Positron annihilation in bioactive glass/poly(glycolide-*co*-L-lactide) composites

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Abstract. Composites made of bioactive glasses and resorbable polymers are promising biomaterials for bone tissue regeneration. In this study several types of composites produced from bioactive glasses, differing in chemical composition (A2 and S2) and poly(glycolide-*co*-lactide) (PGLA) were obtained. The resulting composite materials were investigated with positron lifetime spectroscopy and Doppler broadening of annihilation line. It was found that for the composites made of S2 bioglass the intensity of the third positron lifetime component coming from the positronium (Ps) annihilation decreased with increasing in volume fraction of bioglass particles exhibiting behaviour characteristic of microcomposites. For the composites produced from A2 bioglass, such a dependence was not found. The differences obtained may be connected with chemical composition of the bioglass and/or its crystallinity.

Key words: poly(glycolide-*co*-L-lactide) • bioglass • composites • positron annihilation

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Introduction

The use of polymer composites in various engineering applications became the state of the art. In recent years polymer-based composites have received more and more attention. The addition of inorganic filler to a polymer matrix is used to modify its structural and mechanical properties including enhancement of conductivity, mechanical toughness, optical and catalytic activity [9]. In the field of biomaterials engineering polymer composites containing bioactive phase, for example, bioactive glass particles, are considered to be promising biomaterials for bone tissue regeneration [17]. Bioactive glasses exhibit excellent bioactivity, manifested by rapid surface reaction and fast bonding with bone without the formation of scar tissue [10]. However, they suffer from low mechanical strength and high brittleness. Therefore, combining them with a polymer matrix may result in creation of materials better adapted into surrounding tissues. Polymer matrices of particular medical interest are resorbable polylactides, polyglicolide and poly(glycolide--*co*-L-lactide) (PGLA). These polymers have been widely used in medical applications as temporary sutures, bone fixation devices, drug delivery systems and more recently as scaffolds for tissue engineering applications [14].

Studies of polymer-based composites include also fundamental research aimed at understanding of physical behaviour of polymer segments in close contact with

the inorganic filler. Positron lifetime spectroscopy is a useful tool to evaluate free volume holes especially in amorphous polymers. There is available only limited experimental information on free volume hole dimensions and size distribution obtained by other methods. Therefore, positron annihilation spectroscopy has become a valuable technique for studying polymer materials including polymer composites important for practical applications such as rubbers with silica, carbon black and other fillers [1, 19, 20] or conductive polymer composites [2].

The aim of this study was to evaluate new polymer/bioglass composites with the use of positron lifetime spectroscopy in order to better understand how addition of the different amount of bioglass influences subnanometer size holes in the resulting materials. To this end several types of composites differing in bioglass concentration and bioglass chemical composition were produced and analysed.

Experimental

In this study two types of composites produced from bioactive glasses and PGLA were obtained. Two bioactive glasses differing in chemical composition: S2 (SiO_2 – 80 mole%, CaO – 16 mole%, P_2O_5 – 4 mole%) and A2 (SiO_2 – 40 mole%, CaO – 54 mole%, P_2O_5 – 6 mole%) were produced by sol-gel process, followed by drying and milling to obtain glass powders with particle sizes < 50 μm [13]. PGLA (molar ratio of glycolide to L-lactide 15:85, number-average molecular mass Mn = 80 kDa, polydispersion index d = 2.1) was produced by ring opening polymerization [3]. The PGLA/bioglass composites were fabricated by mixing bioglass powder with PGLA solution in methylene chloride, followed by slip casting of the mixture on glass Petri dishes, drying in air and in vacuum. The volume fraction of bioglass in the composites was adjusted to 12 vol.%, 21 vol.% and 33 vol.%. The obtained composite foils had a thickness of 110 μm.

Positron lifetime spectra were measured using a conventional fast-fast spectrometer with BaF_2 scintillators. The time resolution of the system was 280 ps full width at half maximum (FWHM). The 30 μCi activity positron source containing ^{22}Na isotope enveloped in a 7 μm thick Kapton foil was sandwiched between two polymer samples. The thickness of the investigated polymer foil was equal to 110 μm. Each sample consisted of the stack of 3 foils. Because the thickness of 3 foils is too low to stop all positrons emitted from the ^{22}Na source, outside the foil stacks the thick Kapton foils were placed. Lifetime spectra containing ca. 2×10^6 counts were measured at room temperature. All obtained spectra were deconvoluted using the LT code [11] subtracting the background. The lifetime of positrons annihilating in Kapton outside the samples should be close to lifetime of the source component in the lifetime spectrum. The density of samples changed from 1.28 g/cm^3 for PGLA to 1.80 g/cm^3 for PGLA with 33 vol.% A2. This caused that the mean positron implantation depth (the reciprocal of the positron linear absorption coefficient α_+) calculated from the semi-empirical formula given in [4] changes from 177 μm to 125 μm. Then, there was taken an additional contribution to source component,

which changed from 16% to 7.3%, respectively. In order to confirm the additional contribution from annihilation in the Kapton foil in the case of PGLA the lifetime spectrum was also measured for the stacks of 6 foils stopping 98% of positron from the source. The positron lifetime spectra after source correction were decomposed into three components. First lifetime value τ_1 was fixed at 0.125 ns. The value of τ_2 decreased from 0.40 ns to 0.39 ns for the composites with increasing A2 bioglass content and increased from 0.40 ns to 0.44 ns for composites with increasing S2 bioglass content. In this study we are discussing the longest-living component, τ_3. Average free volume radius was calculated according to the semi-empirical model [6, 18] combining the pick-off lifetime τ_3 with the average free volume radius of a spherical hole $V_f = 4\pi R^3/3$:

$$(1) \qquad \tau_3 = \frac{1}{2} \left[1 - R / (R + \Delta R) + (\frac{1}{2}\pi) \right. \\ \left. \cdot \sin (2\pi R / (R + \Delta R)) \right]^{-1}$$

where R is the radius of the hole and ΔR is the electron layer thickness. The value of ΔR was estimated as 1.66 Å by fitting the longest lifetime value to known free volume sizes of molecular crystals. Value of τ_3 and intensity of that lifetime component for PGLA were compared with the result of our previous measurements [16]. The values of τ_3 were equal within the error limits. Intensity I_3 was slightly higher, i.e. 19.3±3%. The positron lifetime measurements were also performed for bioglasses A2 and S2. In this case the samples were the pellets (10 mm in diameter and 3 mm thick) made from glass powders using a press. Additionally, the coincidence Doppler broadening (CDB) measurements were performed using a coincidence spectrometer with an HpGe detector (energy resolution FWHM equal to 1.37 keV interpolated for 511 keV) and a scintillator detector NaI(Tl). We used a ^{68}Ge/^{68}Ga positron source (50 μCi) enveloped in the Kapton foil. The achieved peak to background ratio was obtained as 5000:1. After background subtraction [5], the spectra were normalized to unity.

For the bioglass samples, the X-ray diffraction was measured using a PANanalytical X'Pert PRO X-ray diffraction system and CuK$_\alpha$ radiation.

Results and discussion

Figure 1a presents the variations of the longest lifetime component intensity I_3 as a function of the bioglass content in both PLGA composites. This component originates from $ortho$-positronium (o-Ps) localized in free volume annihilating in pick-off processes. For the PGLA composite with A2 bioglass, the value of I_3 decreases with bioglass content. For the PGLA composite with S2 bioglass changes of I_3 do not exhibit a definite trend. It has been shown that for polymer microcomposites with micron-sized filler particles and micron-sized grains the total o-Ps, $para$-positronium (p-Ps) and free positron intensities are the weighted averages of intensities of those components in filler and matrix [7, 15]. Then, the linear relationship between the filler content and the intensities of o-Ps, p-Ps and free positron annihilation components in microcomposite is observed. In particular, for the third lifetime component coming from o-Ps annihilation:

(2) $$I_{3c} = w_f I_{3f} + (1 - w_f) I_{3m}$$

where subscripts c, f, and m indicate the composite, filler and matrix, respectively, I_3 is the intensity of the third lifetime component and w_f is the filler content. The linear dependence of I_3 consistent with linear averaging relationship (2) was observed by Winberg *et al.* [21] in silica filled polydimethylsiloxane with addition of micron-sized silica. In the case of nanosized silica, I_3 also decreased with increasing silica content but did not follow the formula (2). That behaviour was explained by the authors as a result of out-diffusion of positrons or/and *o*-Ps from the filler particles to the matrix in heterogeneous systems with very small particles. Hence the intensity of *o*-Ps annihilation in the polymer matrix was higher.

In the case of rubber composites with carbon black the presence of carbon black particles causes decrease of I_3 partly by a decrease of the rubber content in the composite by incorporation of the filler [19]. However, the presence of a rubber shell around the filler particles confirmed by nuclear magnetic resonance (NMR) studies [12] affects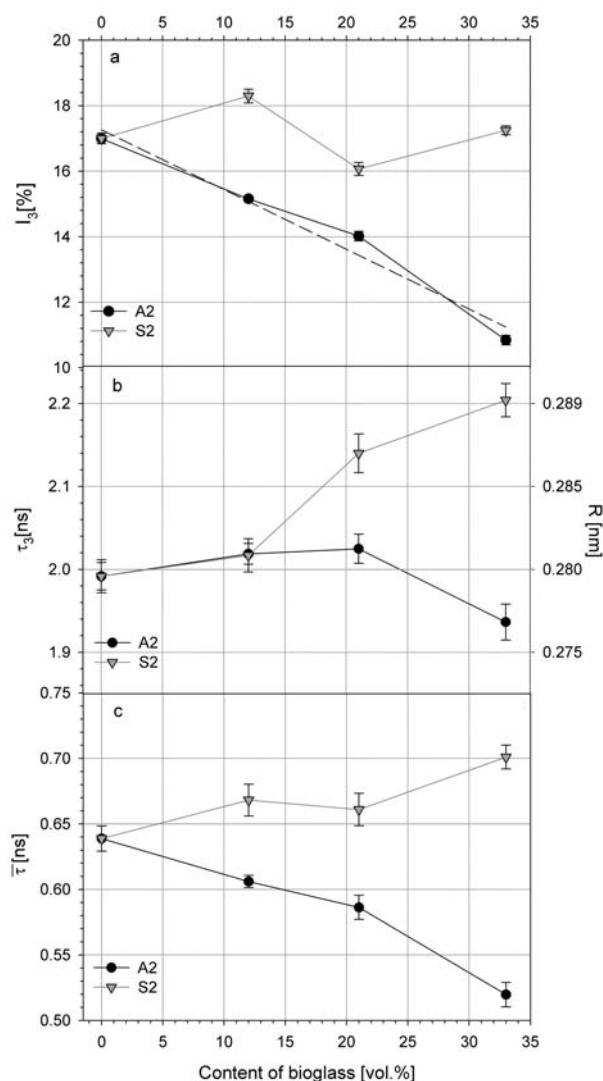 the properties of compound by increasing the effective filler volume, which is important for nanosized filler particles. In this bound rubber shell the formation of free volume holes is reduced [20], what influences the intensity of *o*-Ps formation and annihilation. Wang *et al.* [20] investigated as well the styrene-butadiene rubber composites with monmorrilonite (MMT). In this case the differences between micron-sized and nanosized composites were also observed. Positron annihilation measurement performed for ethylene-propylene-diene (EPDM) rubber with silica filler [1] revealed the differences in the positron lifetime spectra obtained for the samples with the same chemical composition but different filler dispersion. Thus, the analysis of the dependence of the lifetime component intensity coming from the *o*-Ps decay can shed light on the filler matrix interaction, especially for polymer composites with small filler particles.

Taking into account formula (2), the measurement of the positron lifetime in the A2 and S2 bioglasses is essential. The lifetime spectra obtained for bioglasses were also deconvoluted into tree components. For A2 bioglass $\tau_2 = 0.383 \pm 0.002$ ns with intensity $I_2 = 77.0 \pm 0.6\%$ and $\tau_3 = 1.35 \pm 0.04$ ns with intensity $I_3 = 6.0 \pm 0.2\%$. The intensity of *o*-Ps annihilation component in A1 bioglass is much lower than in PGLA. It should be also taken into account that the bioglass samples were not bulk samples and annihilation of positronium on the surface of glass particles also takes place and contributes to intensity I_3. The dashed line in Fig. 1a presents the least squares fit of the linear function of the experimental points for composite with A2 bioglass. The value of the third lifetime component intensity for filler, I_{3f} in formula (2), obtained from this fit is close to zero. For S2 bioglass, the values obtained from the lifetime spectrum analysis are the following: $\tau_2 = 0.485 \pm 0.006$ ns with intensity $I_2 = 67.1 \pm 0.3\%$ and $\tau_3 = 2.49 \pm 0.02$ ns with intensity $I_3 = 16.2 \pm 0.2\%$. The intensity of *o*-Ps decay obtained for S2 bioglass is similar to that obtained for PGLA. Then, in agreement with the formula (2), I_3 depends weakly on the bioglass content.

The bioglasses A2 and S2 used as fillers in PGLA composites differ in chemical composition. In addition, X-ray diffraction showed that they also differ in crystallinity. Figure 2 shows the diffraction patterns obtained for both samples. It can be seen that S2 bioglass is amorphous, but A2 bioglass X-ray diffracrion pattern
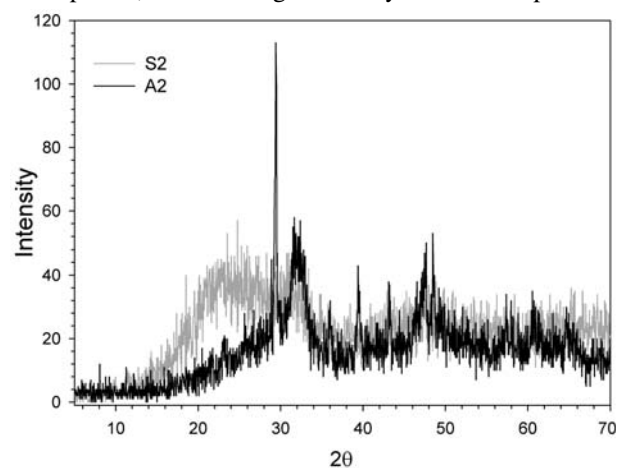

Fig. 1. a – *o*-Ps intensity, I_3; b – lifetime, τ_3, free volume radius, R (right axis); c – mean positron lifetime in PGLA/bioglass composites as a function of bioglass content. Dashed line is a least squares fit of linear function.

Fig. 2. Diffraction patterns obtained for A2 and S2 bioglasses.

exhibits diffraction peaks. Both chemical composition and degree of crystallinity may be the reason of the differences in the positron lifetime spectra. The influence of the glass crystallinity on the positron lifetime spectrum is confirmed by the studies of silicate glasses performed by Hautojärvi and Pajanne [8]. They found that when glass starts to crystallize the structural changes are big enough to be clearly visible in positron lifetime spectrum. Intensities of the longer lifetime components decrease. Much smaller intensity I_3 for A2 bioglass than for S2 bioglass correlates well with partly crystal structure.

Figure 1b shows the dependence of τ_3 on bioglass content. Changes of τ_3 with the bioglass content, distinct for the two fillers, are clearly visible. For composites with A2 bioglass, the τ_3 value for the lower filler content composites does not change in the limit of error and for the sample with 33 vol.% of filler it is slightly lower. For composites with S2 bioglass, τ_3 increases with filler content from 1.99 ± 0.02 ns to 2.20 ± 0.02 ns. Changes of τ_3 with the bioglass content correlate with the values of τ_3 obtained for the filler, i.e. if τ_3 for bioglass is higher than for PGLA τ_3 increases, if τ_3 for bioglass is lower than for PGLA τ_3 decreases. Because free volume holes in polymer exhibit some distribution of their sizes, the value of τ_3 should be treated as an average positron lifetime. Addition of filler changes this distribution and shifts τ_3 to the values characteristic of the filler itself.

Dependences of the mean positron lifetime (calculated as the weighted average of discrete components in the positron lifetime spectrum) on the filler content are shown in Fig. 1c. Mean positron lifetime as a robust parameter scarcely affected by the spectrum deconvolution procedure reflects the tendencies visible in the shown above dependencies of I_3 and τ_3 on the filler content.

Figure 3 presents the ratio curves obtained by dividing the Doppler broadening spectra for PGLA, PGLA with 33 vol.%S1 and PGLA with 33 vol.%A1 composites by the spectrum for pure (99.999%) annealed aluminium. Additionally, the ratio curve for pure silicon is also presented. Though aluminium is not prese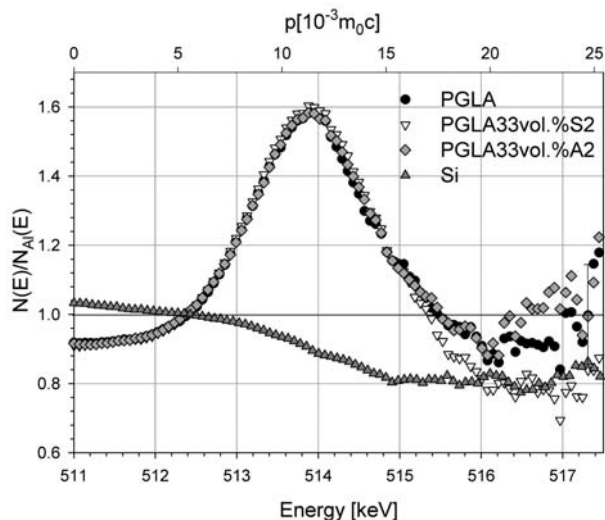nt in the samples, its spectrum was chosen as a reference because it is often used for comparison of pure elements' spectra. It can be seen that up to the momentum ca. 15×10^{-3} m_0c the ratio curves for PGLA and composites do not differ significantly. The differences for higher momentum region ($p > 15 \times 10^{-3}$ m_0c) may be caused by the lower positronium formation probability for the composite with A2 bioglass than for PGLA and the composite with S2 bioglass. On the other hand, the content of SiO_2 in S2 bioglass is two times higher than in A2 bioglass and lower values of the ratio curve for the composite with S2 bioglass in this region may be caused by higher probability of the positron annihilation with core electrons of silicon. This consideration is qualitative because it does not include the influence of the other difference in chemical composition of the bioglasses, i.e. the CaO content.

Conclusions

The positron lifetime measurements of PGLA/bioglass composites shows that o-Ps yield follows the linear relationship with the volume content of the bioglass in the case when the intensity I_3 for the bioglass is definitely lower than for the matrix PGLA. There is no deviation from the behaviour characteristic of polymer composites with micron-sized filler particles. Then, the influence of the interface between the filler particles and the polymer matrix on the positron lifetime spectra was not observed.

Fig. 3. Ratio curves obtained by dividing the coincidence Doppler broadening spectrum for PGLA, PGLA 33%vol.S2 bioglass, PGLA 33%vol.A2 bioglass and silicon (single crystal) by the spectrum for pure Al (99.999%).

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