terms of structure, *i.e.*, polymers. A large number of polymers are biocompatible with living organisms and their further modification with inorganic compounds may result in obtaining bioactive functions, for example in dental fillings, where addition, among other additives, of phosphorus compounds to the polymer matrix results in creation of chemical bonds between the filling and the tooth tissue [4]. Polymer matrixes without any inorganic additives are used in ophthalmology to produce, among other things, intraocular lenses (IOLs).

The first intraocular implants were manufactured on the basis of poly(methyl methacrylate) (PMMA), which is a biocompatible material, though stiff, which was connected with making excessive incision of the external tissues of an eye in order to insert the lens into an eyeball. The discovery of the phacoemulsification used to remove the cloudy natural lens allowed introducing elastic materials, which can be rolled and implanted through a small incision inside the eye [5]. The next step in making the use of intraocular lenses more functional was introducing the UV and blue light chromophores into structures of materials. Although the UV light is a well-known factor causing cataract, among other things, the effect of blue light on the damage of the sight organ, particularly of the retina of the eye, is not widely known. It turns out that blue light is one of the factors causing AMD (age-related macular degeneration). The use of chromophores causes the reduction of transmission of blue light into the retina of the eye, which is beneficial for prevention of this type of diseases [6].

Modification of the material of an intraocular lens towards achieving the absorption of blue light involves introducing molecules or atoms, which absorb the light-wave of the 400–500 nm range. At the same time it becomes important for the chromophore to become an integral part of the material of a lens material, due to which it will not be possible to leach it out of the inside into the surrounding tissues, which may lead to immunologic reactions. In order to obtain a homogeneous material, chromophores of appropriate optic properties, containing in their structures polymerizable functional groups, are used. To make the whole chromophore a durable molecule that does not change its optical properties, it is necessary to separate the group responsible for absorption from reactive groups by means of so-called spacing-groups. The final material is obtained as a result of polymerization of the main component of the material of the lens with the UV and blue light chromophores. The number of chromophores used for blue light should not exceed 0.1% of the weight material, at 1.9% of the weight material for all the chromophores in the material [7].

Observation of the impact of modification of a polymer chain on the parameters of the internal structure of the material is an important aspect from the technological point of view. Positron annihilation lifetime spectroscopy (PALS) seems to be a proper tool to watch such small modifications of the internal structure. Due to its sensitivity, the method is capable of measuring changes in the internal structure of empty spaces of the size above 1 Å and concentrations of modifications of 1 ppm [8].

The purpose of our study was checking, by means of the PALS technique, to what extent the modification with blue light chromophores changes the internal structure of an intraocular lens and what the UV-vis spectrum of thus modified structure looks like.

2. Methods – PALS theory

The effect of PALS technique is based on the interaction of elementary particles – positrons, created as a result of decay of an radioactive isotope, with the electrons of their material medium. Due to interacting with different annihilation centers, different positron lifetimes are obtained. The basic phenomenon taking place in the material is free annihilation, the effect of which is transformation of mass of the positron-electron pair into the gamma quantum energy with the most probable two-quanta process. The free annihilation lifetime is about 200 to 300 ps. Positrons can also be trapped by inter-atomic empty spaces, where they stay a little longer until the moment of annihilation. In this case, positron lifetime is about 300 to 500 ps. In amorphous materials, where large empty spaces can be found in the internal structure, there occurs the phenomenon of creation of a hydrogen-like atom called positronium. Due to mutual spin positioning of the positronium creating a positron-electron pair, there are the singlet parapositronium (p-Ps) state and triplet orthopositronium (o-Ps) state that stand out. The p-Ps state is characterized by anti-parallel positioning of spins and annihilates up to two gamma quanta after the time of 125 ps regardless of its medium, whereas o-Ps is characterized by parallel positioning of spins and, in the vacuum, it annihilates up to three gamma quanta after 142 ps. The time can be shortened to a few nanoseconds in a material medium. The phenomenon which allows to shorten o-Ps lifetime is called pick-off and involves annihilation of the positron creating positronium with an electron of the medium with an anti-parallel spin, which results in a two-quanta positron annihilation [9, 10].

As a result of PALS measurements, positron lifetime spectra are obtained and are later resolved into components. Each spectrum component is responsible for a given annihilation phenomenon. In case of polymers, there are usually three components obtained, where the first component is responsible for free annihilation and p-Ps in bulk material and is a mixed parameter, the second component refers to positron annihilation from the state localized in positron traps of multivacancy type, whereas the third component with the longest lifetime corresponds to the o-Ps annihilation from free volumes [11, 12].

Another approach towards spectrum distribution assumes determination of the first component as the one responsible only for the p-Ps annihilation, the second component responsible for free annihilation and annihilation from localized states, whereas the third component is responsible for o-Ps annihilation from free volumes [13, 14].

In order to determine the sizes of free volumes in the studied material, the Tao–Eldrup model is used [15, 16], according to which, the o-Ps lifetime in a free volume is proportional to its radius, which can be denoted by the following formula:

$$\tau_{\text{o-Ps}} = \frac{1}{2} \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1}$$

where $\Delta R = 0.166$ nm and describes thickness of the electron layer with which o-Ps interacts in the pick-off process. Next, assuming a spherical shape of free volumes, it is possible to determine their size

$$V_f = \frac{4}{3}\pi R^3$$

and their concentration inside the material

$$f_V = CV_f I_{\text{o-Ps}}$$

where $C = 0.0018$, and $I_{\text{o-Ps}}$ is the intensity of the o-Ps component [17].

3. Experiment

3.1. Materials

The material of the study were brand new Alcon intraocular lenses prepared by the manufacturer. Lens models SA60AT and SN60AT of 6 mm diameter and 1 mm thickness were used. The lenses that are the object of the study are hydrophobic materials based on copolymer of 2-phenylethyl acrylate (PEA) and 2-phenylethyl methacrylate (PEMA). 1,4-butanediol diacrylate (BDDA) was applied as a cross-linking agent. Apart from that, a UV light chromophore, *i.e.*, 2-(3'-methallyl-2'-hydroxy-5'-methyl phenyl) benzotriazole (o-MTP) was added to both lenses. The structure of the SN60AT lens was additionally modified with a blue light chromophore of the azo family compounds, namely N-2-[3-(2'-methylphenylazo)-4-hydroxyphenyl] ethyl methacrylamide. The prepared mixtures containing the components of lens materials were subjected to thermal free-radical polymerization. In case of the SA60AT lens, the percentage of PEA, PEMA, BDDA and o-MTP was 65%, 30%, 3.2% and 1.8%, respectively, whereas for the SN60AT lens it was 65%, 30%, 3.2% and 1.75%. Mass fraction of the added blue light chromophore was 0.05% [7, 18].

3.2. PALS measurements

PALS measurements were carried out with the use of Ortec spectrometer in start-stop configuration. Detailed description of the system was presented in [19]. Peak resolution of the system was 300 ps and was estimated with the use of the ^{60}Co isotope. The source of positrons was the ^{22}Na isotope of 400 kBq activity, closed in Kapton film. The positron source together with samples was placed between two scintillation counters forming a "sandwich" type system. The experiment was carried out in the temperature of 22°C with air humidity not exceeding 40%. The measurements yielded positron lifetime spectra made up of 1×10^6 – 2×10^6 counts, which provided appropriate statistics.

3.3. UV-vis-NIR measurements

The experimental setup for absorbance/transmission measurements is presented in Fig. 1. The DT-MINI-2-GS lamp was used as a light source. According to the device datasheet, the light output power coupled into UV/vis fiber and measured in the range of 200–1100 nm was 9.4 μW for the deuterium bulb and 7.0 μW for the tungsten halogen bulb. The examined intraocular lens was placed horizontally on the holder. The sample was illuminated from above by collimating lenses connected with fiber wire with a lamp. The transmitted light was collected by the second collimating pair of lenses coupled with the spectrometer via fiber wire.

4. Results and discussion

At the beginning, measurements with the use of the UV-vis-NIR spectroscopy were carried out in order to check in what way an addition of such a small amount of blue light chromophore influences transmission and absorption of light. The experimental setup presented in Fig. 1 is very sensitive when such objects as lenses are measured. The collimated lenses CL1 and CL2 must be perfectly aligned. A small variation causes significant changes in the signal recorded by the spectrometer. The examined samples had an optical power of +25 and +30 diopters, which greatly hampered the measurements. Most of the light was scattered and only a small part has been detected by the spectrometer. For this reason, the scale in Fig. 2 has an arbitrary unit. The experiment was carried out in UV-vis-NIR region and covered the spectral range of 200–1000 nm. Both of the intraocular lenses stop the harmful UV radiation up to 400 nm. In the visible region of 400–800 nm, the absorbance spectra are different. SN60AT absorbs radiation by 400–500 nm stronger than SA60AT. Human eye detects this radiation as a violet and blue color. The optical spectra of the examined samples in longer wavelength 520–1000 nm coincide with one another and they are approximately the same. Thus, it results from the performed measurements that a slight modification of the structure is able to limit light emission quite effectively, whereas modification with the use of UV chromophore in the amount of only 1.8% weight is significantly more effective than the modification with the use of 0.05% weight of blue light chromophore.

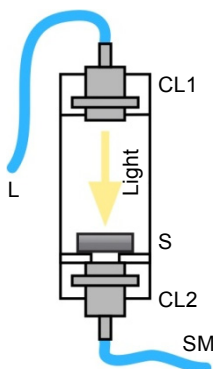


Fig. 1. Transmission/absorbance experimental setup; L – fiber wire from lamp, CL1 – collimating lenses 1, S – sample, CL2 – collimating lenses 2, SM – fiber wire connected to spectrometer.

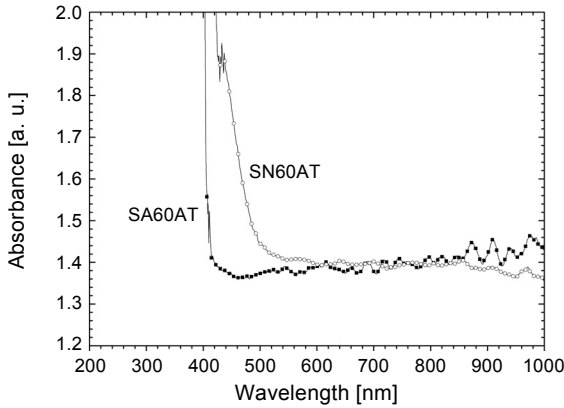


Fig. 2. Absorbance spectrum of examined samples.

As a result of the PALS measurements, positron lifetime spectra in the examined samples were obtained. Measurements were carried out on the same samples. In order to obtain reproducible results, four measurements for each sample were made. Each spectrum was decomposed into components with the use of the LT9 program for spectrum analysis [20]. The best matching was obtained for decomposition into three components, where the p-Ps annihilation and positron free annihilation were assigned to the τ_1 component, positron annihilation from the states localized in traps of the multivacancy type was assigned to the τ_2 component, whereas the o-Ps annihilation in free volumes was assigned to the τ_3 component. One decomposition, characterized by the best matching of the χ^2 parameter, was selected for analysis. A model positron lifetime spectrum with detailed decomposition into components is presented in Fig. 3.

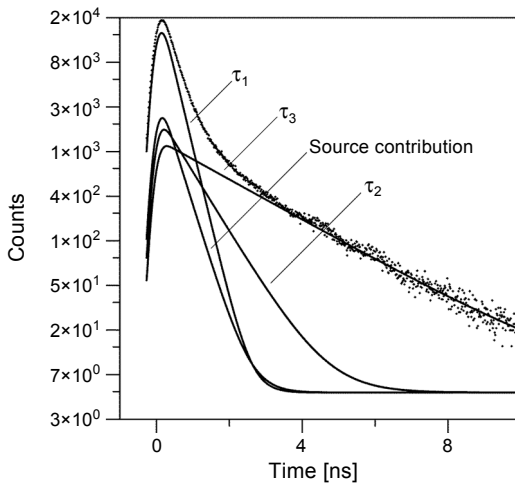


Fig. 3. Decomposed PALS spectrum of SA60AT sample.

Table 1. Results of PALS spectra decomposition and Tao–Eldrup calculation.

	Sample	
	SA60AT	SN60AT
τ_1 [ns]	0.291 ± 0.002	0.283 ± 0.002
I_1 [%]	65.50 ± 0.29	63.20 ± 0.08
τ_2 [ns]	0.748 ± 0.009	0.727 ± 0.011
I_2 [%]	13.10 ± 0.33	14.82 ± 0.08
τ_3 [ns]	2.197 ± 0.012	2.169 ± 0.006
I_3 [%]	21.42 ± 0.20	21.98 ± 0.06
R [Å]	3.1	3.0
V_f [Å ³]	120.0	116.5
f_V [a. u.]	4.63	4.61

Results of decomposition for both samples, together with values calculated for the Tao–Eldrup model are presented in Table 1.

It is evident from the results collected in Table 1 that the PALS method is sensitive to the modification applied to the material of the lens. The third component, responsible for the o-Ps annihilations, in which slight changes in lifetimes and intensities were detected, was subjected to interpretation. During structural modification the τ_3 component drops, whereas the I_3 intensity rises, which can be explained by higher packing of the structure of the material to which the blue light chromophore was added. However, one should not believe that modification resulted in deposition of particles of the chromophore in free volumes, because firstly there was a new structure formed as a result of polymerization of the mixture containing chromophore, and secondly a particle of chromophore is too large to fit into a free volume of the basic material. It is evident in the Tao–Eldrup model that modification of the structure resulted in decreasing the free volume radius, which was translated into its smaller size V_f . Concentration of free volumes f_V decreased in spite of the increased I_3 intensity. It is, therefore, the evidence confirming the fact of denser packing of the modified structure. As for the first two components, changes in lifetimes and their intensities can also be observed here. In case of the first component, the decrease of τ_1 time is connected with free annihilation in the new structure of bulk material, so it indirectly characterizes the modified bulk material. Decreasing of I_1 intensity in modified structure suggests the existence of lower free annihilation probably related with lower concentration of free electrons or point defects in the form of non-terminated polymer chains with negative charge.

Changes of τ_2 , the second component of lifetime and its I_2 intensity, have the same tendency as the third component. Hence, one can conclude that the sizes of multivacancy-type positron traps decreased during structural modification, what is indicated by decreasing τ_2 lifetime component. On the other hand, increasing of I_2 intensity can be explained by higher concentration of positron traps, which are formed in result of structure modification.

5. Conclusions

Polymer materials used as intraocular implants were examined in this study. Internal structures of materials were examined, one of which contained a blue light chromophore in the amount 0.05% of weight.

During the study carried out with the UV-vis-NIR method it was found that such a small modification can effectively limit light transmission within 400–500 nm. It was noticed, however, that modification of both internal structures with UV-chromophore in the amount of 1.8% of weight is much more effective. Such an attitude is probably determined by the intention to eliminate the effect of the harmful factor, *i.e.*, UV radiation and only to limit blue light transmission, in order not to lower the sharpness of vision.

The study with the PALS method revealed changes in positron lifetimes in the structure modified with a blue light chromophore. After adding particles of a chromophore, sizes and concentrations of free volumes as well as sizes of positron traps in the material were decreased. A change in the lifetime of the first component was also detected, which is the evidence of changes in the structure of the solid material. The study showed that the PALS method is a sensitive method for such a small structural modification.

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