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Void volume variations in contact lens polymers

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ABSTRACT

Aim: In this study, void size and free volume properties in different contact lens materials have been investigated in their hydrated state using positron annihilation lifetime spectroscopy (PALS).
Methods: PALS is used to characterize the void size distributions inside the lens materials. Three different types of contact lenses were used (Balafilcon A, Hilafilcon B and Polymacon).
Results: Measurements on different contact lenses reveal significant differences between the materials, up to ∼100% difference in void volume was observed between Hilafilcon B and Balafilcon A, the latter having larger voids. As oxygen diffusion is strongly correlated with the void sizes, the results are in good agreement with the usage recommendations of the specific lens types (daily disposable lenses or 1 month continuous use lenses). The void sizes in monthly lenses (Balafilcon A) were found to decrease 25% under artificial aqueous tear (albumin–water solution) exposure in 4 weeks leading to a significant decrease in the oxygen permeation rate through the contact lens. Yet, the voids were still significantly larger than in disposable or semi-disposable lenses.
Conclusions: We have showed that PALS is a viable method to probe the microstructure of biotechnologically relevant polymers and can be used to quantify the void properties in different types of contact lenses. Usage recommendations correlate well with measured void sizes and the median void size decreases during the incubation of albumin solution as a function of time. We anticipate the use of PALS for any polymer-based intracorneal/intraocular device in which diffusivity plays a crucial role.

1. Introduction

The local free volume of a polymer structure (void), corresponding to the unoccupied regions accessible to segmental motions, is an important parameter in the overall diffusion of atoms and molecules, either in gaseous or solid states, through the polymer. Positron annihilation lifetime spectroscopy (PALS) has been widely used to characterize atomic scale defects in semiconductors and metals and is also routinely used to study void distributions in polymer materials and in characterizing structural parameters such as the glass transition temperatures [1]. Lately we have employed this method to study also biological materials, such as lipid bilayers [2] as well as intact crystalline intraocular lenses [3]. Diffusion of molecules is largely determined by the presence and volume of voids in any material, and hence PALS can give direct information of the diffusion properties of the material in question.

Oxygen diffusion is one of the most important factors in contact lens (CL) materials. Typically the permeation of oxygen through the CL is much less efficient in soft disposable CLs compared to harder CLs designed for daily long term use. In an earlier study by Singh et al. [4] where PALS and measurements of gas diffusion rates were compared, it was shown that oxygen diffusion through CLs was strongly dependent on the void sizes. This effect was explained by the fact that gas permeability is the product of solubility and diffusion coefficient, causing the permeability to change with free volume. In another PALS study on CLs, Deepa and Ranganathaiah [5] reported that calcification of CLs reduced the void volume of these lenses, as the calcium deposits filled the voids. The focus of that work was, however, on the optical properties of the CLs before and after calcification. Both of these studies show that PALS is applicable to study ready-to-use CLs (instead of representative polymer samples) of different types.

Different types of CLs have different specifications on how long these should be used continuously. This is partly dependent in the oxygen permeability of each CL polymer. Furthermore, the contamination of CL by proteins, ions, and impurities present in the tear fluid will eventually reduce the diffusion properties of the CL by filling the voids within the polymer. In this work we have studied the void size distributions (and hence the diffusion characteristics) of different types of CLs. We also exposed different types of CLs to aqueous albumin solution and followed changes in the void volume as a function of time.

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2. Positron annihilation lifetime spectroscopy in polymers

When an energetic positron from a radioactive source (^{22}Na in most cases) enters molecular media, it thermalizes rapidly after interacting with the surrounding molecules through inelastic collisions. A fraction of positrons forms a bound state with spin parallel electrons (ortho-positronium, o-Ps) that preferentially localizes in the free volume pockets in the material. In vacuum, o-Ps has a relatively long lifetime of 142 ns, compared to 125 ps for p-Ps (bound state of a positron and an electron with opposite spins). In a medium, the o-Ps prefers to undergo so-called pick-off annihilation with an electron of opposite spin during collision with molecules in the cavity wall in which it is localized. The pick-off process reduces the lifetime of o-Ps down to a few nanoseconds. The smaller the cavity size, the higher the frequency of collisions and the shorter the o-Ps lifetime, hence the o-Ps lifetime provides information of the size of the free volume pockets (i.e., voids).

A quantitative semi-empirical relation has been established by Tao and Eldrup [6] (work on positronium trapping to voids in polymers) correlating the o-Ps lifetime (τ_{polymer}) with the radius (R) of a spherical trap:

$$\tau_{\text{polymer}}\ (\text{ns}) = \frac{1}{2}\left[1 - \frac{R}{R+C} + \frac{1}{2\pi}\,\sin\left(\frac{2\pi R}{R+C}\right)\right]^{-1}, \qquad (1)$$

where C is a semi-empirical constant of 0.166 nm [7]. The model applies directly to spherical voids and as such it is not directly applicable to characterize accurately the void sizes in CLs, as the specific form and distribution of forms of the voids is not known. However, the Tao–Eldrup model can be used to provide an order-of-magnitude estimate and means to compare the void sizes in polymers.

3. Experimental methods

3.1. Instrumentation

The PALS measurements were performed using a sandwich-geometry of the sample material and the positron source. The positron/positronium lifetime is measured with a pair of scintillation detectors, one detecting the birth of a positron and the other its annihilation. When the positron source (^{22}Na) decays, it produces simultaneously one positron and one ∼1.27 MeV γ-quantum. When this quantum denoting the birth of the positron is detected, the pulse acts as a START-signal for the equipment. When the positron annihilates in the sample, as a free positron, p-Ps or o-Ps (pick-off) it produces two γ-quanta of about 511 keV each, either of which act as the STOP signal. The time difference of START- and STOP-pulses gives the positron lifetime (τ) in the material. In this study the annihilation spectrum was measured with a normal digital lifetime setup, consisting of two scintillation detectors with large scintillation heads producing a broad time resolution (full-width at half-maximum, FWHM, of the Gaussian resolution function ∼550 ps for the setup for preliminary measurements, ∼320 ps/260 ps for the further studies described later on) but with high efficiency. A broad time resolution is not optimal for lifetime separation, but as the measurements were planned to be performed in the hydrated state, the short duration of measurement was an important factor: the lenses were placed inside a sealed plastic bag, and the liquid (borate-buffered saline from the lens containers) drained slowly from the lenses to the bottom of the bag due to the horizontal geometry of the measurement setup. The setup is characterized in more detail in Ref. [8]. The lifetime spectra were analyzed first with PALSfit [9] to analyze the properties of the time resolution of the setup and then analyzed with MELT [10] in order to minimize possible fitting problems due to continuous void size distributions, the mathematical basis of the aforementioned tools are presented in the references. Statistics of ∼2 to 3 million events were collected in each annihilation spectrum and the analysis was performed using a free fit with no source corrections resulting to 3–4 lifetime components depending on the sample and whether the water-lifetime ($\boldsymbol{\tau_3}$) could be separated from the polymer lifetime ($\boldsymbol{\tau_4}$), the two shortest components representing the annihilation of free positrons and p-Ps ($\boldsymbol{\tau_1}$) as well as a ∼1 ns long o-Ps component ($\boldsymbol{\tau_2}$). Goodness of the fits was evaluated with the χ^2-output of the analysis software and similar range of values (1.1–1.2) was observed in all cases.

3.2. Contact lens materials and their measurement

Preliminary experiments were performed with three different types of lenses, all from the same manufacturer, (Bausch & Lomb, B&L). The purpose of these experiments was to characterize the differences of lifetimes in different types of CLs. The studied lenses were: B&L Daily Disposable (DD, 59% water), B&L Soflens® (SL, 38%), and B&L Purevision® (PV, 36%). The lenses were chosen to have profound differences in their usage recommendations, ranging from the short term use (DD) to lenses that can be used continuously for a month (PV). The B&L Soflens is a CL that can be reused but is not recommended for continuous use. The base materials in these CLs are polymer-based Hilafilcon B (DD), Polymacon (SL) and a silicone–hydrogel based Balafilcon A (PV).

We measured contact lenses in their “in-use” hydrated state, containing reasonable amounts of water (36–59%) and hence some of the o-Ps always annihilated in water. Because the lifetime components of some of the studied polymers were quite near the o-Ps lifetime in water, the measured lifetime component was in most cases an intensity weighted sum of water and polymer lifetimes. This effect is more significant in the samples measured with a PALS setup with broader time resolution. Due to this and other factors (e.g., chemical interactions of o-Ps with the material), the measured o-Ps lifetimes are, as usual in polymers, not discrete, but a distribution. Hence the radius R obtained by using the Tao–Eldrup model (Eq. (1)) should be interpreted as the mean radius of the free volume pockets.

A layer consisting of at least five contact lenses was placed on both sides of the small ($2 \times 2 \times 0.003$ mm) positron source, surrounding the small source completely and thus the vast majority of positrons annihilated in the lenses based on the estimate of positron range in the CL polymers. The positron sources (approximately 0.5 MBq each) were manufactured by injecting ^{22}NaCl saline inside a thin aluminium foil package and the package was dried to prevent radioactive contamination when handling the source package; additionally, each source package was used only once for enhanced radiation safety.

The sample sandwich was placed inside a hermetically sealed Minigrip$^{\text{TM}}$ bag and moisturised with the borate (Hilafilcon B, Balafilcon A) or phosphate (Polymacon) buffered saline from the lens packages, keeping the lenses moist during the measurement and preventing instantaneous drying. The drying of the lenses was observed to happen within 12–24 h after placement inside the bag as the saline slowly drained to the bottom of the bag. The PALS measurements were performed in normal room temperature of 20 °C and the duration of each measurement was maximally 3–4 h for each annihilation spectrum (the total measurement time of each sample sandwich was at most 12 h). For studies on the possible filling of the voids during the submersion time in artificial tears (water–bovine serum albumin (Sigma–Aldrich) solution), Balafilcon A (PV) CLs were used based on the results of the preliminary studies: the voids in the Balafilcon A (PV) CLs were large enough to produce an o-Ps lifetime component that could be separated from the o-Ps annihilating in water with high certainty. All CLs