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Structure and properties of polymer membranes based on polyelectrolyte complexes

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Using physicochemical and physicomechanical methods, the structure and properties of polymer membranes based on polyelectrolyte complexes chitosan-pectin, chitosan-alginate, chitosan-CMC were investigated. The obtained complexes were studied for the sorption of Cu^{2+} and Ag^{+} cations from aqueous solutions. The formation of polyelectrolyte complexes was confirmed using the IR spectroscopy method. It was found that the obtained chitosan-pectin complexes are characterized by a semi-crystalline structure, while the chitosan-alginate and chitosan-CMC polymer systems exhibit an amorphous structure. The degree of crystallinity of the chitosan-pectin PEC is 73 %. It was found that the chitosan-pectin polymer system has a higher sorption capacity for Cu^{2+} and Ag^{+} cations than other complexes.

Keywords: polymer membranes, polyelectrolyte complexes, structure, thermal stability, thermomechanical properties, sorption capacity

Структура та властивості полімерних мембран на основі поліелектролітних комплексів. *В.Л. Демченко, D. Zeng, М.В. Юрженко, Н.П. Рибальченко, В.Б. Долгошей, В.О. Овсянкіна, Т.В. Рибальченко, О.М. Кислиця*

За допомогою фізико-хімічних та фізико-механічних методів було досліджено структуру та властивості полімерних мембран на основі поліелектролітних комплексів хітозан-пектин, хітозан-альгінат, хітозан-КМЦ. Отримані комплекси були досліджені щодо сорбції катіонів Cu^{2+} та Ag^{+} із водних розчинів. За допомогою методу ІЧ-спектроскопії було підтверджено утворення поліелектролітних комплексів. Було встановлено, що отримані комплекси хітозан-пектин характеризуються напівкристалічною структурою, тоді як полімерні системи хітозан-альгінат та хітозан-КМЦ проявляють аморфну структуру. Ступінь кристалічності ПЕК хітозан-пектин становить 73 %. Встановлено, що полімерна система хітозан-пектин має вищу сорбційну ємність щодо катіонів Cu^{2+} та Ag^{+} порівняно з іншими комплексами.

1. Introduction

Polymeric materials are of significant scientific and practical interest, as they are widely used in modern technology and medicine [1-3]. Polymers have unique physicochemical, mechanical, and biological properties [4–9].

In modern life, the problem of ensuring access to high-quality water remains relevant. This is due to global challenges, such as increasing industrial production, increasing demand, climate change and dwindling supplies of drinking water. Membrane water purification and secondary extraction technologies, as a key method of water treatment, require modernization of production to meet modern needs[10].

Most often, such pollutants as heavy metals, synthetic dyes and residues of petrochemical products are found in water resources. In addition, in recent years, there has been increasing attention to micropollutants, particularly from pharmaceuticals and personal care products, due to increased awareness of their impact on the environment, public health, and the economy [11–15]. Systematic discharge of wastewater containing significant concentrations of heavy metals such as As, Pb, Cd, Cr, Cu, Ni, Hg, and Zn poses a serious threat to humans and aquatic ecosystems [16–20].

In this regard, the development of membranes for water purification based on polymeric materials is an important and urgent task. Polyelectrolyte complexes (PECs) are often used to develop effective polymer membranes. PECs obtained on the basis of polysaccharides deserve special attention, since they are considered as promising materials for creating membranes for ecological purposes. Their advantages are biocompatibility, the ability to selectively sorb ions of heavy metals, as well as the ability to adjust the structure by varying the complexation conditions [21]. At the same time, the issue of the relationship between the chemical structure of polyelectrolytes, the supramolecular organization of PEC and their functional properties remains insufficiently investigated.

The properties of polymer membranes based on polyelectrolyte complexes are determined by a set of factors, among which the chemical nature of oppositely charged polyelectrolytes plays an important role, in particular, their molecular weight, the type of ionogenic groups, the flexibility of the polymer chain, and the charge density. The conditions for formation of complexes, namely the concentration of cationic and anionic polyelectrolytes before the moment of mixing, the pH value, the temperature of the reaction medium, as well as the ratio of components and the order of their introduction into the system, have an equally significant influence. Depending on the combination of the specified parameters, different types of polyelectrolyte complexes can be formed, in particular soluble, colloidally stable and coacervate. In addition, according to the molar ratio of cationic and anionic polyelectrolytes, PECs are divided into stoichiometric and non-stoichiometric. The increased interest of researchers in polymer membranes on polyelectrolyte complexes is due primarily to their practical significance [22-24].

The purpose of this work is to study the structure and properties of polymer membranes based on polyelectrolyte complexes of oppositely charged polyelectrolytes with different chemical composition.

2. Experimental

Anionic and cationic polyelectrolytes of different chemical composition were used to form polymer membranes based on polyelectrolyte complexes. Chitosan-pectin, chitosan-alginate, chitosan-CMC polymer membranes were formed by mixing aqueous solutions of oppositely charged polyelectrolytes in a given molar ratio at $T = 20\pm2$ °C.

Copper and silver salts were used to study the sorption capacity of the obtained samples. The interaction between the components of polymer membranes was studied using FTIR-spectroscopy in the membrane lumen in the frequency range $\nu = 500 \div 4000$ cm^{-1}.

The structure of the membrane materials was studied by the method of wide-angle X-ray diffraction on an XRD-7000 diffractometer (Shimadzu, Japan); the X-ray optical scheme on the lumen used CuK_α radiation ($\lambda = 1.54$ Å) monochromatized by a Ni filter at a temperature of $T = 20\pm2$ °C. The automatic step-by-step scanning was carried out in the scattering angle range from 3 to 40 degrees in the mode U = 30 kB, I = 30 mA, the exposure time was 5 s.

The thermal stability of the samples was investigated using a TGA 55 device in an atmosphere of dry air in the temperature range from 20 to 700 °C with a linear heating rate of 20 °C/min. The thermomechanical behavior of the samples was studied by the penetration method in the temperature range from 0 to +300 °C.

3. Results and discussion

Fig. 1 presents the IR spectra of polysaccharides and polymer membranes based on them. In the IR spectrum of pectin and chitosan, there are characteristic absorption bands in the frequency range from 1030 to 1180 cm^{-1}, which are associated with the vibrations of C–O groups of glucopyranose fragments (curves 1, 2). In the frequency range from 2500 to 3800 cm^{-1}, there are absorption bands associated with the vibrations of –OH and –CH groups. In the spectra of pectin there are absorption bands of C=O groups with a band of 1730 cm^{-1}, which belong to carboxyl groups. In the spectrum of the chitosan sample, there is a band at a frequency of 1650 cm^{-1}, which is attributed to C=O vibrations of the amide group located in the chitosan links. The band at a frequency of 1600 cm^{-1} is due to NH vibrations of the amino and amide groups. The spectrum of polyelectrolyte complexes has two bands in the frequency range of 1415–1425 cm^{-1} and 1615–1625 cm^{-1}, which can be attributed to symmetric and asymmetric deformation vibrations of ionized carboxyl groups; this confirms the formation of n complexes (curve 3) [25].

Analysis of wide-angle X-ray diffraction patterns of the studied samples showed that pectin and Na-CMC are characterized by an amorphous structure (Fig. 2, curves 1, 2), while sodium alginate and chitosan exhibit a semicrystalline structure (curves 3, 4).

Analysis of structural features of polymer membranes based on polyelectrolyte complexes showed that chitosan-pectin and chitosan-alginate are characterized by a semi-crystalline structure, while the polymer system chitosan-CMC exhibits an amorphous structure (Fig. 3, curves 1–3). It was found that the structure of polymer membrane complexes differs from the structure of individual anionic and cationic polyelectrolytes, which is evidence of the formation of polyelectrolyte complexes.

The average distance between macromolecular chains in amorphous and semicrystalline polymers was determined according to the Wulff –Bragg equation [26, 27]:

$$d = n\lambda(2\sin\theta_m)^{-1},$$

where n is the ordinal number of the diffraction maximum (in studies of all types of polymers it is equal to one, since the structure of high-molecular compounds has a relaxation character); $2\theta_m$ is the angular position of the diffraction maximum on the scattering profile.

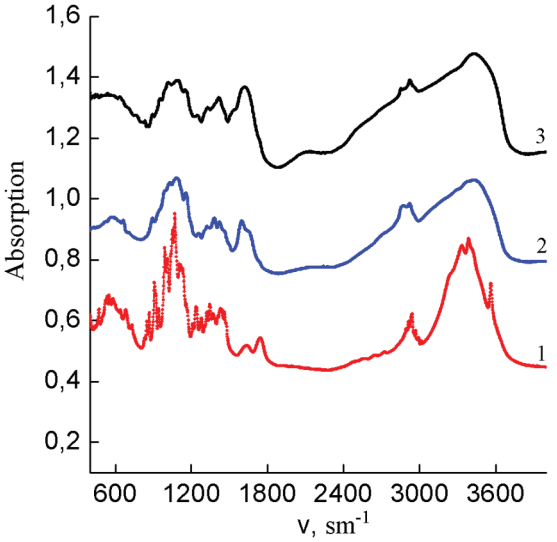

Fig. 1. IR spectra of samples of pectin (1), chitosan (2) and PEC chitosan–pectin (3)

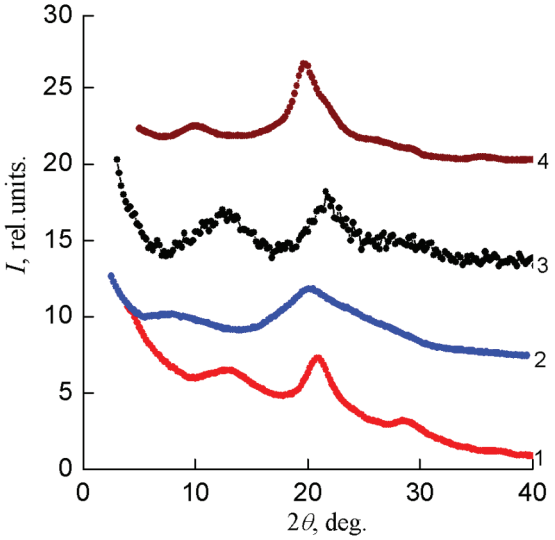

Fig. 2. Wide-angle X-ray diffraction patterns of pectin (1), Na-CMC (2), sodium alginate (3), chitosan (4).

According to the Wulff-Bragg equation, the average value of the short-range order period of fragments of macromolecular chains of oppositely charged polyelectrolytes in polymer membranes is the average Bragg distance between the macromolecular chains of oppositely charged polyelectrolytes in the polymer membranes. For chitosan-pectin samples, this distance is greatest, 4.2 Å, while for chitosan-alginate samples, it is smallest, 3.0 Å. This is due to the chemical structure and interaction characteristics of oppositely charged polyelectrolytes in polymer membranes (Table 1).

The relative level of crystallinity (X_{cr}) of semicrystalline polymers was estimated according to the Mathews method [28]:

Table 1. Structural and physicochemical parameters of the studied polymer systems

Sample	d, Å (WAXS)	X_{cr}, % (WAXS)	$T_{g(PEC)}$,°C (TMA)	ε, % (T =120 °C) (TMA)
chitosan– pectin	4.2	73	51.5	14.4
chitosan–alginate	3.0	-	75	11.5
chitosan– CMC	3.9	-	73	15.0

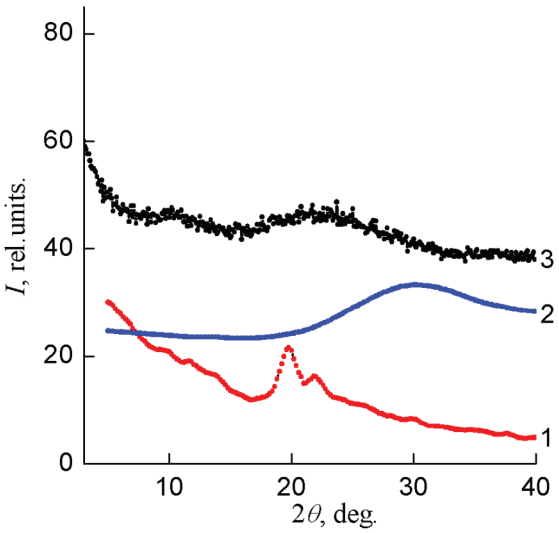

Fig. 3. Wide-angle X-ray diffraction patterns of polyelectrolyte complexes chitosan–pectin (1), chitosan–alginate (2), chitosan–CMC (3).

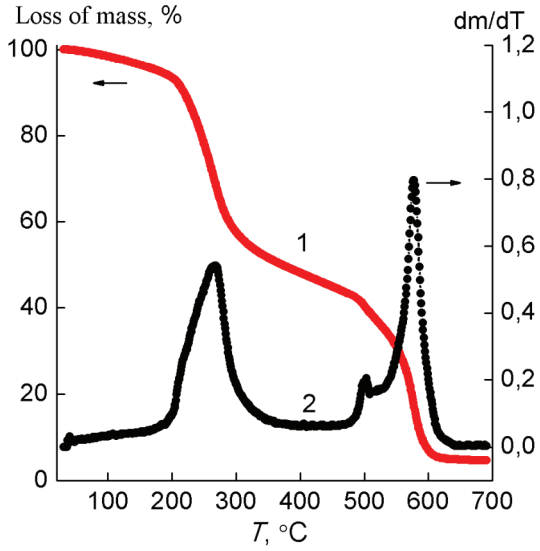

Fig. 4. TGA (1) and DTGA (2) curves for polymer systems chitosan–pectin.

$$X_{cr} = Q_{cr}(Q_{cr} + Q_{am})^{-1}\times 100,$$

where Q_{cr} is the area of diffraction maxima that characterize the crystalline structure of the polymer; $Q_{cr} + Q_{am}$ is the area of the entire diffraction spectrum in the interval of scattering angles ($2\theta_1 \div 2\theta_2$), in which the semicrystalline structure of the polymer is manifested.

The evaluation of the relative level of crystallinity of polymer membranes showed that the X_{cr} for chitosan-pectin samples is 73% (Table 1).

The mass loss of polyelectrolyte complexes was studied by the thermogravimetric method. Analysis of the thermogravimetric curves of pectin-chitosan samples showed that in the temperature range from 30 to 200 °C the water contained in the polymer membranes evaporates (Fig. 4). Thermal destruction of the original chitosan and pectin polymers begins at temperatures of 244 °C and 220 °C, respectively. Earlier, it was established that the temperature of the onset of destruction for the studied chitosan-pectin samples is 217 °C. In general, the thermal stability of the studied polymer membranes is determined by the thermal stability of individual polymers. It should be noted that the decomposition of polymer membranes at different stages differs from the destruction of individual polyelectrolytes, which is evidence of the formation of complexes (Fig. 4) [25].

Studies of the thermomechanical behavior of the samples showed that the glass transition temperature for chitosan–alginate and chitosan–CMC polymer membranes is higher than that of chitosan–pectin polymer systems (Fig. 5, Table 1). The higher values of the glass transition temperature for the chitosan–alginate and chitosan–CMC samples indicate the limitation of the mobility of macromolecular chains, which may be associated with the formation of a more rigid three-dimensional structure. This makes such materials promising for use under conditions of elevated temperatures.

Previously, using the example of the chitosan-pectin polymer system, the dependence of the experimental value of $T_{g(PEC)}$ (Table 1) and the total glass transition

Table 2. Sorption capacity of the studied films

Polyelectrolyte complex	A, mmol/g	
	Cu^{2+}	Ag^{+}
chitosan–pectin	2.5	3.9
chitosan–alginate	1.3	3.2
chitosan–CMC	1.6	3.3

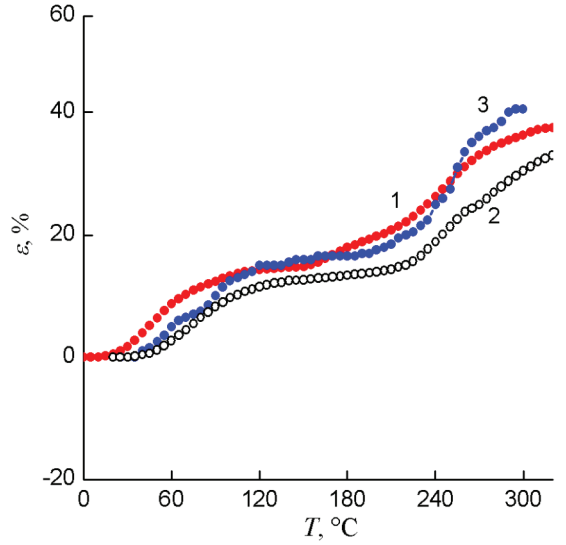

Fig. 5. Thermomechanical curves of polyelectrolyte complexes chitosan–pectin (1), chitosan–alginate (2), chitosan–CMC (3)

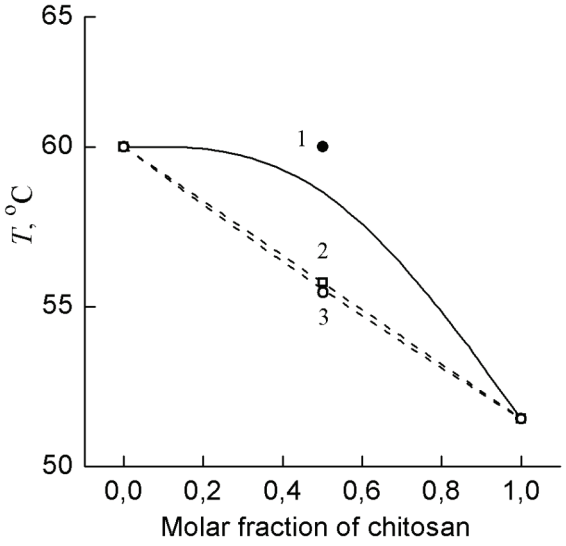

Fig. 6. Concentration dependence of experimental values of $T_{g(PEC)}$ (1) and calculated from the Wood (2) or Fox (3) equations of $T^*_{g(PEC)}$ for polyelectrolyte complexes chitosan–pectin

temperature of anionic and cationic polyelectrolytes $T^*_{g(PEC)}$ on concentration was constructed. $T^*_{g(PEC)}$ was calculated using the Wood or Fox equations $T^*_{g(PEC)} = w_1 T_{C1} + w_2 T_{C2}$ or $T^{*-1}_{g(PEC)} = w_1 T_{C1}^{-1} + w_2 T_{C2}^{-1}$ (w_1 and w_2 are the mole fractions of oppositely charged polyelectrolytes, ($w_1 + w_2 = 1$), T_{C1} and T_{C2} are the glass transition temperatures of PEC components). The pectin–chitosan polymer system demonstrated a positive deviation of the experimental concentration dependence of $T_{g(PEC)}$ compared to the $T^*_{g(PEC)}$ graphs calculated according to the equations of Wood or Fox based on the values of the initial polyelectrolytes; this indicates the formation of complexes (Fig. 6) [29].

4. Conclusions

The structural features, thermal, thermomechanical and sorption properties of chitosan-pectin, chitosan-alginate, chitosan-CMC polymer membranes were investigated and analyzed. The formation of polymer membranes based on polyelectrolyte complexes was confirmed by IR spectroscopy. Analysis of wide-angle X-ray diffraction patterns of the studied polymer membranes showed that the obtained chitosan-pectin complexes have a semi-crystalline structure, while the chitosan-alginate and chitosan-CMC polymer systems are characterized by an amorphous structure. The degree of crystallinity of chitosan-pectin polymer membranes is 73%. It was established that the chitosan-pectin polymer system has a higher sorption capacity for Cu^{2+} and Ag^{+} cations compared to other chitosan-alginate and chitosan-CMC complexes. In particular, for chitosan-pectin samples with Cu^{2+} A=2.5 mmol/g, and with Ag^{+} A=3.9 mmol/g. The results obtained confirm the prospects of using polyelectrolyte complexes based on polysaccharides as effective materials for creating polymer membranes of ecological purpose for wastewater filtration.

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References

1. V. Demchenko, V. Shtompel', S. Riabov, et al., *Nanoscale Research Letters*, **10**, 479–485 (2015).
2. O.O. Sapronov, A.V. Buketov, D.O. Zinchenko, et al., *Composites: Mechanics, Computations, Applications. An International Journal*, **8(1)**, 47-65 (2017).
3. V. Demchenko, S. Riabov, and V.Shtompel', *Nanoscale Research Letters*, **12**, 235 (2017).
4. W. Sikorska, M. Zięba, M. Musioł, et al., *Polymers*, **12 (5)**, 1167–1181 (2020).
5. A. Buketov, S. Smetankin, P. Maruschak, et al., *Transport*, **35(6)**, 679-690 (2020).
6. E.A. Lysenkov, V.V. Klepko, V.M. Golovanets, et al., *Ukrainian Journal Physics*, **59 (9)**, 906–914 (2014).
7. A. Buketov, O. Sapronov, K. Klevtsov, et al., *Polymers*, **15**, 3449 (2023).
8. P.D. Stukhlyak, M.M. Mytnyk, V.O. Orlov, *Materials Science*, **37(1)**, 80-86 (2001).
9. P.D. Stukhlyak, K.M. Moroz, *Materials Science*, **46(4)**, 455-463 (2011).
10. S. Aziz, A.R. Mazhar, A. Ubaid, et al., *Appl Water Sci*, **14**, 169 (2024).
11. K.O. Badmus, J.O. Tijani, E. Massima, et al., *Environ. Sci. Pollut. Res. Int.*, **25**, 7299–7314 (2018).
12. P. Vazquez-Roig, V. Andreu, C. Blasco, et al., *Sci. Total Environ.*, **440**, 24–32 (2012).
13. D. Zhang, R.M. Gersberg, W.J. Ng, et al., *Environ. Pollut.*, **184**, 620–639 (2014).
14. J. Rivera-Utrilla, M. Sanchez-Polo, M.A. Ferro-García, et al., *Chemosphere*, **93**, 1268–1287 (2013)
15. Q. Sui, X. Cao, S. Lu, et al., *Emerg. Contamin.*, **1**, 14–24 (2015).
16. U. Upadhyay, I. Sreedhar, S.A. Singh, et al., *Carbohydr. Polym.*, **251**, 117000 (2021).
17. T. Mahmood, M.T. Saddique, A. Naeem, et al., *Chem. Eng. J.*, **171**, 935–940 (2011).
18. W. Wei, S. Kim, M.-H. Song, et al., *J. Taiwan Inst. Chem. Eng.*, **57**, 104–110 (2015).
19. C. Li, H. Duan, X. Wang, et al., *Chem. Eng. J.*, **262**, 250–259 (2015).
20. G.K. Kinuthia, V. Ngure, D. Beti, et al., *Sci. Rep.*, **10**, 8434 (2020).
21. L. Fu, Z. Wang, A. Dhall, et al., *Carbohydrate Polymers.*, **273**, 118558 (2021).
22. S.E. Herrera, M.L. Agazzi, E. Apuzzo, et al., *Soft Matter*, 19, 2013-2041 (2023).
23. D.K. Danso, M.M. Alhajeri, J. Bicerano, et al., *Applied Energy*, 392, 125966 (2025).
24. I. Dogaris, I. Pylypchuk, G. Henriksson, et al., *Drug Deliv. and Transl. Res.,* **14**, 3452–3466 (2024).
25. V. Demchenko, S. Riabov, S. Sinelnikov, et al., *Carbohydrate Polymers*. **242**, 116431, (2020).
26. V. Demchenko, P. Zaremba, N. Rybalchenko, et al., *Scientific Reports*, **15 (1)**, 35087 (2025).
27. V. Demchenko, Ye. Mamunya, I. Sytnyk, et al., *ACS Applied Materials & Interfaces*, **17 (38)**, 53312-53326 (2025).
28. A. Galchun, N. Korab, V. Kondratenko, et al., *Nanoscale Research Letters*, **10**, 138–143 (2015).
29. V.L. Demchenko, Nanocomposites based on polyelectrolyte complexes of polysaccharides and nanoparticles of copper and silver: dissertation ... Dr. of Chemical Sciences: 02.00.06 / V. L. Demchenko. Kyiv. 2021. 324 p.