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TETIANA VISLOHUZOVA* (ORCID: 0000-0002-4071-4329), **RITA ROZHNOVA**** (ORCID: 0000-0003-3284-3435), **TETIANA KISELOVA** (ORCID: 0000-0001-5606-6904), **GALYNA KOZLOVA** (ORCID: 0000-0001-8114-4812)
Institute of Macromolecular Chemistry of the NAS of Ukraine, 48 Kharkivske Highway, Kyiv, 02155, Ukraine,
*e-mail: rudenchyk@gmail.com
**e-mail: rozhnovarita@gmail.com

IN VITRO INVESTIGATION OF THE BIODEGRADATION CAPACITY OF POLYURETHANE-UREAS WITH GRAFTED COPOLYMER FRAGMENTS OF POLYVINYL ALCOHOL-POLYETHYLENE GLYCOL IN STRUCTURE

The study of biodegradation capacity in vitro is one of the essential stages in the development of polymers for medical applications, as it allows predicting the behavior of the materials in vivo. Therefore, the purpose of this work was to investigate the biodegradation capacity of polyurethane-ureas (PUUs) with fragments of 4,4'-diaminodiphenylmethane (DADPh) as a chain extender and grafted copolymer polyvinyl alcohol-polyethylene glycol (PVA-PEG) as a hydrophilic component under in vitro conditions. The biodegradation capacity was evaluated based on the changes in the structure, physical-mechanical, and thermophysical properties of PUUs under the influence of biological medium 199 (BM 199) over incubation periods of 1, 3, and 6 months, using methods such as IR spectroscopy, physical-mechanical testing, and differential scanning calorimetry (DSC). Based on the results of IR spectroscopy studies, under the influence of BM 199, a process of biodegradation of the studied PUUs occurs, which is accompanied by the cleavage of chemical bonds, changes in hydrogen interactions, and structural transformations of the polymer matrix. Based on physical-mechanical tests, after 6 months of incubation, a decrease in strength of 11.9–26.7% and in relative elongation at break of 5.9–13.7% was observed in PUUs compared to the control. DSC analysis revealed that after 6 months of incubation in BM 199, an increase in Tg of 10.6–51.3% and an increase in ΔCp during vitrification of 17.5–46.5% were observed, indicating structural changes during the biodegradation process. Considering the obtained results, the investigated PUUs with DADPh fragments and graft copolymer PVA-PEG in the structure demonstrate biodegradation capacity in vitro with simultaneous structural changes in the polymer matrix. The synthesized PUUs could be a promising polymer matrix for developing bioactive polymer materials with temporary functionality and require further investigation.

Keywords: *polyurethane-urea, grafted copolymer polyvinyl alcohol-polyethylene glycol, biodegradation, biological medium 199.*

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Тетяна Віслогузова, Ріта Рожнова**, Тетяна Кісельова, Галина Козлова*
Інститут хімії високомолекулярних сполук НАН України, 48, Харківське шосе, Київ, 02155, Україна,
*e-mail: rudenchyk@gmail.com
**e-mail: rozhnovarita@gmail.com

ДОСЛІДЖЕННЯ ЗДАТНОСТІ ДО БІОДЕГРАДАЦІЇ ПОЛІУРЕТАНСЕЧОВИН ІЗ ФРАГМЕНТАМИ ПРИЩЕПЛЕНОГО КОПОЛІМЕРУ ПОЛІВІНІЛОВИЙ СПИРТ-ПОЛІЕТИЛЕНГЛІКОЛЬ У СТРУКТУРІ В УМОВАХ *IN VITRO*

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Дослідження здатності до біодеградації за умов *in vitro* є одним із важливих етапів при створенні полімерів медичного призначення, оскільки дає змогу спрогнозувати поведінку досліджуваних матеріалів за умов *in vivo*. Тому метою роботи було дослідження здатності до біодеградації поліуретансечовин (ПУС) із фрагментами 4,4'-діамінодифенілметану (ДАДФ) як подовжувача макроланцюга і прищепленого кополімеру полівініловий спирт-поліетиленгліколь (ПВС-ПЕГ) як гідрофільного компонента за умов *in vitro*. Здатність до біодеградації оцінювали за зміною структури, фізико-механічних і теплофізичних властивостей ПУС під впливом біологічного середовища 199 (БС 199) протягом 1, 3 і 6 місяців інкубації методами ІЧ-спектроскопії, фізико-механічними випробуваннями та методом ДСК. За результатами ІЧ-спектроскопічних досліджень, під впливом БС 199 відбувається процес біодеградації досліджуваних ПУС, який супроводжується розщепленням хімічних зв'язків, зміною водневих взаємодій і структурними перетвореннями полімерної матриці. За даними фізико-механічних випробувань, після 6 місяців інкубації ПУС порівняно з контролем спостерігається зменшення міцності на 11,9–26,7 % та відносного подовження при розриві на 5,9–13,7 %. Методом ДСК встановлено, що після 6 місяців інкубації ПУС у БС 199 спостерігається підвищення T_c на 10,6–51,3 %, а також підвищення ΔC_p при склуванні на 17,5–46,5 %, що є свідченням структурних змін в процесі біодеградації. Враховуючи отримані результати, досліджувані ПУС із фрагментами ДАДФ і прищепленого кополімеру ПВС-ПЕГ у структурі проявляють здатність до біодеградації за умов *in vitro* з одночасними структурними змінами полімерної матриці. Синтезовані ПУС можуть бути перспективною полімерною матрицею для створення на їх основі біологічно активних полімерних матеріалів тимчасового терміну дії та потребують подальших досліджень.

Ключові слова: поліуретансечовина, прищеплений кополімер полівініловий спирт-поліетиленгліколь, біодеградація, біологічне середовище 199.

Introduction

Polyurethane-ureas (PUUs) with hydrophilic fragments of the grafted copolymer polyvinyl alcohol-polyethylene glycol (PVA-PEG) and the chain extender 4,4'-diaminodiphenylmethane (DADPh) in their structure [1] are a promising polymer matrix for obtaining biologically active polymeric materials for medical applications.

One of the most important characteristics of polymeric materials intended for medical use is their biodegradation capacity in environments that simulate the conditions of the human body. The biodegradation processes of the polymer matrix are accompanied by changes in its structure, which in turn lead to changes in its properties. Factors such as the chemical composition of the polymer, the hydrophilicity of the polymer matrix, etc., influence the biodegradation process [2, 3]. Specifically, it is known that an increase in the hydrophilic component in the polymer matrix structure leads to an increase in biodegradation rate [4, 5].

For example, the authors [6, 7] conducted studies on the biodegradation capacity of PUUs with fragments of the hydrophilic copolymer N-vinylpyrrolidone with vinyl acetate and vinyl alcohol (VP-VA) and the chain extender 1,6-hexamethylenediamine in the structure. It was found that PUUs with minimal copolymer content remain biostable, while with increasing copolymer content they exhibit biodegradation capacity. Thus, increasing the hydrophilic component in the polymer structure leads to enhanced biodegradation. Block copolyurethanes with hydrophilic copolymer VP-VA fragments in their structure are also known, which degrade within 7 days after incubation in BM 199 [8]. At the same time, PUUs with fragments of poly(vinyl butyral-vinyl acetate-vinyl alcohol) copolymer in their structure remain stable for 6 months after incubation in BM 199 [9].

In addition, studies were conducted to analyze the influence of soft and hard segments on the biodegradation processes in the PUU structure. The *in vitro* degradation of PUUs with poly(D,L-lactic acid) diol as a soft segment and 1,6-hexamethylene diisocyanate and piperazine as hard segments was studied. Piperazine was also used as a chain extender. According to the obtained results, varying the component ratios can significantly affect the stability and degradation rate of PUUs. Therefore, by adjusting the component ratios, it is possible to predict a specific degradation rate for PUUs to restore bone defects [10, 11]. The authors [12] investigated the biodegradation of segmented PUUs based on 2,6-diisocyanato methyl caproate, poly(ε-caprolactone diol), and the chain extender 1,4-butanediamine with different soft segment lengths. According to the research results, seg-

mented PUUs with longer soft segments, leading to higher hydrophobicity, showed a lower degradation rate. A narrow molecular weight distribution could also be one of the reasons for the slower degradation of the studied PUUs. The results of studies [13] indicate that the degree of biodegradation of the multiblock copolymer poly(urethane-urea-amide) depends on the pH of the medium and the type of hard segment (amide chain extender). The polymers showed a sharp decrease in viscosity at neutral pH, while the amide bonds were resistant to degradation in an alkaline medium.

Since the chemical composition of the polymer material affects the biodegradation process of the polymer matrix, it is necessary to investigate the biodegradation capacity of PUUs containing the PVA-PEG copolymer and DADPh in their structure. The results of *in vitro* studies will allow predicting changes in the properties of the studied materials under *in vivo* conditions when used in medical practice.

Therefore, the aim of this study was to investigate the biodegradation capacity of polyurethane-ureas containing PVA-PEG as a hydrophilic component and DADPh as a chain extender by analyzing the changes in their structure, physical-mechanical, and thermophysical properties under the influence of a model medium for 1, 3, and 6 months under *in vitro* conditions.

Experimental part

Materials. For the synthesis of PUU, the following components were used: polyoxypropylene glycol (POPG) (Rokopol, MM = 1052), 2,4-; 2,6-toluene diisocyanate (TDI, 80/20) (Merck, MM = 174.16; ρ = 1.22 g/cm^3; T_{boil} = (133 ± 1) °C), 4,4'-diaminodiphenylmethane (DADPh) (Fluka, MM = 198.27; T_{melt} = 88–92 °C), graft copolymer polyvinyl alcohol–polyethylene glycol (PVA-PEG) KOLLICOAT® IR (Sigma-Aldrich, % OH = 6.445), dimethyl sulfoxide (DMSO) (MM = 78.13; ρ = 1.1004 g/cm^3; T_{boil} = 189 °C).

To study biodegradation capabilities, a biological medium 199 (BM 199) (BioTestLab, Ukraine, pH 7.4–7.7) was used as a model medium, simulating blood plasma and comprising a complex mixture of proteins, amino acids, carbohydrates, fats, salts, hormones, enzymes, antibodies, and dissolved gases.

Synthesis of PUUs. The objects of study were PUUs based on diisocyanate prepolymer (DPP) (synthesized from POPG and TDI), chain extender DADPh, and grafted copolymer PVA-PEG, obtained at different molar ratios of DPP:DADPh:PVA-PEG (1.0:0.7:0.3; 1.0:0.8:0.2; 1.0:0.9:0.1) (Table 1) [1].

Table 1. **Component ratio in the synthesis of PUUs**

PUUs	DPP:DADPh:PVA-PEG, mole
PUU1	1.0:0.7:0.3
PUU2	1.0:0.8:0.2
PUU3	1.0:0.9:0.1

Incubation in BM 199. Samples were placed in sterile containers, filled with 25 ml of model biological medium, and kept in a thermostat at a temperature of (37 ± 1)°C for periods of 1, 3, and 6 months. The medium solutions were changed daily. After the specified periods in the model medium, the samples were removed, washed with distilled water, and dried to constant weight at room temperature.

Characterization. The structure was investigated using a Fourier transform infrared spectrometer "Tensor-37" (Bruker) by the attenuated total reflection (ATR) method in the range of 500–4000 cm^{-1}, using a diamond crystal trapezoidal prism (number of reflections N = 1, incident angle φ = 39°).

Physical-mechanical properties, such as tensile strength (σ, MPa) and relative elongation at break (ε, %) of the synthesized PUUs were measured on a tensile testing machine R5 in accordance with the current regulatory documentation [14].

The thermophysical properties (glass transition temperature (T_g), change in heat capacity at the glass transition (ΔC_p) were investigated by DSC. The studies were conducted in the temperature range of –90°C to 200 °C (TA Instrument Q2000) at a heating rate of 20 °C/min in a nitrogen atmosphere.

Results and Discussion

To study the biodegradation capacity of PUUs with PVA-PEG copolymer fragments synthesized at different molar ratios of DPP:DADPh:PVA-PEG (1.0:0.7:0.3, 1.0:0.8:0.2, 1.0:0.9:0.1), samples were incubated in BM 199 for periods of 1, 3, and 6 months. The effect of the model medium was

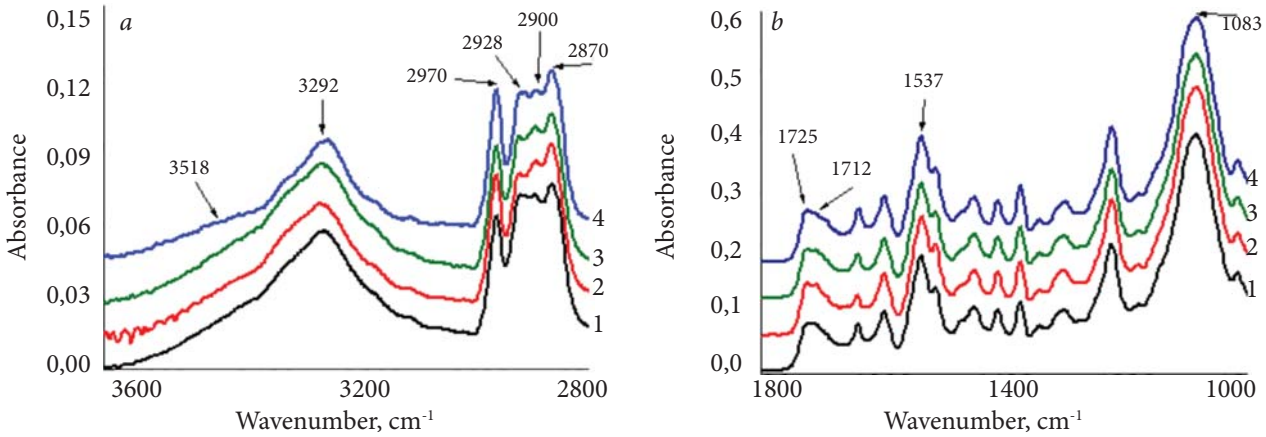

Fig. 1. IR spectra of PUU1 before (*1*) and after incubation in BM 199 for 1 month (*2*), 3 months (*3*) and 6 months (*4*) in the range of 3600–2800 cm^{-1} (*a*) and 1800–1000 cm^{-1} (*b*)

evaluated based on the changes in their structure, physical-mechanical, and thermophysical properties by comparing samples before (control) and after incubation.

According to the results of IR spectroscopic studies of PUUs samples before and after exposure in the model medium, no significant changes in chemical structure occurred. However, the chan-ges were observed in the stretching vibration region, which is sensitive to hydrogen bonding (Fig. 1–3).

For PUU1 in the IR spectral range of 3600–2800 cm^{-1} under the influence of BM 199 for up to 6 months of incubation, a decrease in the intensity of the absorption bands of ν(NH-bound) at 3292 cm^{-1} and ν(NH-free) at 3518 cm^{-1} was observed, which is associated with a decrease in the amount of free and hydrogen-bonded NH groups on the surface layer of the samples (as the IR spectra were recorded from the surface of the polymer materials) and a redistribution of the intensity of the absorption bands of ν(C–H) (2900 cm^{-1}, 2928 cm^{-1}, and 2970 cm^{-1}) (Fig. 1 *a*).

In the 1800–1000 cm^{-1} frequency range (Fig. 1*b*), there is a redistribution of the absorption intensity of the carbonyl group of the urethane fragment: unassociated C=O groups with a maximum at 1725 cm^{-1} and associated C=O groups with a maximum at 1712 cm^{-1}. After one month of incubation, both bands are more clearly defined, and after six months, an increase in the intensity of the unassociated C=O absorption band at 1725 cm^{-1} and a decrease in the intensity of the associated C=O band at 1712 cm^{-1} are observed, indicating an increase in the number of unassociated C=O groups on the sample surface after incubation in BM 199. There is also an increase in the intensity of the absorption band δ_{NH} at 1537 cm^{-1}, indicating increased hydrogen bonding or the formation of new bonds between the NH groups of the polyurethane-urea and the components of the medium. In the IR spectra of PUUs, there is also a decrease in the absorption intensity of the ν(C=O) band at 1641 cm^{-1}, which is associated with a reduction in the number of C=O groups involved in hydrogen bonding in the initial state, as new, stronger bonds are formed with the components of the biological medium. In addition, an increase in the intensity of the ν(C–O) absorption band with a maximum at 1083 cm^{-1} is observed over the six months of incubation, which is likely associated with intensified bonding or structural changes in the polymer caused by the influence of the biological medium.

For PUU2 (Fig. 2) and PUU3 (Fig. 3), in the IR spectra range of 3600–2800 cm^{-1} under the influence of the biological medium, similar changes in the intensities of the absorption bands of ν(NH-free) at 3518 cm^{-1} and ν(NH-bound) at 3292 cm^{-1}, ν(C-H) (2900 cm^{-1}, 2928 cm^{-1}, and 2970 cm^{-1}), ν(C=O) unassociated at 1725 cm^{-1} and $\nu_{C=O}$ associated at 1712 cm^{-1}, δ_{NH} at 1537 cm^{-1}, $\nu_{C=O}$ urea groups at 1641 cm^{-1}, and νC-O at 1083 cm^{-1} were observed, as in the previous case. A distinguishing feature is the increase in the intensity of the absorption band of $\nu_{NH\text{-}free}$ at 3518 cm^{-1} and $\nu_{NH\text{-}bound}$ at 3292 cm^{-1} after 1 month of incubation, followed

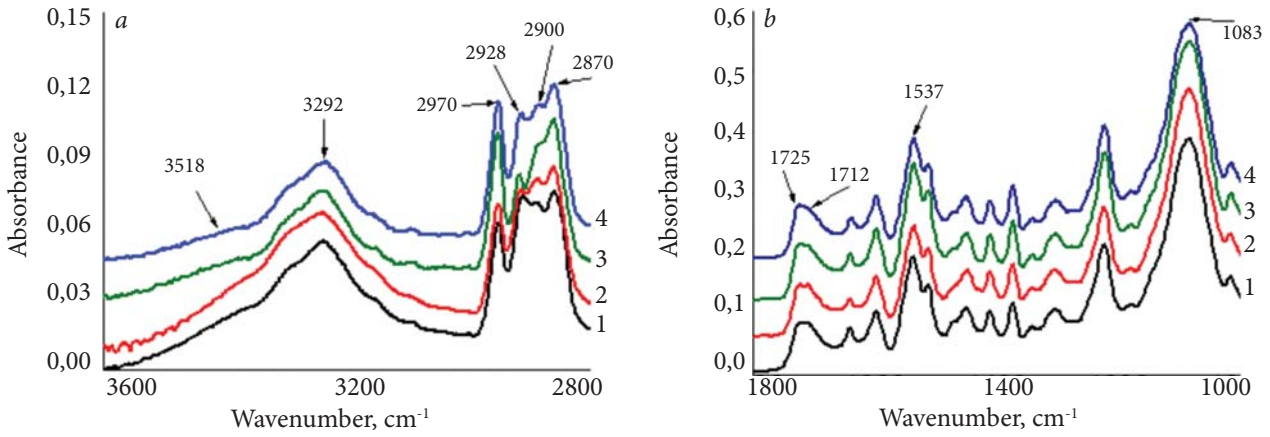

Fig. 2. Fragments of IR spectra of PUU2 before (*1*) and after incubation in BM 199 for 1 month (*2*), 3 months (*3*) and 6 months (*4*) in the range of 3600–2800 cm^{-1} (*a*) and 1800–1000 cm^{-1} (*b*)

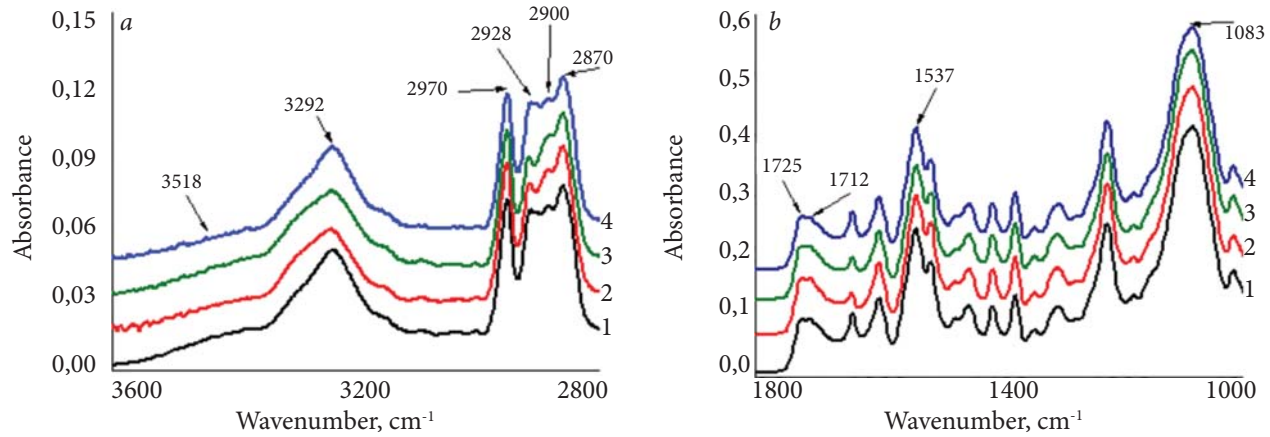

Fig. 3. Fragments of IR spectra of PUU3 before (*1*) and after incubation in BM 199 for 1 month (*2*), 3 months (*3*) and 6 months (*4*) in the range of 3600–2800 cm^{-1} (*a*) and 1800–1000 cm^{-1} (*b*)

by a decrease for PUU2 (Fig. 2 *a*), and a decrease in the absorption intensity of δ_{NH} at 1537 cm^{-1} of the urethane fragment for PUU3 (Fig. 3 *b*).

Thus, according to the results of IR spectroscopic studies, changes in absorption bands were detected for groups involved in the formation of hydrogen bonds under the influence of the biological medium. Decrease in the absorption intensity of free ($\nu_{NH\text{-}free}$ 3518 cm^{-1}) and hydrogen-bonded ($\nu_{NH\text{-}bonded}$ 3292 cm^{-1}) NH groups, redistribution of absorption intensity of $\nu_{C\text{-}H}$ bands (2900 cm^{-1}, 2928 cm^{-1}, and 2970 cm^{-1}), redistribution of associated ($\nu_{C=O}$ associated 1712 cm^{-1}) and unassociated C=O groups ($\nu_{C=O}$ unassociated 1725 cm^{-1}) in the urethane fragment, redistribution of the absorption intensity of NH groups in the urethane fragment (δ_{NH} 1537 cm^{-1}) and $\nu_{C=O}$ urea groups 1641 cm^{-1}, and an increase in the absorption intensity of C-O groups ($\nu_{C\text{-}O}$ 1083 cm^{-1}) were observed. These changes are associated with biodegradation processes in the polymer matrix, accompanied by a redistribution of the system of intra- and intermolecular hydrogen bonds and enhancement of intermolecular interactions.

Thus, according to IR spectral data, conclusions can be drawn regarding the cleavage of chemical bonds during biodegradation. Spectral analysis reveals changes in functional groups participating in hydrogen bonding, which serve as crucial indicators of structural transformations in the polymer matrix. In particular, the decrease in the intensity of absorption bands corresponding to free ($\nu_{NH\text{-}free}$ 3518 cm^{-1}) and bound ($\nu_{NH\text{-}bonded}$ 3292 cm^{-1}) NH groups indicates a decrease in the number of these

groups or changes in their state due to biological influence. This may indicate disruption of internal hydrogen bonds within the polymer matrix. Furthermore, the redistribution of the absorption intensities of the carbonyl groups (associated and unassociated) of the urethane fragment indicates a reorganization of the intermolecular bond system. Specifically, an increase in the absorption intensity of unassociated C=O groups ($\nu_{C=O}$ unassociated 1725 cm^{-1}) and a decrease in that of associated groups ($\nu_{C=O}$ associated 1712 cm^{-1}) suggest the weakening of old hydrogen bonds and the formation of new ones. Changes in urea groups (δ_{NH} 1537 cm^{-1}, $\nu_{C=O}$ 1641 cm^{-1}, ν_{C-O} 1083 cm^{-1}) observed in the spectra indicate structural reorganization of the polymer under the influence of the biological medium. This may be due to the breaking of hydrogen bonds or the formation of new, stronger interactions between the medium components and the polymer. Thus, the IR spectroscopy data confirm that the biodegradation process of the studied PUUs involves cleavage of chemical bonds, changes in hydrogen interactions and structural transformations of the polymer matrix.

According to the results of physical-mechanical tests, it was found that the physical-mechanical properties of the samples after incubation in BM 199 for 1, 3, and 6 months undergo changes, depending on the duration of incubation.

For PUU samples, the tensile strength decreases over the 6 months of incubation and has a non-linear character. The greatest loss in tensile strength, from 28.6% to 61.3%, is observed after 3 months of incubation. After 6 months of incubation in BM 199, an increase in tensile strength was observed for all PUU samples compared to the previous incubation period. However, compared to the control, a decrease of 11.9% to 26.7% in this indicator was observed after 6 months of incubation (Table 2).

The obtained results, in our opinion, are related to the specific nature of PUU biodegradation under the influence of the model biological medium, particularly with the structuring of the polymer matrix due to the redistribution of the system of intra- and intermolecular hydrogen bonds along with the simultaneous progression of biodegradation. Considering that BM 199 is a complex multicomponent biological system, the increase in tensile strength can also be explained by the formation of new hydrogen bonds between the components of the biological medium and the polymer. BM 199 contains various molecules, such as proteins, polysaccharides, and ions that can interact with the functional groups of polyurethane-urea (NH, C=O, and C–O–C).

The value of relative elongation at break of PUUs also changes non-linearly over the 6 months of incubation in BM 199 (Table 2). For all PUU samples, an increase in relative elongation of 9.0–122.1% was observed after 1 month of incubation. After 3 months of incubation, a decrease in relative elongation was observed compared to the previous period. However, after 6 months of incubation in BM 199, an increase in relative elongation was

Table 2. **Physical-mechanical properties of PUUs before and after incubation in BM 199**

PUUs	Periods of incubation, month	σ, MPa	ε, %
PUU1	control	0.60	68.0
	1	0.50	151.0
	3	0.33	69.7
	6	0.44	117.4
PUU2	control	0.31	47.4
	1	0.19	76.8
	3	0.12	38.0
	6	0.23	40.9
PUU3	control	0.42	186.0
	1	0.33	202.8
	3	0.30	129.4
	6	0.37	175.1

Table 3. **Thermophysical properties of PUUs before and after incubation in BM 199**

PUUs	Periods of incubation, month	T_g, °C		ΔC_p, J/ (g ·°C)	
		1st heating cycle	2nd heating cycle	1st heating cycle	2nd heating cycle
PUU1	control	−16.04	−28.41	0.4285	0.3485
	1	−16.92	−16.02	0.3989	0.4022
	3	−16.81	−15.84	0.401	0.4325
	6	−18.17	−17.27	0.418	0.4413
PUU2	control	−15.11	−31.99	0.4872	0.3389
	1	−15.36	−24.75	0.4784	0.4102
	3	−15.63	−16.45	0.4395	0.4257
	6	−15.78	−15.58	0.4833	0.4966
PUU3	control	−11.97	−17.25	0.478	0.3941
	1	−12.01	−15.59	0.4977	0.4765
	3	−15.05	−15.27	0.4572	0.4895
	6	−10.48	−15.42	0.4553	0.4629

observed compared to the previous period. Nevertheless, compared to the control, a decrease in this indicator of 5.9–13.7% was observed for PUU2 and PUU3 after 6 months of incubation, while for PUU1, relative elongation increased of 72.7%.

According to the DSC data, after incubation of PUU samples in BM 199, an increase in glass transition temperature (T_g) and a change in heat capacity (ΔC_p) at the second heating glass transition (Table 3) was observed, which correlates with the results of physical-mechanical tests (a decrease in strength and relative elongation at break was observed after incubation of PUUs in BM 199). To eliminate the influence of the thermal and mechanical history of the polymer material, two heating cycles were performed. The results of the second heating are the most reliable material characteristics.

After 6 months of incubation of PUUs in BM 199, T_g increased by 10.6–51.3%, and the value of ΔC_p increased by 17.5–46.5%.

During the biodegradation of PUUs in the model biological medium, an increase in T_g and ΔC_p was observed compared to the control, which can be explained as follows. In the process of biodegradation under the influence of the model medium, the breakdown of weaker (soft) segments of polyurethane-ureas may occur, leading to an increase in the proportion of hard segments, a decrease in the segmental mobility of macromolecular chains, and a decrease in the free volume. Thus, the increase in T_g and ΔC_p indicates structural changes, such as densification of the structure, restriction of segmental mobility, and enhancement of intermolecular interactions that occur during biodegradation in the biological medium.

Considering the obtained in vitro test results, PUUs with fragments of DADPh chain extender and grafted PVA-PEG copolymer demonstrate biodegradability and can be proposed as a polymer matrix for the preparation of biologically active polymeric materials for temporary medical applications.

Conclusions

The biodegradation capacity of PUUs with fragments of DADPh chain extender and grafted PVA-PEG copolymer *in vitro* was studied on the basis of changes in structure, physical-mechanical, and thermophysical properties under the influence of the model biological medium for 1, 3, and 6 months of incubation. It was found that in the model BM 199, the biodegradation processes of the studied PUUs occur, as evidenced by a reduction in strength and relative elongation at break, accompanied by chemical bond cleavage, changes in hydrogen interactions, and structural transformations of the polymer matrix.

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