

Network Properties of Ureasil-Based Polymer Matrixes for Construction of Amperometric Biosensors as Probed by PALS and Swelling Experiments

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Network properties of ureasil-based polymer matrixes suitable for construction of amperometric biosensors were probed by positron annihilation lifetime spectroscopy and swelling experiments. Temperature dependences of the ortho-positronium (*o*-Ps) lifetimes and their relative intensities were measured in a temperature range of 15–350 K. Glass transition temperatures and expansion coefficients of microscopical free-volume for the investigated polymers were determined. Differences in network behavior for the aged samples and the effect of chalcogenide (As₂S₃) particles on the free volume of ureasil network were observed. Swelling experiments using ethyl alcohol showed that the structure of the aged sample network had less swelling ability for the pure ureasil as well as composite. This suggests that the one of factors influencing swelling is the change of the basic ureasil network due to ageing. It is supposed that the network properties obtained by positron annihilation lifetime spectroscopy and swelling experiments could be very helpful to understand better the bio-functionality of the constructed biosensor based on the ureasil–chalcogenide glass composite.

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1. Introduction

Recently, innovative amperometric biosensors for monitoring the level of wastewater pollution have been constructed [1] on the surface of the gold planar electrodes C220AT “DropSens” by using the organic-inorganic ureasil-based composites as host polymer matrixes and immobilized commercial laccase from *Trametes versicolor*. In fact, urea-silicates or ureasils are well-known as representatives of organic-inorganic hybrid polymer materials successfully examined as dispersion media for luminescent Eu³⁺ salts [2], ion conducting Li⁺ salts [3], organic dyes [4], semiconductor and metal nanoparticles [5–8], and, for the first time, the ureasil-based composites were tested for immobilization of laccase and construction of biosensors [1]. It has been found that the biosensor based on the ureasil-chalcogenide glass composite was characterized by very high sensitivity to be 38.3 times higher in compare with pure ureasil. On the other hand, application of the ureasil-chalcogenide glass composite with incorporated silver nanoparticles synthesized by high-dose 30 keV Ag⁺ ion implantation results

in decrease of the biosensor sensitivity up to 2390 times. Therefore, knowing the properties of the microstructure of such materials is important in terms of optimizing the regulated properties of the biosensors.

The present work is aimed to study the free-volume and swelling properties of various samples of pure ureasil and ureasil-chalcogenide glass composite by means of positron annihilation lifetime spectroscopy (PALS) and swelling experiments.

2. Experimental

2.1. Sample preparation

The synthesis of the pure ureasil matrix (K0) was performed as follows: (i) O,O'-bis(2-aminopropyl)-polypropylene, glycol-block-polyethylene glycol-block-polypropylene, glycol-500 (Jeffamine ED-600) were dried under vacuum for 30 min; (ii) 3-isocyanatopropyltriethoxysilane (ICPTES), tetraethoxysilane (TEOS, 98%) and *n*-butyl amine were used as received; (iii) Jeffamine and ICPTES were mixed in stoichiometric ratio 1:2 in order to obtain a liquid ureasilicate monomer; (iv) Thereupon, TEOS (1.12 mmol) and *n*-butylamine were added to the mixture, which was kept under stirring for more than 20 min; (v) the mixture was transferred into a plastic Petri dish and

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jellified under appropriate conditions; (vi) the obtained gels were heated in a vacuum furnace at 60 °C at ambient conditions; (vii) a non-rigid, homogeneous and highly transparent xerogel in form of a disk with a diameter of 40 mm and a thickness of 0.25 mm was obtained within 1 day.

The synthesis of the ureasil-chalcogenide glass As_2S_3 composite matrix (K4) was performed as follows: (i) the chalcogenide glass As_2S_3 ingots were synthesized by melt quenching method from As (5N) and S (5N) in sealed quartz ampoules at 650 °C; (ii) the melt was quenched to room temperature, and the obtained glassy samples were finely grounded in powder form and dissolved in organic solvent (3 ml of *n*-butylamine) to the 0.4 M concentration; (iii) the As_2S_3 + ureasil composite was obtained by mixing of the ureasilicate monomer with the solution of chalcogenide clusters. The stiff gel was obtained as described.

The images of investigated samples used for the research are shown in Fig. 1.

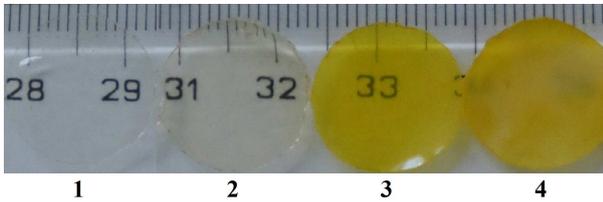


Fig. 1. Images of the investigated polymers used for the research: 1 — ureasil fresh (2 months after preparation): K0-fresh, 2 — ureasil aged (1 year after preparation): K0-aged, 3 — As_2S_3 + ureasil fresh (2 months after preparation): K4-fresh, 4 — As_2S_3 + ureasil aged (1 year after preparation): K4-aged.

2.2. PALS experiment

The positron annihilation lifetime spectra were taken using plastic scintillators coupled to photomultiplier tubes as detectors with the ^{22}Na positron source, deposited on a pure Kapton foil, and placed between two sandwiched samples. This source-sample assembly was covered by a special tube and placed between two detectors to acquire lifetime spectra in a vacuum at different temperatures. The time resolution (FWHM) of spectrometer was about 320 ps, measured by defect free Al sample. Analysis of lifetime spectra was carried out using the free of charge LT program with source correction of 21.8%. Three component fitting procedure for PALS data treatment was applied, that gave the best fit, and long-lived lifetime component τ_3 and its intensity I_3 , ascribing to the *ortho*-positronium (*o*-Ps) pick-off annihilation in free-volume holes in accordance with the conventional interpretation [9], were finally taken into account for analysis. The low-temperature measurements were performed in the range of 15–350 K using helium cryostat (Closed Cycle Refrigerator, Janis Research Company, Inc., USA) and vacuum equipment (Pfeiffer Vac-

uum, HiCUBE, Germany). The accuracy for the each selected temperature was ± 1 K and vacuum in the system was automatically controlled. The samples were measured in the cycles of “cooling-heating” with step of 20 K and elapsed time of 3–5 h per point.

2.3. Swelling experiment

The investigated samples were swollen in anhydrous ethyl alcohol (EtOH) during 8 days at 301 K. One was weighed the initial weight of samples (m_0) and then the samples after 24 h during 8 days. The equilibrium was achieved after 6–7 days, and on the 8th day the weight was not changed. So we have the maximum saturated weight (m_{swollen}). After that the samples at room temperature were dried at 333 K in argon atmosphere by using thermogravimetric analysis (TGA) method where the weight of dry sample (m_{dry}) was obtained as the minimum saturated mass. The percent equilibrium mass swelling (S) was estimated from the equation

$$S = \left[\frac{m_{\text{swollen}} - m_{\text{dry}}}{m_{\text{dry}}} \right] \times 100\%. \quad (1)$$

The molecular weight between two crosslink points, M_c , was estimated based on the Flory–Rehner equation [10, 11]:

$$\nu = \frac{1}{M_c} = - \left[\frac{(V_r + \chi V_r^2 + \ln(1 - V_r))}{\rho_p V_0 (V_r^{1/3} - V_r/2)} \right], \quad (2)$$

where ν is the crosslinking density, ρ_p is the bulk density of the polymeric sample, and V_r is the volume fraction of the polymer in the swollen state given by equations

$$V_r = 1/(1 + Q), \quad (3)$$

$$Q = \left[\frac{(m_{\text{swollen}} - m_0)\rho_p}{m_0\rho_{\text{liquid}}} \right], \quad (4)$$

where ρ_{liquid} is the density of the liquid and V is the molar volume of the liquid. For EtOH V is 57.62 cm³/mol. The parameter χ is the Flory–Huggins interaction parameter between the polymer and the liquid. The values of χ for polymer-solvent interaction were calculated via the cohesive energy of atomic groups.

The density of the investigated polymeric samples was estimated based on the gravimetric method (Archimedean principle). The samples were immersed into EtOH at 301 K. The bulk density of individual samples was calculated by using the following equation:

$$\rho = \rho_{\text{EtOH}} \left[\frac{m_0}{m_0 - m_1 + m_{\text{wire}}} \right], \quad (5)$$

where ρ_{EtOH} is the density of ethanol at the temperature of 301 K, m_{wire} is the weight of the wire in EtOH and the values of m_0 and m_1 are the sample weights on air and after immersion into EtOH.

3. Results and discussion

Figure 2 shows the *o*-Ps lifetimes and their relative intensities for the investigated samples as a function of temperature in the range of 15–350 K. The temperature

where the free volume (*o*-Ps lifetime) changes slope is assigned as a glass transition temperature T_{g1} .

The determined values of free-volume ($V_h(T_{g1}) = 4\pi R^3/3$) in the glass transition temperature (T_{g1}) and thermal expansion coefficient ($\alpha_{fv1} = (1/V_h(T_{g1}))(\Delta V_h/\Delta T)$ [9]) of microscopical free-volume are gathered in Table I. The lower temperature at which the slope of the $V_h(T)$ also changes in some cases is designated as T_{g2} .

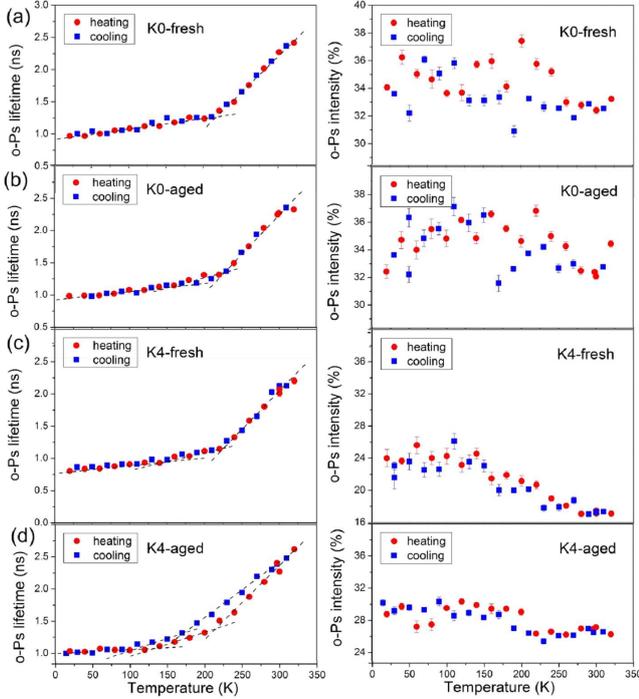


Fig. 2. *o*-Ps lifetime τ_3 (left) and intensity I_3 (right) versus temperature for (a) K0-fresh, (b) K0-aged, (c) K4-fresh, and (d) K4-aged polymers. The samples are marked as shown in Fig. 1. The error bars for *o*-Ps lifetime data are within the size of the symbol. The dashed lines are drawn as a guide for the eye.

TABLE I

Free-volume V_{h1} at glass transition temperature T_{g1} ; lower temperature at which $V_h(T)$ changes the slope T_{g2} ; thermal expansion coefficient α_{fv1} of the microscopical free-volume near T_{g1} for the investigated polymers. The samples are marked as shown in Fig. 1.

Sample	V_{h1} [nm ³]	T_{g1} [K]	T_{g2} [K]	α_{fv1} [$10^{-4}/K$]	
				$T < T_{g1}$	$T > T_{g1}$
K0-fresh (c&h)	0.123 ± 0.002	216 ± 13	–	25 ± 3	286 ± 21
K0-aged (c&h)	0.123 ± 0.003	230 ± 19	166 ± 89	53 ± 22	273 ± 99
K4-fresh (c&h)	0.104 ± 0.001	227 ± 18	126 ± 38	48 ± 1	344 ± 63
K4-aged (c)	0.134 ± 0.001	178 ± 19	88 ± 58	46 ± 17	206 ± 56
K4-aged (h)	0.123 ± 0.004	228 ± 38	130 ± 38	56 ± 22	237 ± 84

Following Fig. 2 and Table I, differences in network behavior for the aged samples and the effect of chalcogenide (As_2S_3) particles on the free volume of ureasil

network are clearly observed. Further research should be focused to resolve the nature of double T_g values in the aged ureasil and As_2S_3 + ureasil composites.

Figure 3 shows the results of swelling experiment for the investigated samples. The numerical parameters such as the bulk density of the polymeric sample ρ_p , and the molecular weight between two crosslink points, M_c are presented in Table II. The higher M_c value, the lower crosslinking density and the higher swellability. Thus, swelling experiments using EtOH showed that the structure of the aged sample network had less swelling ability for the pure ureasil as well as composite. This suggests that the one of factors influencing swelling is the change of the basic ureasil network due to ageing.

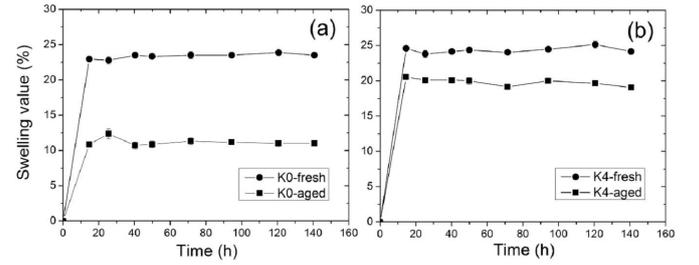


Fig. 3. Swelling value versus time curves for (a) K0-fresh and K0-aged and (b) K4-fresh and K4-aged polymers in EtOH at room temperature. The samples are marked as shown in Fig. 1. The error bars are within the size of the symbol.

TABLE II

Bulk density of the polymeric sample (ρ_p), molecular weight between two crosslink points (M_c) and comparative analysis of crosslinking density or swellability for the investigated polymers. The samples are marked as shown in Fig. 1.

Sample	ρ_p [g/cm ³]	M_c	Crossl.	Swell.
K0-fresh	1.1778 ± 0.0021	92.47	–	+
K0-aged	1.1814 ± 0.0012	44.0	++	--
K4-fresh	1.2015 ± 0.007	99.22	--	++
K4-aged	1.2170 ± 0.003	76.52	+	–

It is supposed that the network properties obtained by PALS and swelling experiments could be very helpful to understand better the bio-functionality of the constructed biosensor based on the ureasil-chalcogenide glass composite [1]. In this respect, to get more information, a comparative analysis of sensitivity of bioelectrodes constructed using the fresh and aged ureasil composites and PALS and swelling results for these samples is required. Such research is currently in progress.

4. Conclusion

Network properties of ureasil-based polymer matrixes suitable for construction of amperometric biosensors have been probed by PALS in the temperature range of 15–350 K and swelling experiments. T_g and α_{fv} values for

the investigated polymers have been determined and differences in network behavior for the aged samples and the effect of As₂S₃ particles on the free volume of ureasil network have been observed. The double T_g values in the aged ureasil and As₂S₃+ ureasil composites have been detected, while their nature remains not understood yet. Swelling experiments using EtOH have proved that the structure of the aged sample network had less swelling ability for the pure ureasil as well as composite, the most probably due to the change of the basic ureasil network with ageing. A comparative analysis of sensitivity of bioelectrodes constructed using the fresh and aged ureasil composites and PALS and swelling results for these samples is still required to understand better a correlation between network properties of polymer matrix and biofunctionality of the constructed biosensor based on the polymer matrix.

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