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ON THE CORRELATION OF NETWORK PROPERTIES OF POLYMER MATRIXES WITH PARAMETERS OF ELECTROCHEMICAL BIOSENSORS

Abstract. In the present work, the influence of organic-inorganic ureasil polymers with different precursors (ICPTES+Jeffamine ED-600 and ICPTES+APTES) on bioanalytical properties of electrochemical biosensors was studied. The parameters of the constructed biosensors were estimated using cyclic voltammetry and chronoamperometric measurements. The network properties (free volume and crosslinking) of the investigated polymers, earlier studied using positron annihilation lifetime spectroscopy technique and swelling measurements, were taken into account for comparative analysis. A correlation of network properties of polymer matrixes with parameters of electrochemical biosensors was found in a good agreement with the previously reported data for ureasil composites of different prehistory (fresh and aged samples) and photocross-linked polymers based on epoxidized linseed oil (ELO). It is concluded that the above mentioned correlation has fundamental origin.

Key words: polymers, positron annihilation, free volume, crosslinking, biosensors.

INTRODUCTION

Application of polymer materials as holding matrixes of immobilized enzyme is an innovative approach in a construction of the amperometric biosensors [1]. The constructed laccase biosensor based on the ureasil/As_2S_3 composite was characterized by a very high sensitivity, but a weak point of the biosensor was very strong unexpected electrochemical noise at chronoamperometric measurement [1]. At the same time, new perspectives of the

ureasil-based polymers for construction of amperometric enzyme biosensors were further found [2–4].

In particular, a correlation between the network properties of the biosensor sensing layers (e.g., free-volume V_h at glass transition temperature T_g and coefficients for the thermal expansion of free-volume voids α_{F1}, α_{F2} as well as their difference ($\alpha_{F2} - \alpha_{F1}$), and swellability or crosslinked density) based on the pure ureasil and ureasil/As_2S_3 composites of different history (fresh and aged samples) and biosensor characteristics (e.g., a maximal current at substrate saturation I_{max}, apparent Michaelis-Menten constant K_M^{app} to ABTS chosen as a substrate, the slope of the calibration curve B, and the sensitivity of bioelectrodes obtained by means of cycle voltammetry and chronoamperometric analysis) was established. On the other hand, vegetable oil-based photopolymers were used as a holding matrix in biosensors [5–8].

Recently, amperometric laccase biosensors for analysis of phenol derivates were constructed using graphite rods (type RW001) as working electrodes and the photocross-linked polymers as a matrix [5]. Such matrix consisted of epoxidized linseed oil (ELO), bisphenol A diglycidyl ether (RD) as reactive diluent and 50% mixture of triarylsulfonium hexafluorophosphate in propylene carbonate as photoinitiator (PI). The synthesis was made by the reaction of ELO and 10 mol.% or 30 mol.% of RD, using 3 mol.% of PI (ELO/10RD and ELO/30RD, respectively). The holding matrixes were used for an immobilization of commercial laccase from the fungus *Trametes versicolor*. The network properties of the polymer matrixes, holding biosensing element, were studied by means of positron annihilation lifetime spectroscopy (PALS) and swelling measurements. The amperometric enzyme biosensor parameters were evaluated using cyclic voltamperometry and chronoamperometric analysis. The next phase of research was nanostructure investigation of soybean oil-based samples and their usage in the construction of biosensors [6–10]. Two groups of the investigated samples contain epoxidized soybean oil (AESO), vanillin dimethacrylate (VDM) and/or vanillin diacrylate (VDA) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as PI. The samples contained different molar ratios of the tested substances.

The aim of the present research is to find correlation between nanostructure and detection properties of the polymer matrixes. It is necessary to find the best material to construct highly sensitive biosensors in order to detect xenobiotics pollution in wastewater. In this work, the influence of ureasil polymers with different precursors on bioanalytical properties of electrochemical biosensors is reported.

EXPERIMENTAL

For the construction of amperometric biosensors, 5 µl of *Trametes zonate* laccase solution with an activity of 12 U·mg^{-1} was applied to the surface of graphite rod electrodes (diameter 3.05 mm, working surface area 7.35 mm^2) and dried for 10 min at room temperature. The formed enzyme layer was covered with 5 µl of polymer solution and dried for 15 min at room temperature. The constructed electrodes were washed with 50 mM acetate buffer (AB), pH 4.5 and kept at 4°C until use.

Cyclic voltammetry and chronoamperometric measurements of laccase-based biosensors with various polymers were performed using an ABTS and/or catechol solution as a calibrator. Nafion as control sample and ureasil polymers with different precursors (Precursor 1 (ICPTES+Jeffamine ED-600) and Precursor 2 (ICPTES+APTES)) marked as Ureasil-1 (100 mol% Precursor 1 : 0 mol% Precursor 2), Ureasil-2 (30.8 mol% Precursor 1

: 69.2 mol% Precursor 2), and Ureasil-3 (0 mol% Precursor 1 : 100 mol% Precursor 2) were selected for research [11]. The measurements were carried out at room temperature in a glass electrochemical cell with a working volume of 50 ml, filled with 10 ml of 50 mM acetate buffer, pH 4.5. The bioelectrodes were placed in a stirred solution and, after establishing the base signal against Ag/AgCl, increasing concentrations of the analyte were introduced into the cell.

RESULTS AND DISCUSSION

A working potential was estimated for ureasil samples as -100 mV vs. Ag/AgCl toward ABTS (Fig. 1) and -50 mV vs. Ag/AgCl (reference electrode) toward catechol.

The chronoamperogram and calibration curves of the control electrode, where the biosensitive layer was covered with a Nafion membrane, for the addition of an increasing concentration of catechol are presented in Fig. 2.

Figure 3 shows the chronoamperogram and calibration response curves for the three tested bioelectrodes for adding analyte of catechol, from which it can be seen that sensors with polymers have better operational parameters compared to the control one (covered with a Nafion membrane).

The dependence of the operational parameters of three laccase biosensors with polymers relative to the control (coated with Nafion) was evaluated according to four main parameters: I_{max} is the value of the response of the biosensor when saturated with the substrate; K_M^{app} is the value of the apparent Michaelis-Menten constant; limits of linearity and sensitivity (Table 1).

For all studied biosensors, an increase in sensitivity of 1.4 is observed; 1.8 and 2.2 times compared to the control. The lowest value of K_M^{app} (1.17 mM) was found for laccase/Ureasil-1, which indicates a better affinity of the biosensitive layer to the analyte, and the control electrode had the widest linear range.

Among the investigated nanomediators towards catechol, the laccase/Ureasil-1 and laccase/Ureasil-2 are the most promising, since the highest sensitivity (190 and 234 $A \cdot M^{-1} \cdot m^{-2}$) is observed when they are used as part of biosensors. The bionanosensors constructed on their basis are promising, probably, for the analysis of phenolic derivatives in real samples of drinking water and wastewater.

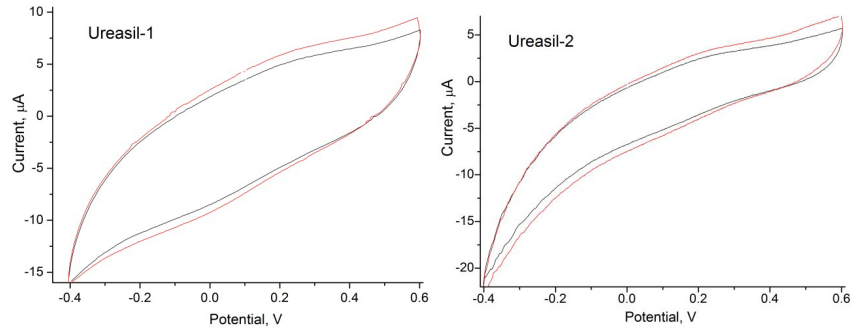

Fig. 1. Cyclic voltammetric response of the bioelectrodes constructed based on laccase immobilized by ureasil samples (Ureasil-1 and Ureasil-2) after addition of an increasing concentration of ABTS

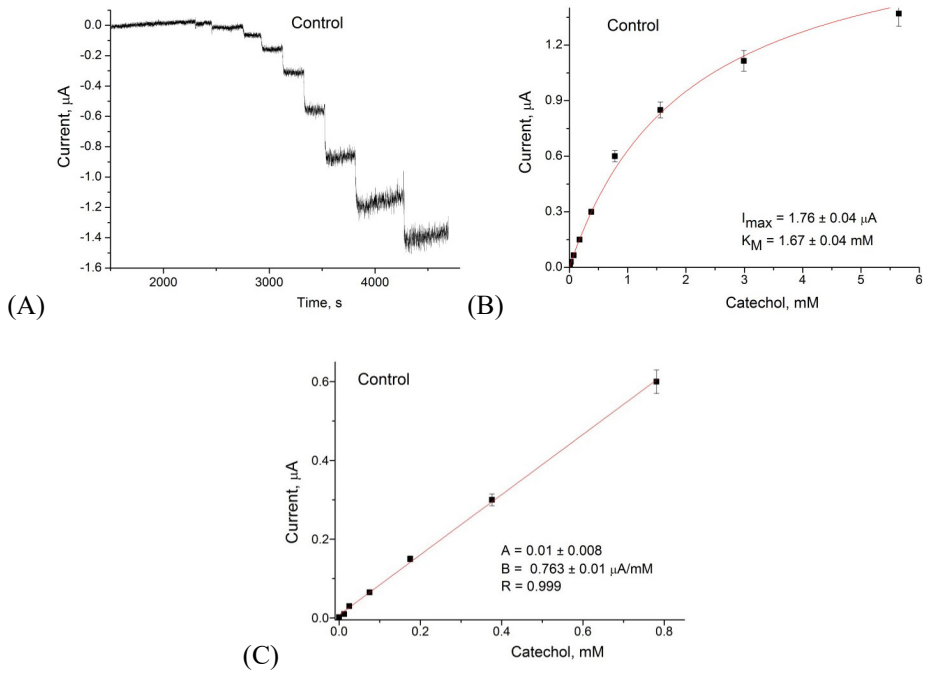

Fig. 2. Amperometric characteristics of bioelectrode laccase/Nafion as control: chronoamperogram (A), dependence of the amperometric signal on the concentration of catechol (B), and calibration curve for determining catechol (C). Conditions: working potential -50 mV vs. Ag/AgCl/3 M KCl in 50 mM acetate buffer, pH 4.5

Notes: *B* is the slope of the calibration curve; *R* is the linear regression correlation coefficient

Figure 4 shows the chronoamperogram and calibration response curves for the laccase/ureasil tested bioelectrodes for adding analyte of ABTS. It was not possible to obtain a good signal using laccase/Ureasil-3 polymer. But it can be seen that sensors with laccase/Ureasil-1 and laccase/Ureasil-2 polymers demonstrated a high sensitivity and a wide range of linearity similarly as in the case of catechol (Table 1).

Amperometric characteristics of bioelectrodes using laccase and ureasil composites of different prehistory (fresh and aged samples) [3] and photocross-linked polymers based on epoxidized linseed oil (ELO) [5] were also gathered in Table 1 for comparison.

The network properties (free volume and crosslinking) of the investigated ureasil polymers with different precursors, earlier studied using positron annihilation lifetime spectroscopy technique and swelling measurements [11], were taken into account for comparative analysis (Table 2).

A correlation of network properties of polymer matrixes with parameters of electrochemical biosensors was found in a good agreement with the previously reported data for ureasil composites of different prehistory (fresh and aged samples) [3; 4] and photocross-linked polymers based on epoxidized linseed oil (ELO) [5]. It is concluded that the above mentioned correlation has fundamental origin.

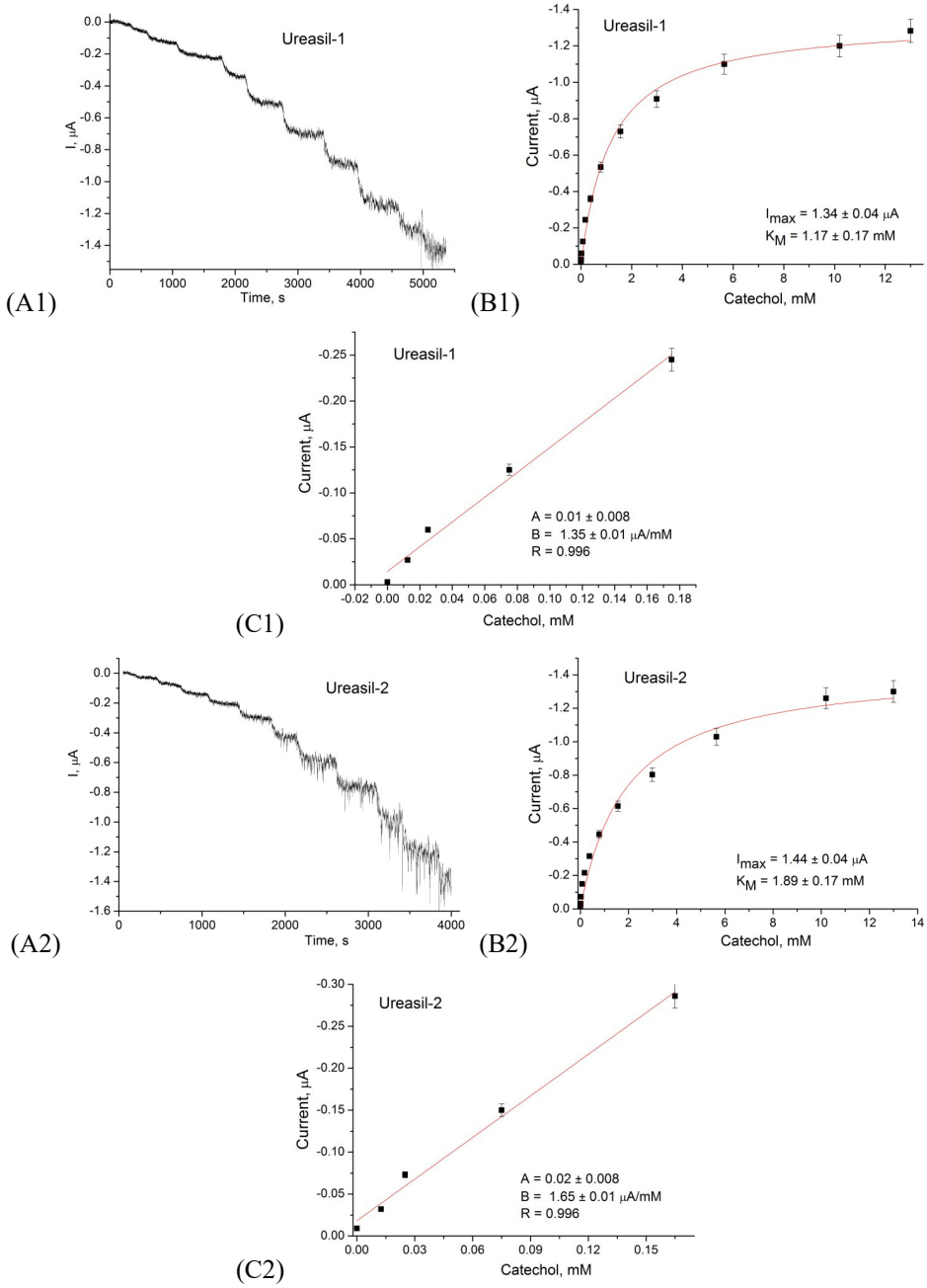

Fig. 3. Amperometric characteristics of bioelectrodes: laccase/Ureasil-1 (A1, B1, C1), laccase/Ureasil-2 (A2, B2, C2), and laccase/Ureasil-3 (A3, B3, C3), where chronoamperograms (A1, A2, A3), dependencies of the amperometric signal on the concentration of catechol (B1, B2, B3), and calibration curve for determining catechol (C1, C2, C3). Conditions: working potential -50 mV vs. Ag/AgCl/3 M KCl in 50 mM acetate buffer, pH 4.5

Notes: *B* is the slope of the calibration curve; *R* is the linear regression correlation coefficient

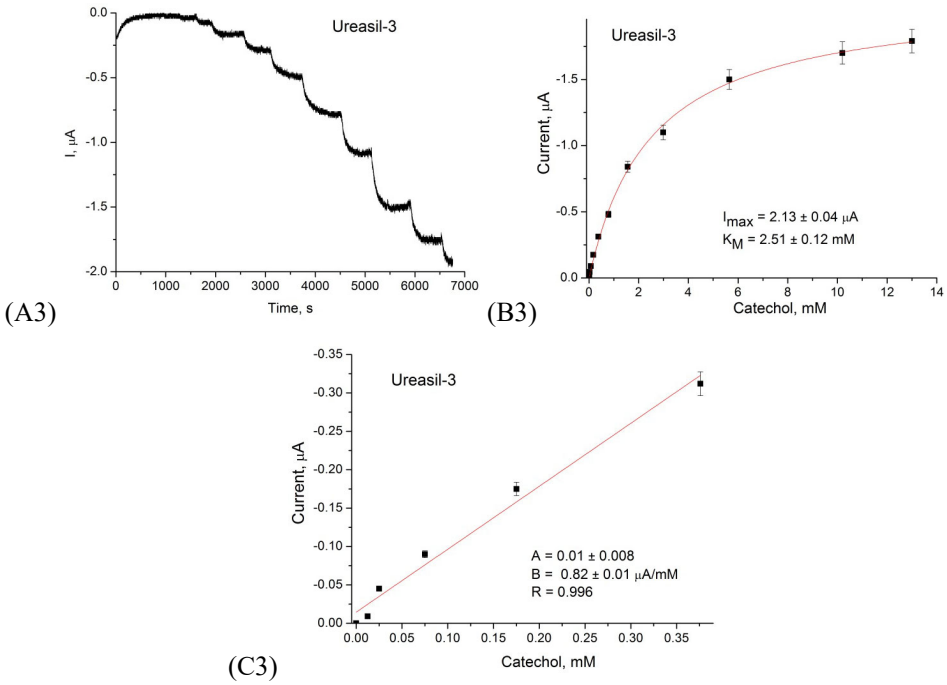

Fig. 3 (continuation)

Table 1

Comparison of analytical properties of the fabricated laccase-based biosensors in this work with previously constructed [3; 5]

Polymers	I_{max} (μ A)	K_M^{app} (mM)	B (μ A·mM^{-1})	Sensitivity (A·M^{-1}·m^{-2})	Linearity, up to (mM)
Catechol (this work)					
Nafion	1.76 ± 0.04	1.67 ± 0.04	0.76 ± 0.01	107	0.80
Ureasil-1	1.34 ± 0.04	1.17 ± 0.17	1.35 ± 0.01	190	0.18
Ureasil-2	1.44 ± 0.04	1.89 ± 0.17	1.65 ± 0.01	234	0.18
Ureasil-3	2.13 ± 0.04	2.51 ± 0.12	0.82 ± 0.01	150	0.18
ABTS (this work)					
Ureasil-1	4.45 ± 0.1	0.51 ± 0.02	7.59 ± 0.05	1080	0.10
Ureasil-2	1.85 ± 0.1	0.38 ± 0.02	3.88 ± 0.05	552	0.18
Ureasil-3	n/a	n/a	n/a	n/a	n/a
ABTS [3]					
K0-fresh	7.62 ± 1.7	0.64 ± 0.17	10.0	794	0.15
K0-aged	10.96 ± 3.4	0.35 ± 0.14	22.2	1762	0.15
K4-fresh	43.77 ± 2.7	0.045 ± 0.005	501.7	39,817	0.04
K4-aged	86.8 ± 0.9	0.030 ± 0.008	761.2	60,413	0.06
ABTS [5]					
ELO/10RD	4.9 ± 0.19	0.36 ± 0.03	12.3	1.673	0.15
ELO/30RD	1.25 ± 0.17	0.11 ± 0.04	9.07	1.234	0.10

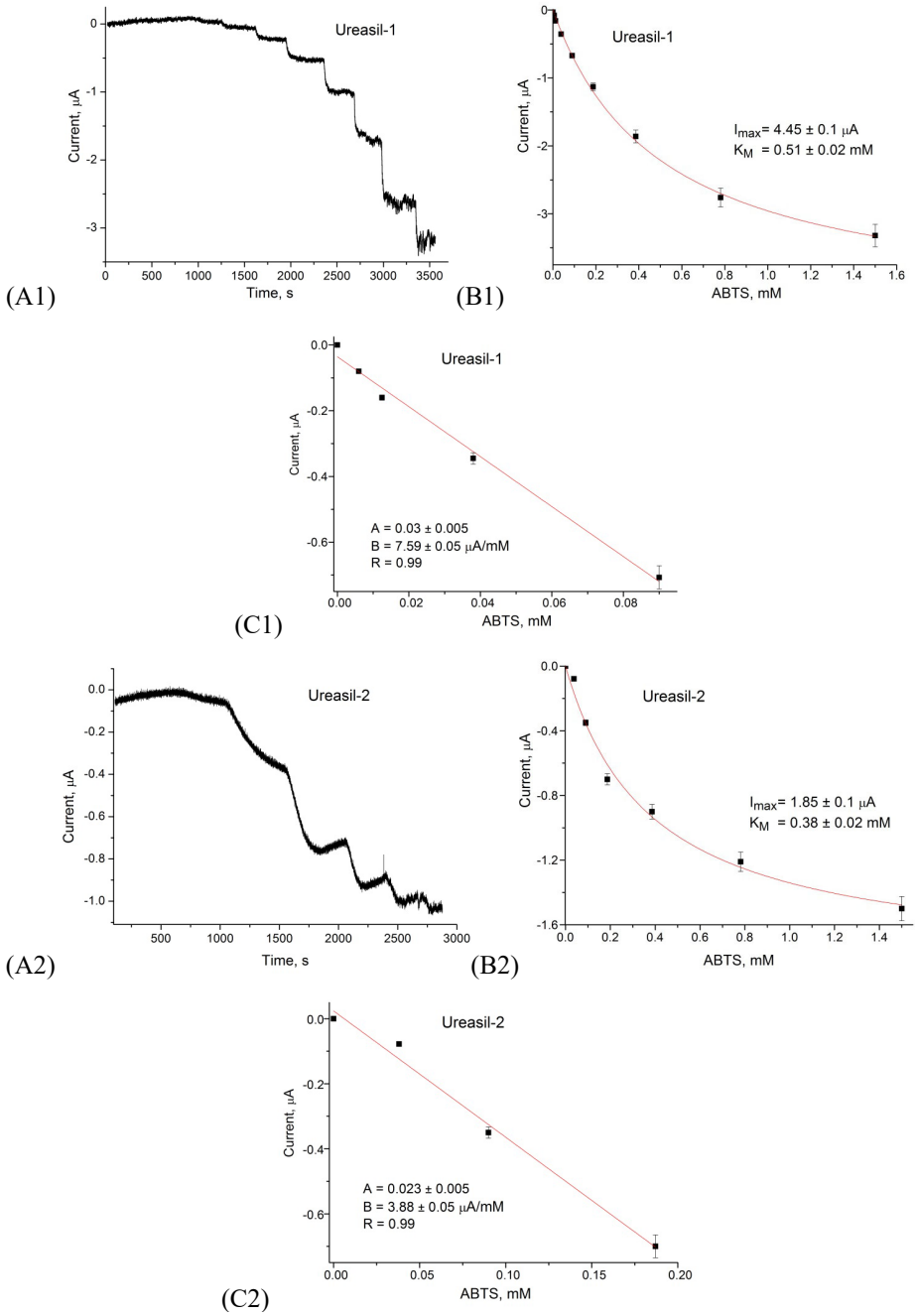

Fig. 4. Amperometric characteristics of bioelectrodes: laccase/Ureasil-1 (A1, B1, C1) and laccase/Ureasil-2 (A2, B2, C2), where chronoamperograms (A1, A2), dependencies of the amperometric signal on the concentration of ABTS (B1, B2), and calibration curve for determining ABTS (C1, C2). Conditions: working potential -100 mV vs. Ag/AgCl/3 M KCl in 50 mM acetate buffer, pH 4.5

Notes: *B* is the slope of the calibration curve; *R* is the linear regression correlation coefficient

Table 2

Hole volume V_h at glass transition temperature T_g, swellability S in EtOH, and slopes α_{F1}, α_{F2} of the $V_h(T)$ dependences in the regions below and above T_g, respectively, as well as their differences for the ureasil-based [3; 4; 11] and photocross-linked polymers [5]. Values for heating and cooling cycles are in the top and bottom part of the boxes, respectively

Polymers	$V_h(T_g)$ (nm^3)	S (%)	α_{F1} (10-4 K-1)	α_{F2} (10^{-4} K^{-1})	$\alpha_{F2} - \alpha_{F1}$ (10^{-4} K^{-1})
Ureasil polymers with different precursors					
Ureasil-1 [11]	0.050 ± 0.009 0.050 ± 0.005	37.8	53 ± 11 44 ± 5	213 ± 40 181 ± 20	160 137
Ureasil-2 [11]	0.049 ± 0.005 0.048 ± 0.001	22.3	39 ± 5 34 ± 9	163 ± 19 131 ± 27	124 97
Ureasil-3 [11]	n/a n/a	-	n/a n/a	n/a n/a	n/a n/a
Ureasil composites with different prehistory					
K0-fresh [3; 4]	0.123 ± 0.002	23.0	25 ± 3	286 ± 21	261
K0-aged [3; 4]	0.123 ± 0.003	11.0	53 ± 22	273 ± 99	220
K4-fresh [3; 4]	0.104 ± 0.001	24.0	48 ± 10	344 ± 63	296
K4-aged [3; 4]	0.123 ± 0.002 0.134 ± 0.001	19.0	56 ± 22 46 ± 17	237 ± 84 206 ± 56	181 160
Photocross-linked polymers					
ELO/10RD [5]	0.057 ± 0.002 0.068 ± 0.002	24.09	3.53 ± 0.30 3.31 ± 0.32	13.02 ± 0.60 11.16 ± 0.55	9.49 ± 0.67 7.85 ± 0.64
ELO/30RD [5]	0.051 ± 0.002 0.049 ± 0.002	24.81	3.47 ± 0.33 3.87 ± 0.83	12.42 ± 0.64 8.96 ± 0.48	8.95 ± 0.72 5.09 ± 0.96

CONCLUSION

On the basis of comprehensive analysis of the results obtained on the nanostructure and detection properties of ureasil and photocross-linked polymers of different prehistory and composition, a correlation of network properties of polymer matrixes with parameters of electrochemical biosensors is verified and it seems to be fundamental in origin. The development of the laccase-biosensor can be used for assay of phenolic compounds in the wastewater and drinking water.

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АНОТАЦІЯ

ПРО КОРЕЛЯЦІЮ СІТКОВИХ ВЛАСТИВОСТЕЙ ПОЛІМЕРНИХ МАТРИЦЬ ІЗ ПАРАМЕТРАМИ ЕЛЕКТРОХІМІЧНИХ БІОСЕНСОРІВ

У даній роботі досліджено вплив органічно-неорганічних уреасильних полімерів з різними прекурсорами (ICPTES+Jeffamine ED-600 та ICPTES+APTES) на біоаналітичні властивості електрохімічних біосенсорів. Параметри сконструйованих біосенсорів оцінювали за допомогою циклічної вольтамперометрії та хроноамперометричних вимірювань. Для порівняльного аналізу були враховані сіткові властивості (вільний об'єм і зшивання) досліджуваних полімерів, раніше вивчені методом часового розподілу анігіляційних фотонів (з англ. positron annihilation lifetime spectroscopy) та вимірювання набухання. Знайдено кореляцію сіткових властивостей полімерних матриць з параметрами електрохімічних біосенсорів, яка добре узгоджується з раніше наведеними даними для уреасильних композитів різної передісторії (свіжі та витримані зразки) та фотозшитих полімерів на основі епоксидованої лляної олії (ELO). Зроблено висновок, що зазначена кореляція має фундаментальне походження.

Ключові слова: полімери, позитронна анігіляція, вільний об'єм, зшивання, біосенсори.