RESEARCH ON THE SORPTION PROPERTIES OF BIOPOLYMER MATRIX BASED ON SOYBEAN OIL FOR THE CONSTRUCTION OF BIOSENSORS TO DETECT XENOBIOTICS*

Magdalena Goździuk, Bożena Zgardzińska

Institute of Physics, Maria Curie-Sklodowska University
Pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland

Taras Kavetskyy

Drohobych Ivan Franko State Pedagogical University
Ivan Franko Street 24, 82100 Drohobych, Ukraine
and
The John Paul II Catholic University of Lublin
Al. Racławickie 14, 20-950 Lublin, Poland

Received 20 September 2022, accepted 2 November 2022, published online 15 November 2022

The biopolymer matrix synthesized from epoxidized soybean oil (AESO) and vanillin dimethacrylate (VDM) in a molar ratio of 1:1 was investigated by the Positron Annihilation Lifetime Spectroscopy (PALS) in the presence of pure water, saline solution, and water contaminated with xenobiotics from a reservoir. The main aim of the research is the construction of a biosensor with a biopolymer matrix for the detection of trace water pollution with xenobiotics, which are carcinogenic and have a negative impact on the human endocrine system. These substances may come from the pharmaceutical industry, households, and are used as plant protection products or food additives. The measurements show that the presence of ions and pollution in water causes the elongation of the absorption process into the matrix. The performance of the biosensor will therefore correlate with the level of ion concentration and pollution.

DOI:10.5506/APhysPolBSupp.15.4-A5

1. Introduction

The development of materials engineering and biotechnology has enabled the production of biopolymers, which are materials of plant origin environ-

* Presented at the 4th Jagiellonian Symposium on *Advances in Particle Physics and Medicine*, Cracow, Poland, 10–15 July, 2022.

mentally friendly and biodegradable. This type of materials has found many applications *e.g.* in medicine [1] and in the production of single-use bioplastics [2]. Biopolymers can also be used to produce enzymatic biosensor matrices, where they fulfill two important roles: immobilizing the enzyme on the detection part of the biosensor and improving the detection properties of biosensors [3].

The Positron Annihilation Lifetime Spectroscopy (PALS) allows for non-invasive investigation of the nanostructure of samples, which enables to predict matrix properties in the macroscale. It is based on the detection of the phenomenon of electron (e^-) and positron (e^+) annihilation. In the free nanovolumes of the sample, a hydrogen-like positronium (Ps) atom can be formed, which is a quasi-stable bound state of the electron and positron. The Ps can exist in two spin configurations: para-positronium (p-Ps) with parallel spins and ortho-positronium (o-Ps) with anti-parallel spins [4, 5]. During the measurements, positron and positronium lifetimes and intensities are obtained. It allows to track the dynamics of the processes taking place in the samples under given humidity conditions [6] and estimate the size of free volumes using the Tao–Eldrup model [7, 8] as shown in [9].

The biopolymer matrices can be also tested in chronoamperometric measurements in order to verify the biosensor parameters [10, 11].

2. Experimental

A biopolymer matrix containing epoxidized soybean oil (AESO) and vanillin dimethacrylate (VDM) in a molar ratio of 1:1 was synthesized in the same way as described earlier [12]. The matrix nanostructure was investigated using the PALS technique to analyse the sorption properties of the sample in the presence of pure water, saline solution, and water contaminated with xenobiotics from a natural water reservoir. The last type of measurements was made in conditions close to the real work of the biosensor. For PALS measurements, a digital spectrometer was used, equipped with two Hamamatsu detectors positioned at an angle of 90° to each other, containing BaF_2 scintillation crystals. The scintillators are used to detect the 1274 keV "START" signal associated with the emission of the positron from the source and the 511 keV "STOP" signal that indicates annihilation in the sample. The time resolution (FWHM) was 0.193 ns. The sample was placed in a chamber with the ^{22}Na positron source, activity of 0.5 MBq in the sandwich configuration [6]. The chamber was connected to the pressure control system and the dosing of vapors from the liquid. The obtained spectra were analyzed with the LT 9.2 software [13].

Measurement on the degassed sample was treated as reference data. Data for fresh degassed biopolymer sample were collected for 24 hours. These data are necessary to compare nanostructure of the sample before and after the

influence of liquid. Then the measurements were performed in the three regimes: *(i)* in the presence of vapour, *(ii)* in the liquid, and *(iii)* measurements of desorption in a vacuum environment after removing the liquid from the measuring chamber [6]. As the liquid environment, we used: (a) pure (deionized) water, (b) 0.9% NaCl (saline solution), and (c) water polluted with xenobiotics taken from the natural water reservoir. The natural water sample was taken from the Dnieper River in Ukraine. The main aim was to check the sorption properties of the sample in pure water (clean environment), in the presence of ions, and in the presence of xenobiotic contamination. The last type of measurements was performed to check the properties of the biosensors matrix in conditions approximating to the real operating environment. The measurement at each stage lasted until the o-Ps intensity, I_3 values were stabilized, and after the system achieved stability (80 h in vapour, 120 in liquid, and 150 h in vacuum), then the next stage of analysis was started. The time constants of the processes taking place in the sample were also determined by fitting the exponential curves according to the following equation:

$$I_3 = I_{30} + I_{3\Delta}\left(1 - \mathrm{e}^{-\frac{t}{\Theta}}\right) ,$$

where I_3 is the o-Ps intensity, I_{30} is the initial o-Ps intensity value, $I_{3\Delta}$ is the maximum o-Ps change as a result of sorption/desorption process, and Θ is the time constant of sorption/desorption process. The comparison of the time constants of the processes makes it possible to determine the rate of water infiltration and removal from the sample.

3. Results

The analysis of the sorption properties of the biopolymer matrices in the presence of three types of used liquids was carried out on the basis of the o-Ps lifetimes and intensities. The results obtained for samples in the presence of pure water, saline solution, and water contaminated with xenobiotics (Fig. 1) show very good sorption properties of the matrix due to the presence of changes in PALS parameters caused by the presence of a liquid medium. The o-Ps lifetimes τ_3 have different values when measuring the sample in liquid depending on the type of water used. In the presence of vapour liquid, the differences in the o-Ps lifetime are small. The lowest values of τ_3 can be observed in the liquid environment in pure water. It can be concluded that the presence of ions and pollution (*e.g.* xenobiotics) in the water hinders the absorption into the sample. In the presence of water (in the vapour and liquid), it can be observed that at the beginning of the measurement o-Ps intensity I_3 was about 25.8%, then decreased during analysis

in vapour and liquid. During the desorption process, I_3 values were higher than o-Ps intensities during measurements in the degassed sample. This proves the presence of water molecules in the nanostructure of the reference sample. The fresh polymer matrix absorbs the water molecules from the vapour. Higher I_3 values obtained during desorption measurements indicate the possibility of removing water molecules from the sample nanostructure.

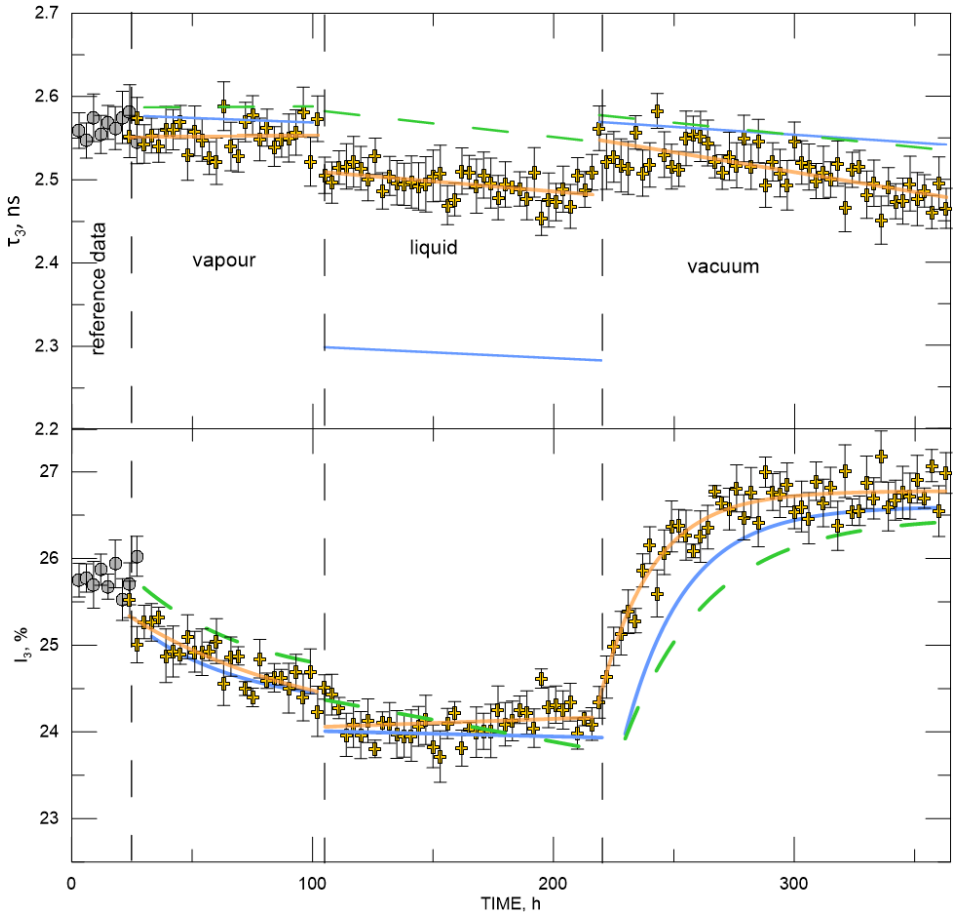

Fig. 1. The o-Ps lifetimes (τ_3) and intensities (I_3) as a function of time in different humidity conditions in the sample AESO: VDM = 1 : 1 (mol). Curves were fitted to experimental points: solid blue line — pure deionized water, green dashed line — saline solution, yellow crosses — water contaminated with xenobiotics, gray dots — measurements in a degassed sample. The figure is divided by dashed lines into sections: reference data, vapor, liquid, and vacuum environment, respectively.

Time constants based on fitted exponential curves of the processes were determined (Table 1) in the sample during sorption measurements Θ_{vap} and desorption process Θ_{vac}.

Table 1. Time constants of the sorption (from vapour) processes Θ_{vap} and during desorption process Θ_{vac}, and the R^2 of fitted curves.

	Θ_{vap}, h	R^2	Θ_{vac}, h	R^2
Pure water	43.33	0.791	25.02	0.828
Saline solution	47.54	0.777	35.39	0.886
Water polluted with xenobiotics	78.77	0.725	21.74	0.907

From the obtained time constans, it can be concluded that the sorption and desorption processes are not time equivalent. The speed of the sorption process in vapour decreases with the presence of ions and xenobiotics in water. The longest time constant was obtained for the vapour sorption of water contaminated with xenobiotics. In the case of the desorption process, the highest time constant was obtained for the saline solution, which may mean that the process time constant increases in correlation with higher level of salinity (the longest desorption process is in saline solution).

4. Conclusion

Measurements made under given humidity conditions allow to investigate changes in the nanostructure of the sample due to the presence of liquid. In this way, the dynamics of the processes taking place can be monitored and the ability of the sample to absorb liquid can be examined. Analysis of desorption process enables checking the possibility of removing water molecules from the matrix. Such measurements allow to predict the sorption properties of the matrix and check its usefulness in the construction of biosensors. Based on the obtained results, it can be predicted that the matrix will be useful in the construction of biosensors. The obtained time constants indicate the dependence of the process speed on the presence of ions and xenobiotics in the water. The sample will also be tested in chronoamperometric measurements in order to verify the results obtained with the PALS technique.

This work was supported in part by the Ministry of Education and Science of Ukraine (projects Nos. 0118U000297, 0119U100671, 0121U109543, and 0122U000874), the National Research Foundation of Ukraine (project No. 2020.02/0100 "Development of new nanozymes as catalytic elements for enzymatic kits and chemo/biosensors"), and The John Paul II Catholic University of Lublin (project No. 1/6-21-20-09-0605-0004-2002). T.K. also acknowledges the SAIA (Slovak Academic Information Agency) for scholarship in the Institute of Physics of Slovak Academy of Sciences in the framework of the National Scholarship Programme of the Slovak Republic.

REFERENCES

[1] R.L. Kronenthal, «Biodegradable Polymers in Medicine and Surgery», *Springer US*, Boston, MA 1975, pp. 119–137.

[2] S. Lambert, «Biopolymers and Their Application as Biodegradable Plastics», in: Vipin Chandra Kalia (Ed.) «Microbial Factories — Biodiversity, Biopolymers, Bioactive Molecules: Volume 2», *Springer*, New Delhi 2015, pp. 1–9.

[3] F. Ejeian *et al.*, *Biosens. Bioelectron.* **118**, 66 (2018).

[4] D.M. Schrader, Y.C. Jean, «Positron and Positronium Chemistry», 1988.

[5] O.E Mogensen, «Positron Annihilation in Chemistry», vol. 58, *Springer Science & Business Media*, 2012.

[6] M. Goździuk *et al.*, *Acta Phys. Pol. A.* **139**, 432 (2021).

[7] S.J. Tao, *J. Chem. Phys.* **56**, 5499 (1972).

[8] M. Eldrup, D. Lightbody, J.N. Sherwood, *Chem. Phys.* **63**, 51 (1981).

[9] M. Goździuk *et al.*, *Materials* **15**, 6607 (2022).

[10] T. Kavetskyy *et al.*, *Acta Phys. Pol. A* **137**, 246 (2020).

[11] T. Kavetskyy *et al.*, *J. Appl. Polym. Sci.* **134**, 45278 (2017).

[12] M. Lebedevaite, J. Ostrauskaite, E. Skliutas, M. Malinauskas, *Polymers* **11**, 116 (2019).

[13] J. Kansy, *Nucl. Instrum. Methods Phys. Res. A* **374**, 235 (1996).