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BENZOYL PEROXIDE DECOMPOSITION BY NANOPOROUS AND NANOSCALE CARBON MATERIALS IN NONAQUEOS MEDIA

This study presents benzoyl peroxide solutions stability in acetone, carbon tetrachloride, butanol, acetic acid, and ethyl acetate. The catalytic activities of nanoporous (KAU and SKN) and nanosized (CNT) carbon materials, their modified forms (oxygen- and nitrogen-containing), and enzyme catalase were determined by calculation of Michaelis constants, according to the kinetics of substrate decomposition. It was shown that nitrogen-containing materials provide the highest catalytic activity in non-aqueous medium. It was found out that the catalytic activity of the investigated materials decreased in the following order: N–KAU > N–CNT > N–SKN > SKN > SKNo > KAUo–NH_2 > CNT > catalase> CNTo > KAU > KAUo. It was shown that catalase activity in non-aqueous is small. It has been proved that the catalytic activity of the studied samples correlated with the surface basicity and presence of quaternary nitrogen groups in the structure. It has been established that presence of nitrogen atoms in carbon materials increases their catalytic activity, while oxygen atoms reduce catalytic activity.

Keywords: carbon materials, activated carbon, carbon nanotubes, benzoyl peroxide, catalytic activity, Michaelis constant.

Introduction

Carbon nanomaterials (nanoporous and nanosized) such as activated carbon (AC), carbon nanotubes (CNT) are widely used for various purposes: for organic and inorganic synthesis as catalysts [1; 2] and catalysts support [3], purification, separation, and extraction (as adsorbents) [4], for the processes of the detoxification (as entero- or haemosorbent) [5], and for other processes. Besides, carbon nanomaterials (CNM) can affect on various important biological processes. CNM can affect on enzymatic processes (hydrolysis of proteins, fats, esters, sucrose inversion, decomposition of peroxide, urea, etc.), i.e. carbon materials exhibit enzyme-mimetic properties [6].

It is well known that a number of factors, namely surface modification by different hetero atoms (such as O, N, S, P, B), presence of a wide range of surface functional groups and structural-sorption characteristics (specific surface area, pore volume and radius) can affect on the catalytic activity of carbon materials. Recently it has been shown that oxidation of carbon materials by HNO_3 leads to the formation of a large number of acidic functional groups, increases surface acidity, leads to hydrophilization of material, gives it ion exchange properties [7]. It has been shown that doping of CNM by nitrogen atoms results in the carbon surface defects formation, which leads to increasing catalytic properties of materials [8].

Enzymatic activity in non-aqueous media attract much attention [9; 10] because it gives a number of advantages: better solubility of the substrate; ability to change the selectivity changing environment, rather than the enzyme; lower risk of microbial contamination and others [11; 12]. Carbon materials used as enzymes carriers for reactions in organic media, CNM improves the stability and catalytic activity of enzymes [13]. However, enzyme-mimetic properties of carbon materials in non-aqueous media practically have not been investigated.

The aim of this work was to study enzyme-mimetic properties of nanoporous and nanoscale carbon materials and comparing their activity to enzyme in a model reaction of benzoyl peroxide decomposition in non-aqueous medium. Decomposition of benzoyl peroxide (BP) by carbon materials can be considered as a model to study the enzyme-mimetic catalase properties of CNM. Investigation of chosen nanoporous and nanoscale carbon materials help find the correlation between their surface chemistry, structural and sorption properties and catalytic ability in the process of peroxides decomposition. The results of these studies can be used to create highly directed action biocatalysts in biotechnology, cosmetology and medicine.

Materials and methods

Activated carbons (AC) (natural – KAU and synthetic – SKN) and carbon nanotubes (CNT), their modified forms (oxidized – SKNo, KAUo and CNTo; and nitrogen containing – N–SKN, N–KAU, KAUo–NH_2, N–CNT) and catalase (from bovine liver, K 1.11.1.6, activity 329 300 au, Fluka) have been used as catalysts in the reaction of BP decomposition. Oxygen containing samples were prepared by nitric acid oxidation method [14]. Nitrogen containing materials were obtained by urea impregnation of oxidized sample and followed by heat treatment (N–SKN, N–KAU, N–CNT) or chemical diaminopentane immobilization on the surface of oxidized sample (KAUo–NH_2) using bifunctional crosslinking agent – water soluble carbodiimine. The investigated samples were characterized: surface area (SA) – by chromatographic method of argon low-temperature adsorption; sorption pore volume (Vs) – by desiccator method and elements composition by Prehlya and Dumas methods [15]. Qualitative and quantitative characterization of functional groups on the surface of carbon nanomaterials samples was performed by Böehm titration [16].

Benzoyl peroxide (Merck KGaA, contains 25 % water); ethyl acetate (Merck KGaA, for liquid chromatography, 99.8 %) are used. Numbers of solvents – ethyl acetate, acetone, tetrachloromethane, butanol, acetic acid – were used to determine the stability of peroxide in non-aqueous media.

Weighted portions of benzoyl peroxide (BP) were solute to prepare solutions with desired concentrations (from 1 to 10 %). BP concentration in the product was determined by modified iodometric titration method [17].

Volumetric method used to determine the kinetic of BP decomposition in non-aqueous media. For analysis, quantitative assessment and comparison of catalytic activity of carbon nanomaterials and their modified forms Michaelis constant (K_M, mM) have been applied. The BP decomposition was conducted in the thermostatted cell with stirring. The reaction mixture temperature was measured with an accuracy of ± 0.5 °C, ambient temperature with accuracy of ± 1 °C, the amount of gases released in the reaction, with an accuracy of ± 0.01 ml. The released gas volume measurements were conducting for 120 minutes. The portion of 10 ml of BP solution in each experiment was taken. Michaelis constant (K_M, mM) was used to quantitative assessment and comparison of carbon nanomaterials and their modified forms catalytic enzyme-mimetic activity. Initial velocity (V_0) of reaction for different concentrations of the substrate was used to Michaelis constant determine [18]. Affinity constants (K_{af}), reverse to Michaelis constant, mM^{-1} has been applied for easy interpretation of experimental data.

Analysis of the reaction products of benzoyl peroxide decomposition was made by temperature-programmed mass spectrometry (TPD MS) [19]. 0.1 g of the sample has been added to 5 % BP solution in dioxane with volume of 50 ml. The suspension was left for 24 hours to establish the adsorption equilibrium. After decomposition the sample of CNM has been filtrated, dried and analyzed by TPD-MS method. TPD-MS experiments were performed using MX-7304 A monopole mass spectrometer with electron impact ionization.

The chemical state of Nitrogen atoms on the surface of samples investigated by X-ray photoelectron spectroscopy (XPS) on the "JEOL" device, with X-ray Al Kα (monochromator) source at room temperature and the working pressure in the chamber $2{,}7\times10^{-6}$ Pa.

Results and discussion

In order to establish the factors that affect on the catalytic activity of carbon nanomaterials, we selected a number of nanoporous (AC) and nanoscale (nanotubes) carbon materials with different structural and sorption characteristics, surface chemistry, and heteroatom presence in its structure. Surface area of investigated samples was in the range of 145–2140 m^2/g according to the chromatographic method. The desiccator method showed that volume of sorption pores varies within 0.30–0.90 cm^3/g. Results of elemental analysis of CNM samples showed that during the oxidation number of oxygen atoms is doubled for SKN and in 20 times for KAU. The increasing number of hydrogen atoms suggests the oxygen-containing functional groups formation on the SKN and KAU samples surface (Table 1).

The results of titration showed the mainly acid character of the surface groups which were formed. Total number of acid groups in the oxidation reaction of carbon increased in the 6, 18, and 20 times for CNTo, SKNo and KAUo respectively. Phenolic, lactone and carboxyl groups are prevalence on the carbon materials surface. They can be involved in catalytic processes. Number of basic surface groups of SKN, N–SKN, N–KAU and KAUo–NH_2 was in the range 0.12 to 1.90 mEq/g (Table 2). According to elemental analysis the smallest nitrogen atoms content of 0.30 % was found in the carbon KAU. The number of nitrogen atoms in the AC structure increases twice as a result of oxidation by nitric acid, possibly because of carbon surface nitration processes. Functionalization of KAU can include nitrogen atoms up to 2.20 %. SKN obtained from the vinylpyridine resin and as a result it contains Nitrogen atoms [20]. The total nitrogen content in synthetic carbon SKN increases with oxidation. SKN was additionally functionalized by urea impregnation to compare the activity of nitrogen contained materials. As a result N–SKN with the nitrogen content of 3.85 % has been obtained.

Table 1. **Characteristics of initial and oxidized samples**

Types of samples	**Elements composition, mass. %**				**V_s, *cm^3/g* (X_1)**	**Surface area, *m^2/g* (X_2)**
	C	H	O (X_6)	N (X_5)		
KAU	99.40	0.20	0.06	0.30	0.50	1070
KAUo	96.30	1.10	2.10	0.60	0.85	1850
N–KAU	89.20	2.33	6.24	2.20	0.91	1470
KAUo–NH_2	78.61	1.98	16.08	3.33	0.56	650
SKN	91.20	0.96	6.50	1.30	0.75	1970
SKNo	85.80	0.90	11.20	2.00	0.80	2140
N–SKN	91.25	1.20	3.70	3.85	0.84	1650
CNT	95.80	0.65	3.27	0.28	0.48	145
CNTo	97.21	0.95	1.43	0.41	0.56	150
N–CNT	99.12	–	0.48	0.40	0.31	145
R^2	–	–	0.01	0.13	0.34	0.01

Table 2. **Functional groups on surface of investigated samples**

Types of samples	**Functional groups, mEq/g**				
	carboxylic	**lactonic**	**phenolic**	**sum of acidic groups (X_3)**	**basic groups (X_4)**
KAU	0.04	0.06	0.02	0.12	0.00
KAUo	0.84	0.20	1.39	2.43	0.00
N–KAU	0.00	0.45	0.05	0.50	1.90
KAUo–NH_2	0.00	0.00	1.27	1.27	0.22
SKN	0.08	0.02	0.02	0.12	0.12
SKNo	1.04	0.10	1.01	2.15	0.00
N–SKN	0.00	0.00	0.73	0.73	1.44
CNT	0.10	0.31	0.03	0.44	0.23
CNTo	0.40	0.40	0.55	1.35	0.00
N–CNT	0.41	0.22	0.09	0.72	0.00
R^2	–	–	–	0.14	0.93

For a quantitative calculation of BP concentration changes during catalytic decomposition by volumometryc method it was needed to establish the reaction stoichiometry. The products of the benzoyl peroxide decomposition in the presence of carbon nanomaterials were investigated by TPD MS method. Benzoyl peroxide TPD MS spectra showed (Fig. 1), availability existence of peaks with mass numbers 122, 105, 77, 44, 28 which correspond to such radicals: benzoic acid, benzoyl peroxide radical, phenyl radical, carbon dioxide and carbon monoxide molecules. It was shown that in all cases the CO and CO_2 but not oxygen molecules were released. Analysis of the TPD spectra of the BP shows that decomposition of 1 mole BP results in 2 mole of gas release that allows realizing quantitative determination of changes in BP concentration in time by the volume of released gas [21].

Solvents affect the stability of benzoyl peroxide [22; 23]. In order differentiation processes of BP decomposition in solution and on a solid surface, we have investigated peroxide benzoyl solutions stability in acetone, ethyl acetate, CCl_4, butanol and glacial acetic acid. It was established that during two hours BP decomposed in ethyl acetate – 0 %; acetone – 0.14 %; CCl_4 – 0.23 %; butanol – 1.37 %; acetic acid – 1.90 % (Fig. 2). Experimental results have been shown to be in agree with literature data which argues that BP solutions are less stable in highly polar solvents as alcohols and acids [22; 24]. For example BP solutions in acetic acid and butanol were the less stable than in other solvents. BP solution in ethyl acetate exhibited the highest stability. Hence, ethyl acetate has been selected as optimal solvent for investigation of BP catalytic decomposition.

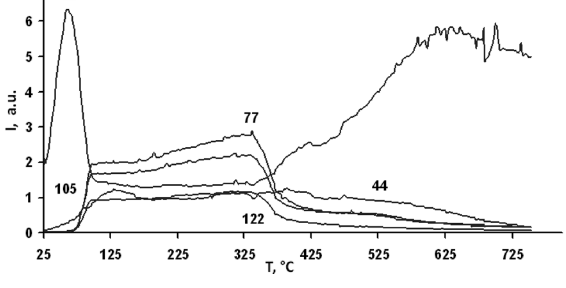

Fig. 1. TPD MS spectrum of benzoyl peroxide decomposition on activated carbon SKN

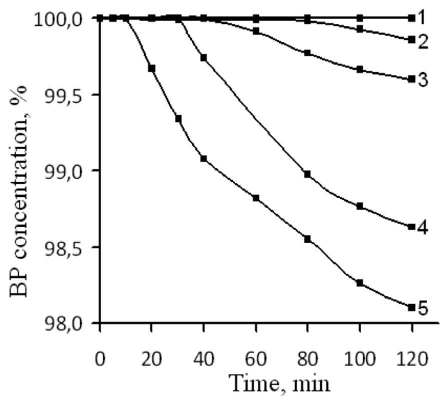

Fig. 2. Stability of BP in different solvents: *1* – ethyl acetate; *2* – acetone; *3* – CCl_4; *4* – butanol; *5* – acetic acid

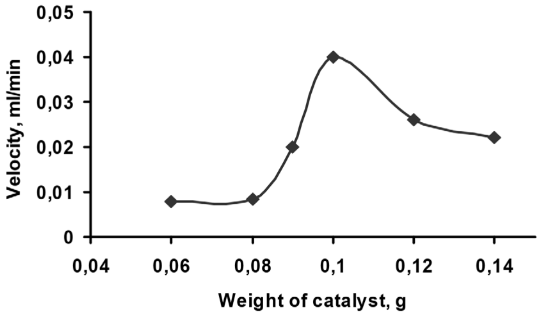

Fig. 3. Dependence of BP decomposition rate by SKNo from its amount

Methodology Michaelis constants require used catalyst of optimum amount in kinetic experiments, while there is a maximum substrate (benzoyl peroxide in ethyl acetate) decomposition rate. Optimal catalyst amount was determined from kinetic data – dependence of BP maximal decomposition rate from amount of catalyst (Fig. 3, Table 3) for all investigated carbon material samples.

Table 3. **Optimal amount of catalyst (m), K_M (mM) and reliability approximation value R^2**

Catalyst	m, g	K_M (mM)	R^2
KAU	0.100	470	0.90
KAUo	0.080	1120	0.98
N–KAU	0.100	29	0.89
KAUo–NH$_2$	0.050	290	0.85
SKN	0.040	176	0.99
SKNo	0.090	250	0.89
N–SKN	0.050	55	0.95
CNT	0.005	320	0.98
CNTo	0.010	430	0.87
N–CNT	0.005	40	0.98
Catalase	0.050	340	0.96

For analysis, quantitative assessment and comparison of catalytic activity of carbon nanomaterials, their modified forms and enzyme catalase, Michaelis constant has been calculated from kinetic data of different concentration BP solutions decomposition (Table 3, Fig. 4).

It was found that the catalytic activity (K_M, mM) of the investigated materials decreased in the following order: N–KAU > N–CNT > N–SKN > SKN > SKNo > KAUo–NH$_2$ > CNT > catalase > CNTo > KAU > KAUo. It was found, that activity highest activity – more then catalase one – exhibit nitrogen containing carbon nanomaterials (N–KAU, N–CNT, N–SKN). N–KAU is most active, N–SKN shows significant activity, which is three times more than the initial SKN. SKNo characterized by less activity. The following materials are less active than the enzyme. KAUo–NH$_2$ material is more active than KAU and KAUo, which has the lowest activity. Thus, nitrogen-containing materials have higher catalytic activity, which can be explained by the fact that nitrogen as electron donor element provides greater mobility of electrons in the carbon matrix and reduces the electron work function at the interface of carbon/liquid or gaseous phase. Oxidation of carbon materials leads to a decrease in their catalytic activity by reducing their electron donor ability. Because of this transfer of electrons to molecules BP is difficult. Catalase occupies an intermediate position between the nitrogen containing carbon materials and samples KAU and CNTo by the activity to decompose BP in non-aqueous medium. This indicates that some carbon nanomaterials may act as biocatalysts in non-aqueous environment and under certain conditions to achieve higher efficiency of the process compared to the enzymes.

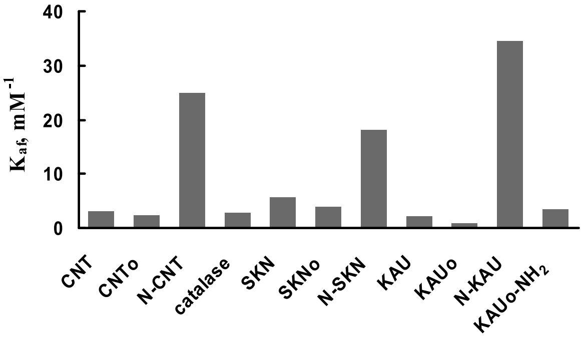

Fig. 4. The affinity constant for carbon nanomaterials samples and enzyme catalase in non-aqueous media (solvent – ethyl acetate)

On the basis of the research work done authors have found factors which determine catalase-mimetic activity of carbon nanomaterials in reaction of BP decomposition in non-aqueous medium. Search correlation (R^2) between catalytic activity (K_{af}, Y) and structural factors (X_1 and X_2) has not given a positive response – $R_1^2 = 0.34$ та $R_2^2 = 0.01$, respectively. The total content of surface acidic groups (X_3) and Oxygen content (X_6) also no affects the catalytic activity – $R_3^2 = 0.14$ and $R_6^2 = 0.01$, respectively. At the same time the correlation between the presence of basic groups and catalytic activity was found: $R_4^2 = 0.93$. It has been suggested that the basicity of surface is related with the presence in structure of CNM nitrogen-containing groups. However, the catalytic activity is not correlated with total nitrogen content (X_5): $R_5^2 = 0.13$. Probably, the catalytic activity nitrogen-containing carbon nanomaterials depend on the nitrogen atoms chemical state but not on the total nitrogen content in the structure [25].

State Nitrogen atoms and their relative content in the studied nitrogen-containing carbon nanomaterials were determined from the analysis of N 1s XPS spectra (Table 4, Fig. 5).

It was shown that the catalytic enzyme-like activity of carbon nanomaterials correlated with the presence of quaternary nitrogen through increasing capacity electron-donating carbon matrix. Higher activity modified nitrogen containing NCM N–KAU and N–SKN compared with SKN can be attributed to the different content of quaternary nitrogen. These data is in agreed with dependence on the activity of the basic groups on the surface of CNM.

Conclusions

It has been shown that carbon nanomaterials exhibit catalase-like catalytic activity in the reaction of BP decomposition. Stability of BP solutions in different solvents was investigated. The highest stability of the BP solutions in different solvents was found in the case of ethyl acetate. It was shown, that catalase activity in non-aqueous media is small. Catalytic ability on carbon nanomaterials in the process of BP decomposition correlate with their surface chemistry. Presence of

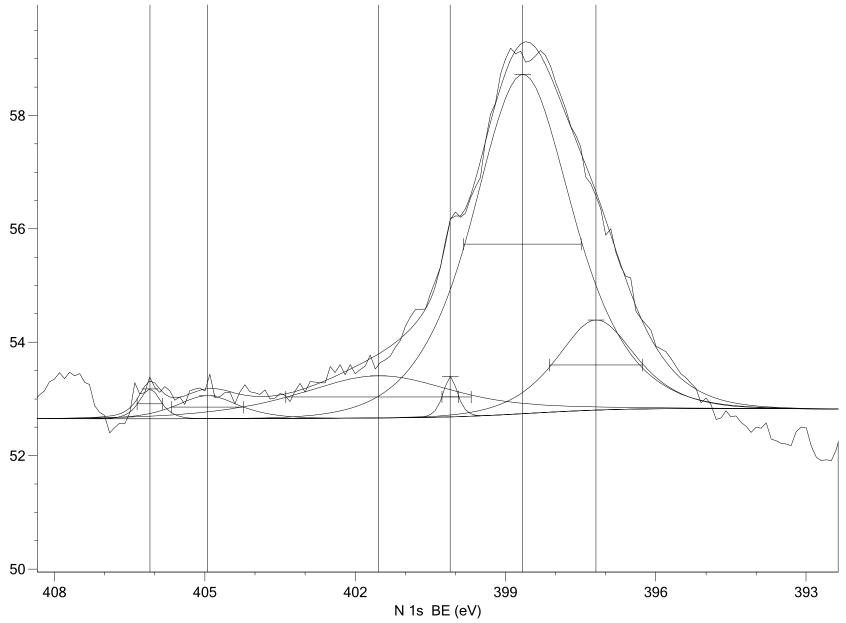

Fig. 5. XPS 1s Nitrogen spectra state for N–KAU

Table 4. **The correlation between the chemical nitrogen state and catalytic activity of CNM**

Sample	State of nitrogen atoms (relative content, %)							K_{af}, mM^{-1} (Y)
	Pyrrolidonic (X_7)	Pyrrolic (X_8)	Pyridinic (X_9)	Pyridine N-oxide (X_{10})	NO_2-Group (X_{11})	C=N (X_{12})	Quaternary (X_{13})	
KAU	0.00	35.59	57.58	3.98	2.85	0.00	0.00	2.12
KAUo	0.00	6.44	89.27	2.83	1.46	0.00	0.00	0.89
N–KAU	0.00	1.12	67.38	0.00	4.09	14.18	13.23	34.48
KAUo–NH_2	35.93	0.00	60.67	1.30	0.00	0.00	2.10	3.44
SKN	48.69	0.00	25.52	10.03	2.19	13.57	0.00	6.17
SKNo	0.00	29.41	45.12	0.35	3.07	21.37	0.00	4.00
N–SKN	0.00	0.00	64.45	2.39	0.23	32.39	0.54	18.18
R^2	0.07	0.14	0.01	0.11	0.14	0.23	0.77	–

nitrogen atoms in carbon materials increases their catalytic activity while oxygen atoms reduce catalytic activity. Catalytic activity of carbon nanomaterials depends on presence of quaternary nitrogen in carbon materials. Hence it is possible to create biocatalysts based on nitrogen-containing carbon nanomaterials for the processes of organic peroxides decomposition.

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РОЗКЛАДАННЯ ПЕРОКСИДУ БЕНЗОЇЛУ НАНОПОРИСТИМИ ТА НАНОРОЗМІРНИМИ ВУГЛЕЦЕВИМИ МАТЕРІАЛАМИ В НЕВОДНОМУ СЕРЕДОВИЩІ

Досліджено стабільність розчинів пероксиду бензоїлу в ацетоні, чотирьоххлористому вуглеці, бутанолі, оцтовій кислоті та етилацетаті. Визначено каталітичну активність нанопористих (КАУ і СКН) і нанорозмірних (ВНТ) вуглецевих матеріалів, їх модифікованих форм (кисень- і азотовмісних) та ферменту каталаза шляхом розрахунку констант Міхаеліса за кінетикою розкладання *субстрату. Показано, що азотовмісні матеріали проявляють найвищу каталітичну активність у неводному середовищі. Встановлено, що каталітична активність досліджуваних матеріалів знижується в такому ряді: N–КАУ > N–ВНТ > N–СКН > СКН > СКНо > КАУо–NH_2 > ВНТ > каталаза > ВНТо > КАУ > КАУо. Показано, що активність каталази в неводних середовищах є низькою. Каталітична активність досліджуваних зразків корелює з основністю поверхні і наявністю груп четвертинного азоту в структурі. Доведено, що наявність атомів азоту у вуглецевих матеріалів підвищує їхню каталітичну активність, а атоми кисню знижують каталітичну активність вуглецевих наноматеріалів.*

Ключові слова: вуглецеві матеріали, активоване вугілля, вуглецеві нанотрубки, пероксид бензоїлу, каталітична активність, константа Міхаеліса.

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РОЗРОБКА ПЛІВКОВИХ МАТЕРІАЛІВ З ДЕКАМЕТОКСИНОМ НА ОСНОВІ ПОЛІУРЕТАНСЕЧОВИН, ЯКІ МІСТЯТЬ У СВОЇЙ СТРУКТУРІ ФРАГМЕНТИ КОПОЛІМЕРУ N-ВІНІЛПІРОЛІДОНУ З ВІНІЛОВИМ СПИРТОМ

На основі діізоціанатного форполімеру, 1,6-гексаметилендіаміну (ГМДА), кополімеру N-вінілпіролідону з вініловим спиртом (ВП-ВС) синтезовано ряд гідрофільних поліуретансечовин (ПУС), які містять у своєму складі декаметоксин за різного співвідношення ГМДА:ВП-ВС. Встановлено, що ПУС, отримані за співвідношення ГМДА:ВП-ВС як 40:60, мають покращені фізико-механічні властивості, є біосумісними та можуть бути використані як плівкові матеріали для лікування ран та опіків.

Ключові слова: поліуретансечовина, декаметоксин, кополімер N-вінілпіролідону з вініловим спиртом, плівковий матеріал.

Вступ

Актуальним і перспективним напрямом хімії високомолекулярних сполук є розробка нових полімерних матеріалів медичного застосування з власною біологічною активністю, зокрема як полімерних покриттів для лікування ран та опіків.

Полімерні плівки є альтернативою таких лікарських засобів, як мазі, пасти, гелі [1; 2]. В останні роки увагу вчених привертають поліуретансечовини (ПУС) як матеріали медичного призначення, які використовують при створенні покриттів на рани [3], контактних лінз [4], катетерів, протезів, судин [5], антитромбогенних виробів [6].

Використання діамінів як подовжувачів макроланцюга при синтезі ПУС покращує їхні експлуатаційні та медико-біологічні характеристики, що дозволяє подальше використання як матеріалів медичного призначення [7–9].

Також серед полімерів – носіїв лікарських речовин (ЛР) – особливе місце посідають полівінілпіролідон (ПВП) та його кополімери завдяки своїм унікальним властивостям. Це насамперед