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# SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITES BASED ON POLYLACTIDE/SILVER NANOPARTICLES, OBTAINED BY THERMOCHEMICAL REDUCTION OF $Ag^+$ IONS BY NATURAL OR SYNTHETIC POLYMERS

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*The addition of silver ions or nanoparticles to impart antimicrobial properties to polymeric or other materials is a widely used method. However, it should be noted that the antiviral and antimicrobial effect of silver nanoparticles that come into contact with the environment, associated with their size, with a decrease in the size of nanoparticles, their effectiveness increases sharply. In the present work, we used a biodegradable polymer polylactide (PLA), which is obtained by condensation of lactic acid or ring-opening polymerization of lactide. These studies will further contribute to the development of new safe materials, in particular for food packaging, which is undoubtedly an urgent problem.*

*The work aims is to obtain the silver-containing polymer composites based on polylactide by thermochemical reduction of $Ag^+$ ions using natural (chitosan) and synthetic (polyethyleneimine (PEI)) polymers and to study the structure, morphology, thermomechanical and antimicrobial properties of the obtained nanocomposites.*

*Thermochemical reduction of $Ag^+$ ions in the bulk of polymer films, containing PLA, silver palmitate as a precursor of Ag NP and reducing agent (PEI or chitosan), has been performed by keeping them at 100–170 °C within 5 minutes. The polymeric film composites, cast from chloroform solution, were heated in an oven using precise thermal regulator VRT-3. As a result of reduction, the films get attained silver color, the Ag content in the bulk of films varied from 1 to 4 wt. %, and the thickness of the films was 110 μm. Structure, morphology, thermomechanical and antimicrobial properties of two types of nanocomposites – PLA-Ag-PEI and PLA-Ag-chitosan, formed by the thermochemical reduction of $Ag^+$ in polymer films have been studied using wide-angle X-ray scattering (WAXS) (a DRON-4-07 diffractometer), a transmission electron microscope (TEM) (JEM-1230 JEOL, Japan), and thermomechanical analysis (a UIP-70M device). Antimicrobial activity of the obtained nanocomposites was investigated applying reference strains of opportunistic bacteria Staphylococcus aureus and Escherichia coli. It has been found that thermochemical reduction of $Ag^+$ ions in the bulk of polymer films, when using synthetic or natural polymers (PEI or chitosan) as a reducing and stabilizing agent of silver nanoparticles occurs at 160 °C during 5 minutes. It has been found that the average size of Ag nanoparticles in the polymeric matrix is equal to ~ 7 and ~ 4 nm for PEI and chitosan, respectively. It has been shown that PLA-Ag-chitosan nanocomposites have much higher antimicrobial activity against S. aureus and E. coli strains as compared to PLA-Ag-PEI nanocomposites.*

***Keywords**: polylactide, polyethyleneimine, chitosan, silver-containing nanocomposite, structure, morphology, thermomechanical properties, antimicrobial activity*

## INTRODUCTION

In the last decade, interest in studying the structural organization and properties of polymer nanocomposites, in particular filled with nanosized particles of metals or their oxides, has been growing rapidly [1]. Such materials are attractive both for basic science, which studies the nature of the influence of particle size at the nanoscale on their chemical activity, structural organization, and a set of properties and for applied science, whit task being to implement nanocomposites in practice [2].

Silver nanoparticles have valuable optical properties, high catalytic and antimicrobial activity. When polymer matrices are filled with silver nanoparticles, they acquire new extremely valuable properties and have potential application in microelectronics, optics, bio-diagnostics, catalysis, optoelectronics, nano-photonics, as well as effective antibacterial and

antiviral drugs in medicine, pharmacology, biochemistry [3].

The formation of nanoparticles by reduction of metal ions is a universal method of controlled synthesis of metal-containing polymer nanocomposites.

Currently, the following methods of Ag-containing nanocomposites production are widely applied: chemical [4, 5], chemical-radiation [5–7], and thermochemical reduction of $Ag^+$ ions in interpolyelectrolyte-metal complexes [8]. The most widely employed chemical reductants are $NaBH_4$ [9], dimethylformamide [10], and hydrazine [11]. Although such approach is simple and effective for getting nanocomposites with controlled structure and properties, the biological toxicity and the environmental hazard of the residual reducing agents are considered as a problem. The principal advantage of the radiation-chemical reduction of metal ions is that there is no need to introduce chemical reductants into reaction, so allowing for nanoparticles to be obtained without admixtures [5–7]. However, this method requires application of special equipment for radiation generating. Recently, the "green" synthesis of silver nanoparticles such as thermochemical reduction of $Ag^+$ ions in polymer films by heating them to a predetermined temperature has been in significant demand. Herewith, the polymer matrix serves as a reducing agent and stabilizer of nanoparticles as well. In comparison with conventional methods, this method is much faster, cleaner and environmentally efficient [8].

So, the aim of the present work was to study structure, morphology, thermomechanical and antimicrobial properties of Ag-containing nanocomposites based on PLA and formed by thermochemical reduction of $Ag^+$ ions by natural (chitosan) and synthetic (PEI) polymers.

## EXPERIMENTAL

The following agents have been used for the production of polymeric systems based on polylactide and silver nanoparticles: PLA filament (MonoFilament, Ukraine, with an average molar mass $M_w = 274000$ g/mol), synthetic polyelectrolyte anhydrous branched polyethyleneimine (PEI) (Aldrich) with $M_n = 1\times10^4$ and $M_w = 2.5\times10^4$ g/mol, natural polyelectrolyte chitosan (low molecular weight, Aldrich). Silver palmitate (AgPalm) was synthesized according to the method described in [12].

***PLA-AgPalm-PEI polymer systems.*** Required quantity of AgPalm was added to PLA solution in chloroform (with vigorous stirring by magnetic stirrer), then the temperature was increased to 60 °C, and then PEI solution in chloroform in small portions was added (molar ratio $NH_2 : Ag^+ = 1 : 1$). The mixture was stirred at 60 °C within 30 minutes, and then it was casted on a Teflon surface. After drying at room temperature, a red-brown colored transparent film has been prepared.

***PLA-AgPalm-chitosan polymer systems*** were obtained in the same way, but instead of PEI solution, 2 wt. % aqueous solution of chitosan in acetic acid was added. After drying at room temperature a white non-transparent film has been obtained. Required quantity of AgPalm was added to PLA solution in chloroform (with vigorous stirring by magnetic stirrer), then the temperature was increased to 60 °C, and then 2 wt. % water solution of chitosan in acetic acid was added (molar ratio $NH_2 : Ag^+ = 1 : 1$). The mixture was mixed at 60 °C within 30 minutes, and then it was cast onto Teflon surface. After drying at room temperature, a white non-transparent film was made.

Thermochemical reduction of $Ag^+$ ions in the bulk of polymer films has been performed by keeping them at 100–170 °C within 5 minutes. The specimens were heated in an oven using precise thermal regulator VRT-3. Temperature regulation precision was ±0.5 °C.

As a result of reduction the films get attained silver color, Ag content in the bulk of films varied from 1 to 4 wt. %, and the thickness of the films was 110 μm.

The structure of nanocomposites based on PLA and Ag particles has been investigated by wide-angle X-ray diffraction using a DRON-4-07 diffractometer, which X-ray optical scheme was used at a "pass" primary-beam radiation through samples. X-ray diffraction studies were performed at $T = 20\pm2$ °C with Cu$K_\alpha$ monochromated radiation and Ni-filter. The size of the Ag nanoparticles and their distribution in the polymer matrix were examined using a transmission electron microscope JEM-1230 (JEOL, Japan) at a resolution of 0.2 nm. Thermomechanical studies of the polymer systems were conducted using the penetration method with uniaxial constant load

($\sigma$ = 0.5 MPa) by a UIP-70M device. Linear heating of the samples was performed at a rate of 2.5 °C/min in the temperature range from +20 to +170 °C. Antimicrobial activity of the Ag-containing nanocomposites was investigated applying reference strains of opportunistic bacteria *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* ATCC 35218 (as model gram-positive and gram-negative bacteria) [13].

## RESULTS AND DISCUSSION

Analysis of the wide-angle X-ray diffraction patterns has shown that the initial PLA, formed at room temperature in chloroform solution, has an amorphous-crystalline structure. This is confirmed by the presence (Fig. 1, curve *1*) of multiple diffraction maxima of discrete type on the background of imaginary amorphous halo with the peak at $2\theta_m \sim 15.1°$ on the diffraction pattern. An average value of *d* period of close location of PLA macromolecular chain fragments, according to Bragg equation [14]:

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

where $\lambda$ is the wavelength of characteristic X-radiation ($\lambda$ = 1.54 Å for Cu$K_\alpha$-radiation), equal to 5.6 Å.

Relative crystallinity level $X_{кр}$ of PLA was calculated according to Mathews method [15]:

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

where $Q_{cr}$ is the square of diffraction maximuma which characterize the crystalline structure of polymer; $Q_{cr} + Q_{am}$ is the total square of diffraction pattern in the interval of dispersion ($2\theta_1 \div 2\theta_2$), where the amorphous-crystalline structure of polymer is observed. Calculations have shown that $X_{кр}$ value is approximately equal to 62.5 %.

The evaluation of effective size of crystallites *L* was calculated according to the Scherrer equation [16]

$$L = K\lambda(\beta\cos\theta_m)^{-1},$$

where *K* is a constant depending on the shape of crystallites (if the shape is unknown then *K* = 0.9), and $\beta$ is the angular semi-width (full width at half maximum) of the diffraction maximum of discrete type; such evaluation has shown that average value of $L \approx 6.9$ nm.

Using PEI as the reductant and stabilizer of nanoparticles during the PLA-AgPalm-PEI preparation at 60 °C from the solution, the partial reduction of $Ag^+$ ions in the polymeric matrix was observed. New diffraction maximum at $2\theta_m$~46,2° in the X-ray pattern of this specimen could be assigned to the crystallographic plane of Miller index (200) of the face-centered cubic (fcc) lattice of Ag.

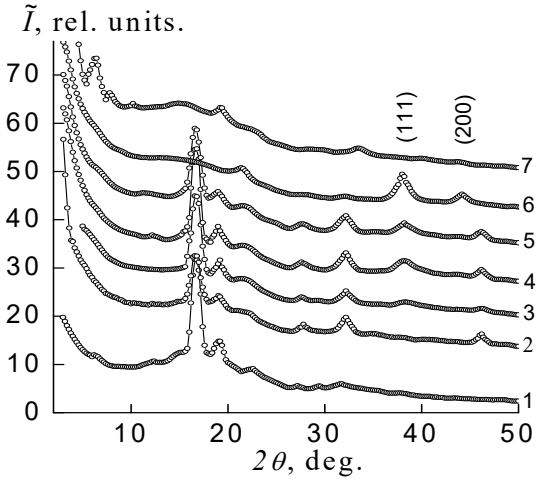



**Fig. 1.** Wide-angle X-ray diffractograms of (*1*) the PLA; (*2*) the PLA-AgPalm-PEI; and (*3–7*) the PLA-4%Ag-PEI nanocomposites, obtained at temperatures: (*3*) 100, (*4*) 130, (*5*) 150, (*6*) 160, (*7*) 170 °C during 5 minutes

This is approved by the presence of diffraction maximum at $2\theta_m$~46,2° in the X-ray pattern of this specimen, it indicates atomic planes of Ag crystalline structure with Miller indices (200) (Fig. 1, curve *2*). In diffraction pattern of the PLA-Ag-PEI nanocomposite, affected by 100°C, two low-intensive diffraction maxima appear at $2\theta_m$~38.4° and 46.2°. They correspond to the crystallographic planes of Miller indices (111) and (200) of the fcc lattice of Ag, respectively. It proves the presence of metallic silver in the nanocomposites (curve *3*). Further, reduction temperature for the $Ag^+$ ions was step-by-step upraised to 160 °C that causes the increase of the Ag nanoparticles content in the PLA-Ag-PEI nanocomposites. It validates by the growth of intensity of respective diffraction maxima characterizing the structure of metallic silver (curves *4–6*). As the result of the nanocomposites formation at 170 °C no Ag nanoparticles were detected (curve *7*). Such an effect may be caused by the melting of PLA preventing $Ag^+$ ions reduction.

When applying chitosan during the PLA-AgPalm-Chitosan formation at 60 °C from the solution, the reduction of the $Ag^+$ ions in the

nanocomposites did not occur (Fig. 2, curve *2*). One can see from the X-ray diffraction patterns of the silver-containing nanocomposites based on PLA and chitosan, that the thermochemical reduction of the $Ag^+$ ions takes place only after heating of the PLA-AgPalm-chitosan at 160 °C (see Fig. 2, curves *3–4*). When the temperature increases up to 170 °C, a worse reduction in the polymer matrix is observed (curve *5*); that is also caused by the melting of PLA. Hence, according to the wide-angle X-ray scattering data, we concluded that the optimal parameters for the development of Ag-containing nanocomposites based on PLA and synthetic or natural polymers (PEI or chitosan) are: 160 °C followed by 5 min duration.

In previous work [17] we have proposed the explanation of the mechanism of thermo-chemical reduction: in brief, it is in the transfer of electron of the nitrogen atoms of PEI or chitosan' amino groups to the $Ag^+$ ions at 160 °C [18].

The effective size of crystallites of the Ag nanoparticles in the volume of nanocomposites based on PEI or chitosan affected by 160 °C temperature within 5 minutes is $L \sim 4.7$ nm.

It was found that while heating of PLA-AgPalm-PEI and PLA-AgPalm-chitosan polymer films from 60 to 170 °C with the further formation of the Ag-containing nanocomposites, the PLA matrix crystallinity degree is varying. With the temperature increase up to 160 °C $X_{cr}$ is growing up, and at $T > 160$ °C it is sharply decreasing. This could be explained by the melting of the PLA crystalline phase (Table 1).

Monitoring of the wide-angle X-ray diffractograms of the native PLA has revealed that it has an amorphous structure in the form of filament, and the PLA formed from the chloroform solution at room temperature demonstrates an amorphous-crystalline structure (Fig. 3, curves *1, 2*). During 5 minutes of staying of the PLA at 100 °C the crystallinity degree increases from 62.5 to 81.5 %. At the same time, when keeping the PLA at 160 °C, its structure becomes almost completely amorphous due to low-speed crystallization (curves *3–4*).

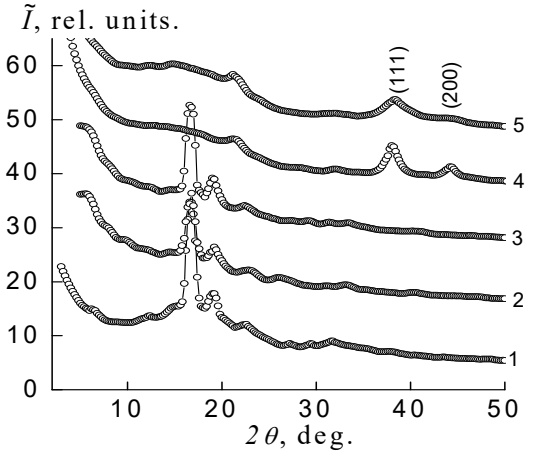



**Fig. 2.** Wide-angle X-ray diffractograms of (*1*) the PLA; (*2*) the PLA-AgPalm-chitosan; and (*3–5*) the PLA-4%Ag-chitosan nanocomposites, obtained at temperatures: (*3*) 150, (*4*) 160, (*5*) 170 °C during 5 minutes

**Table 1.** Structural parameters of the studied polymeric systems

| Specimen | Heating temperature, °C | Heating time, minutes | $X_{cr}$, % | $L$, nm |
|---|---|---|---|---|
| PLA | – | – | 62.5 | 6.9 |
| PLA | 100±0.5 | 5 | 81.5 | 6.3 |
| PLA | 160±0.5 | 5 | – | – |
| PLA-PEI-4%Ag | 60±0.5 | 30 | 61.5 | 6.31 |
| PLA-PEI-4%Ag | 100±0.5 | 5 | 72.7 | 6.31 |
| PLA-PEI-4%Ag | 130±0.5 | 5 | 80.0 | 6.31 |
| PLA-PEI-4%Ag | 150±0.5 | 5 | 75.0 | 5.6 |
| PLA-PEI-4%Ag | 160±0.5 | 5 | – | – |
| PLA-chitosan-4%Ag | 60±0.5 | 30 | 80.0 | 6.88 |
| PLA-chitosan-4%Ag | 150±0.5 | 5 | 83.0 | 6.88 |
| PLA-chitosan-4%Ag | 160±0.5 | 5 | – | – |

Transformation of the polymer systems based on PLA, Ag palmitate and PEI or chitosan into the Ag-containing nanocomposites is acknowledged by the TEM data (Fig. 4 *a*, *b*).

Evaluation of the microphotographs shows that the average size of the Ag nanoparticles in the polymer matrix, when using PEI, is equal to 6.7 nm with a broad size distribution, but while involving chitosan the average size is smaller (4.2 nm) in a narrow range.

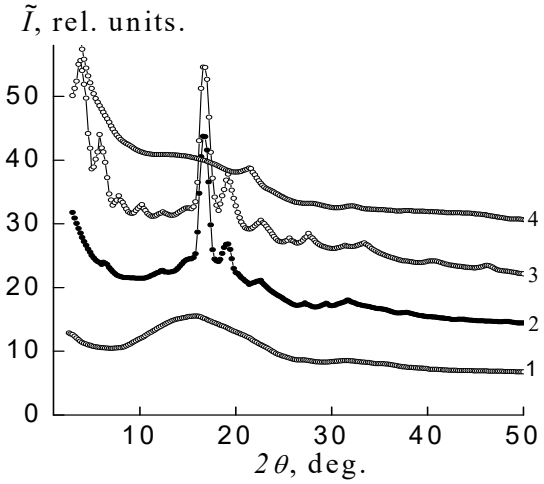
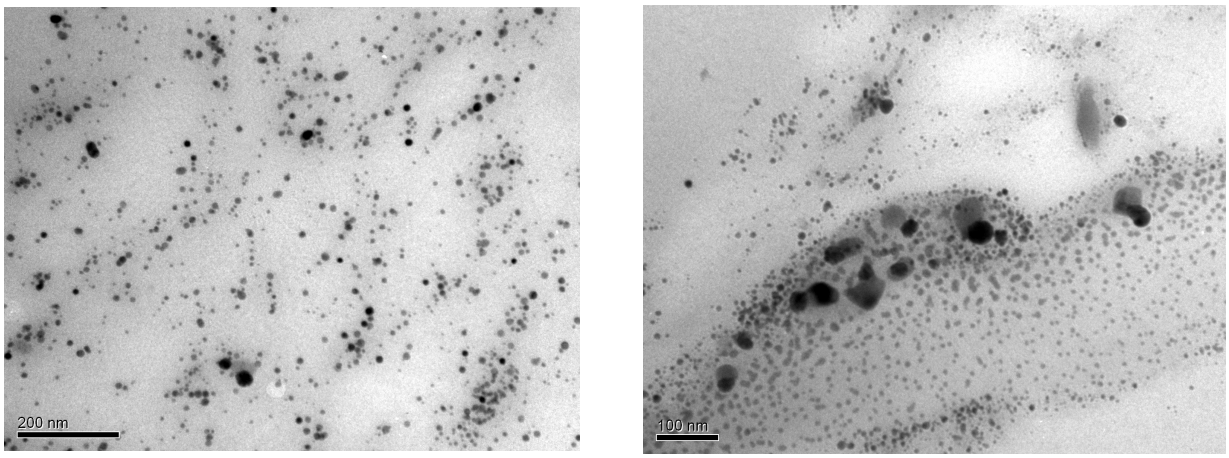



**Fig. 3.** Wide-angle X-ray diffractograms of (*1*) PLA filament; (*2*) the PLA films formed from the solution and the PLA films obtained at (3) 100 °C and (4) 160 °C during 5 minutes




*a* *b*

**Fig. 4.** TEM images of PLA-4 %Ag-PEI (*a*) and PLA-4%Ag-chitosan (*b*) nanocomposites obtained by thermochemical reduction of $Ag^+$ ions in the polymer films at $T$ = 160 °C during 5 minutes

It becomes clear from the microphotographs that during $Ag^+$ ions reduction both with PEI and chitosan, a significant portion of the silver nanoparticles is more or less uniformly distributed in the polymer matrix (Fig. 4 *a*, *b*).

***Thermomechanical behavior of the polymer nanocomposites.*** Thermomechanical behavior of the Ag-containing nanocomposites has been tested simultaneously with the investigation of their structural organization and morphology.

On the thermomechanical curves of the PLA-Ag-PEI and the PLA-Ag-chitosan nanocomposites with the Ag nanoparticles content between 1 and 4 wt. %, in the temperature range between 20 and 90 °C, and between 155 and 170 °C one can detect glass-transition temperature and flow transition (Fig. 5 *a*, *b*). The Ag-containing nanocomposites based on PLA and chitosan are characterized with a much higher relative deformation index

comparing to the nanocomposites based on PLA and PEI (see Fig. 5 *a*, *b* and Table 2).

From the analysis of thermomechanical curves of the polymer nanocomposites based on PLA and PEI or chitosan, it is clear that with the growing of the Ag nanoparticles content, a tendency is seen of subsiding of the glass transition temperature of the polymer matrix (Table 2). From the similar analysis of thermomechanical curves of the neat PLA formed from chloroform solution at room temperature, and of the films heated to 100 and 160 °C becomes evident the higher temperature of specimen heating the higher its glass transition temperature (see Fig. 5 *c* and Table 2).

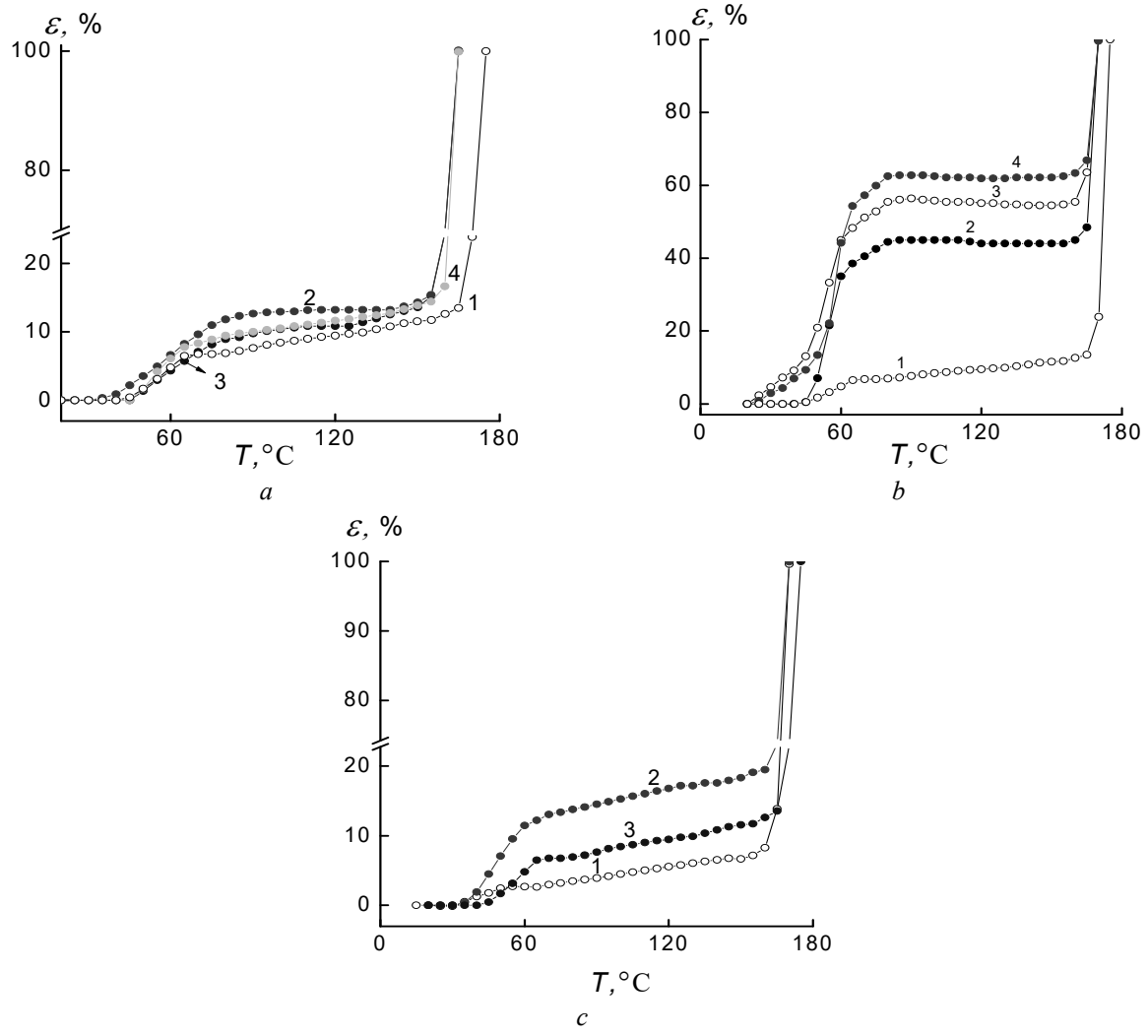



**Fig. 5.** *a* – Thermomechanical curves: (*1*) the PLA, (*2)* the PLA-1%Ag-PEI, *(3)* the PLA-2%Ag-PEI, *(4)* the PLA-4%Ag-PEI, obtained via the thermochemical reduction of $Ag^+$ ions in the polymer films at $T$ = 160 °C during 5 min; *b* – Thermomechanical curves: (*1*) the PLA, (*2)* the PLA-1%Ag-chitosan, *(3)* the PLA-2%Ag-chitosan, (4) the PLA-4%Ag-chitosan, obtained via the thermochemical reduction of $Ag^+$ ions in the polymer films at $T$ = 160 °C during 5 min; *c* – Thermomechanical curves of the (*1*) PLA, formed from the solution at room temperature and the PLA films obtained at: (*2*) 100 and (*3*) 160 °C during 5 min

Mechanical tests of samples of PLA-PEI materials with a content of $\varphi$ = 1, 2, 3, 4 wt. % have shown that the mechanical strength decreases with increasing concentration of the filler and, respectively, is $\sigma$ = 27.0; 26.1; 25.6; 25.1 ± 0.01 MPa, whereas for the original PLA film $\sigma$ = 28.8 ± 0.01 MPa.

***Antimicrobial Properties of the polymer nanocomposites.*** The PLA-Ag-chitosan nanocomposites formed via thermochemical

reduction of $Ag^+$ ions in the polymer films at $T = 160$ °C within 5 min demonstrate higher antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* strains as compared to the PLA-Ag-PEI nanocomposites formed in a similar way. After 24 hours of incubation at 37 °C, it was possible to define a precise zone around films contours. This claims the inhibition of bacteria growth (Table 3).

One can also observe an enhancement of antimicrobial activity of both types of Ag-containing nanocomposites based on PLA and chitosan or PEI with raising of the Ag nanoparticles content in the polymer matrix (Table 3).

**Table 2.** Temperature transitions and related deformations of the investigated polymers

| Polymer system | Reduction temperature, °C | Reduction time, minutes | $T_g$, °C | $T_f$, °C | $\varepsilon$, % |
|---|---|---|---|---|---|
| PLA | – | – | 41.3±0.5 | 164.3±0.5 | 4.7 |
| PLA | 100±0.5 | 5 | 48.5±0.5 | 165.0±0.5 | 15.3 |
| PLA | 160±0.5 | 5 | 55.0±0.5 | 169.1±0.5 | 8.4 |
| PLA-PEI-1%Ag | 160±0.5 | 5 | 59.5±0.5 | 158.0±0.5 | 12.9 |
| PLA-PEI-2%Ag | 160±0.5 | 5 | 59.0±0.5 | 158.0±0.5 | 10.3 |
| PLA-PEI-4%Ag | 160±0.5 | 5 | 54.7±0.5 | 159.8±0.5 | 10.5 |
| PLA-chitosan-1%Ag | 160±0.5 | 5 | 55.5±0.5 | 164.0±0.5 | 45.0 |
| PLA-chitosan-2%Ag | 160±0.5 | 5 | 43.7±0.5 | 164.0±0.5 | 56.0 |
| PLA-chitosan-4%Ag | 160±0.5 | 5 | 43.3±0.5 | 164.0±0.5 | 62.0 |

**Table 3.** Antimicrobial activity of the nanocomposites with various content of the Ag nanoparticles

| Polymer system | Diameter of inhibition zone, mm | |
|---|---|---|
| | *Staphylococcus aureus* | *Escherichia coli* |
| PLA | 0 | 0 |
| PLA-PEI | 0 | 0 |
| PLA-chitosan | 0 | 0 |
| PLA-PEI-1%Ag | 0 | 12.5±0.6 |
| PLA-PEI-2%Ag | 14.0±0.6 | 14.5±0.8 |
| PLA-PEI-4%Ag | 14.0±0.6 | 14.5±0.8 |
| PLA-chitosan-1%Ag | 20.5±1.0 | 17.0±0.8 |
| PLA-chitosan-2%Ag | 20.5±1.1 | 21.6±1.1 |
| PLA-chitosan-4%Ag | 25.8±1.2 | 25.0±1.2 |

For the control specimens (polymer films without nanoparticles) the active growth of investigated bacteria and lack of zones with the inhibited growth are noticed (Table 3).

So, it can be declared that the higher antimicrobial activity of the PLA-Ag-chitosan nanocomposites comparing to the PLA-Ag-PEI nanocomposites is associated with much less size of the Ag nanoparticles (see Fig. 4 and Table 3).

## CONCLUSIONS

In this paper, we have demonstrated a simple technique to design antimicrobial nanocomposites based on polylactide and Ag nanoparticles. Peculiarities of the structural organization of nanocomposites formed via thermochemical reduction of $Ag^+$ ions in the PLA–AgPalm–PEI and PLA–AgPalm–chitosan films at the temperature interval of 100–170 °C have been investigated by the WAXS method.

The method of X-ray diffraction analysis found the optimal temperature ($T$ = 160 °C) and the duration of reduction ($t$ = 5 min) at which the structural manifestation of the metallic phase of silver is fully realized.

It is found that with increasing heating temperature the degree of crystallization of silver-containing nanocomposites increases, and at $T$ > 160 °C this degree sharply decreases due to melting of the crystalline phase of PLA.

It has been determined that the average size of Ag nanoparticles in the polymer matrix using PEI as a reducing agent and stabilizer is ~ 7 nm, while in the matrix with chitosan the average size is found to be ~ 4 nm.

The polymer nanocomposite of polylactide with Ag and chitosan was found to have much higher antimicrobial activity compared to the nanocomposite with Ag and PEI against *S. aureus* and *E. coli* strains, which is probably due to the smaller size of nanoparticles in this nanocomposite.

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## Синтез та характеристика нанокомпозитів на основі полілактиду і наночастинок срібла, отриманих шляхом термохімічного відновлення іонів $Ag^+$ природним чи синтетичним полімерами

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*Для створення різноманітних матеріалів з антимікробними властивостями широко використовуються іони або наночастинки срібла, які вводяться, зокрема, в полімерні композити. Однак противірусна та протимікробна дія наночастинок срібла, що контактують з навколишнім середовищем, пов'язана з їхнім розміром, зі зменшенням розміру наночастинок, їхня ефективність різко зростає. У цій роботі як полімерну основу використовували біодеградабельний полімер полілактид (ПЛА), який отримують шляхом поліконденсації молочної кислоти або полімеризації лактиду з розкриттям циклу. Ці дослідження в подальшому сприятимуть розробці нових безпечних матеріалів, зокрема при створенні пакувальних матеріалів для харчових продуктів, що на сьогодні, безперечно, є актуальною проблемою.*

*Метою роботи було одержання срібловмісних полімерних композитів на основі полілактиду шляхом термохімічного відновлення іонів $Ag^+$ з використанням природного (хітозан) та синтетичного (поліетиленімін (ПЕІ)) полімерів та вивчення структури, морфології, термомеханічних та протимікробних властивостей одержаних нанокомпозитів.*

*Термохімічне відновлення іонів $Ag^+$ у об'ємі полімерних плівок, що містили ПЛА, пальмітат срібла та відновник, проводили, витримуючи їх при температурі 100–170 °C протягом 5 хвилин. Зразки нагрівали в пічці з використанням високоточного терморегулятора ВРТ-3. Точність регулювання температури становила ± 0.5 °C. В результаті відновлення плівки набувають сріблястого кольору, вміст Ag в об'ємі плівок становив від 1 до 4 мас. %, товщина плівок становила 110 мкм. Структура, морфологія, термомеханічні та антимікробні властивості двох типів нанокомпозитів ПЛА-Ag-поліетиленімін (ПЕІ) та ПЛА-Ag-хітозан, сформованих шляхом термохімічного відновлення $Ag^+$ у полімерних плівках, досліджено за допомогою ширококутного розсіювання рентгенівських променів на приладі ДРОН-4-07, трансмісійної електронної мікроскопії (ТЕМ) (JEM-1230 JEOL, Японія), термомеханічного аналізу (УІП-70 М), а також антимікробних випробувань. Встановлено, що термохімічне відновлення іонів $Ag^+$ в об'ємі полімерних плівок при використанні синтетичного або природного полімера (ПЕІ або хітозану) як відновника та стабілізуючого агента наночастинок срібла відбувається при 160 °C протягом 5 хвилин. Встановлено, що*

*середній розмір наночастинок Ag у полімерній матриці дорівнює ~ 7 та ~ 4 нм при використанні ПЕІ та хітозану відповідно. Показано, що нанокомпозити ПЛА-Ag-хітозан мають значно вищу протимікробну активність щодо штамів S. aureus та E. coli порівняно з нанокомпозитами ПЛА-Ag-ПЕІ.*

***Ключові слова**: полілактид, поліетиленімін, хітозан, срібловмісний нанокомпозит, структура, морфологія, термомеханічні властивості, антимікробна активність*

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