

## Structures and Antibacterial Properties of PLA-based Ciprofloxacin Composite Films Deposited by Low-Electron Beam Dispersion

Beibei Li<sup>1</sup>, Chun He<sup>1</sup>, Xiaohong Jiang<sup>1\*</sup>, M.A. Yarmolenko<sup>1,2\*</sup>, D.G. Piliptsov<sup>1,2</sup>,  
A.A. Rogachev<sup>1,2</sup>, A.V. Rogachev<sup>1,2</sup>, Bin Du<sup>3</sup>

<sup>1</sup>International Chinese-Belorussian Scientific Laboratory on Vacuum-Plasma Technology, Nanjing University of Science and Technology, 200, Xiaolingwei str., Nanjing 210094, China

<sup>2</sup>Francisk Skorina Gomel State University, 104, Sovetskaya str., Gomel 246019, Belarus

<sup>3</sup>Department of Orthopaedic, Affiliated Hospital of Nanjing University of Chinese Medicine, Nanjing, China

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### Abstract

Poly(lactic acid) (PLA)-based ciprofloxacin (Cip) antibacterial films with mass ratio PLA:Cip=1:1 were prepared by low-electron beam dispersion (EBD). The molecular structure, chemical composition and morphology of PLA-based ciprofloxacin antibacterial films were investigated by XPS, FTIR, liquid NMR and SEM. The antibacterial activity of composite films was tested against *E. coli* ATCC 25922 and *S. aureus* ATCC 12600 using the agar diffusion method on the solid LB agar medium. XPS and FTIR analysis showed the presence of an antibacterial ingredient in the composite films. Using NMR, it has been shown that the molecular structure of a monolayer of ciprofloxacin is fully consistent with the molecular structure of the initial ciprofloxacin powder. High antibacterial activity of the composite films has been also established and the layers still possess antibacterial activity with regard to *S. aureus* even after 7 days of leaching in an isotonic solution. The thermal treatment indicates that the composite films can withstand temperatures of 180 °C and keep its structure unchanged.

## 1. Introduction

Nowadays, hospitals and outpatients use a lot of indwelling medical devices or transplants to help patients' physiological function and improve their quality of life. Some of these devices need to be inserted into the human body for the time being, while others need permanent implantation. However, the use of these medical devices can cause inflammation, rejection, allergic reactions, and the formation of biofilms with pathogen adhesion. More than 65% of all infectious diseases are believed to be caused by microorganisms that exist in the form of biofilms [1, 2], therefore, inhibiting biofilms formation has become an important way to reduce bacterial infection in medical devices.

Currently, in order to fight against bacterial adhesion and the subsequent formation of biofilms, the main methods are to prepare instruments by novel methods, to remove contaminated devices and to modify the surface of medical devices [3]. One of the most effective and simple methods is to use functional coatings on the surface of medical devices. These directional antibacterial films can make the drug concentration higher than the minimum effective concentration and avoid the systemic use of the drug.

Poly(lactic acid) (PLA) has good thermal stability, excellent biocompatibility and degradability, there is no pollution in the production process which can be extracted from rice or corn. Due to PLA natural origin good processability and low cost which can help alleviating the energy crisis as well as reducing the dependency on fossil fuels of our society [4], researchers have examined different methods, such as controlling PLA surface energy, surface

\*Corresponding authors.

E-mail: [jiangxh24@njust.edu.cn](mailto:jiangxh24@njust.edu.cn) (X. Jiang)  
[simmak79@mail.ru](mailto:simmak79@mail.ru) (M.A. Yarmolenko)

charge and surface roughness or the introduction of other components to modify the PLA. The increasing number of functional PLA-based polyesters provides the opportunity to study the relationships between structure and functionality of the polymers used for the fabrication of various products such as trays, cups, tubs, and films. Due to its degradability and biocompatibility in the human body, PLA can be used to manufacture delivery system materials, covering membranes, or tissue engineering, as well as in dermatology and cosmetics.

Fluoroquinolones were widely used in human and veterinary medicine for the treatment of infectious diseases [5–7]. Ciprofloxacin, a fluoroquinolone antibacterial agent [8, 9], has a wide range of antibacterial activity, which is highly active against various Gram-positive and Gram-negative bacteria. It is very useful for the treatment of urinary tract infection and prostatitis and for acute diarrheal disease caused by *E. coli*, *S. aureus* and *Klebsiella* [10].

Electron beam dispersion is conducive to uniform films of high purity and density. Evaporating the materials under vacuum can help to avoid the contamination and oxidation of the prepared materials [11], which also allows the formation of thin antibacterial layers with prolonged release of the drug component [12, 13]. Under the conditions of multi-turn evaporation deposition, multilayer composite materials or gradient structural materials with various compositions are obtained by controlling the deposition process parameters to meet the design requirements of the materials [14–17].

The aim of this paper is to study the structure, composition and antibacterial properties of PLA-based ciprofloxacin films deposited by EBD, providing a promising method for formation of the antibacterial surface of medical devices. Preparing the films by this method, the structure of the drug molecule has not been destroyed, which ensures the integrity of ciprofloxacin. And the temperature of the standard sterilization has no effect on the antibacterial properties of the deposited films. With the degradation of PLA, the ciprofloxacin embedded in the PLA base films is gradually released, and the long-time antibacterial effect can be maintained.

## 2. Materials and methods

The following materials and reagents were used in the study: Polylactide (PLA, Purac), Ciprofloxacin (Cip, KRKA), 0.9% Sodium chloride (NaCl), Anhydrous ethanol, Peptone, Agar and Deionized water.

The targets were made by mixing thoroughly the PLA powder and ciprofloxacin and mixtures were carried out using a vibrating mill. The composite films were formed by means of low-energy electron beam dispersion exposure in a vacuum of the targets based on PLA and Cip. The electron beam density was  $j = 0.01\text{--}0.03\text{ A/cm}^2$ , the energy  $E$  comprised up to 1600 eV. The formation of the composite films was carried out when the residual gas pressure in the vacuum chamber was  $\approx 4 \times 10^{-3}\text{ Pa}$ .

The properties of the single-component films of ciprofloxacin were not studied in the paper. This is due to the fact that such films are rapidly destroyed in aqueous media. This may contribute to the emergence of resistant pathogens in the body.

As a substrate material, KBr plates (IR analysis), silicon plates (XPS, SEM analysis) and titanium plates (microbiological analysis) were used.

The chemical analysis of the deposited films was performed using the XPS. The XPS measurements were conducted on the PHI Quantera II Scanning XPS Microprobe spectrometer using the Al  $K\alpha$  as a source of monochromatic X-ray radiation ( $h\nu = 1486.6\text{ eV}$ ). All the binding energies of the XPS spectra were corrected by C1s peak at 284.8 eV of the surface adventitious carbon. The processing of the results was carried out using the mathematical application OriginPro.

Fourier transform infrared (FTIR) spectroscopic studies were performed on Thermo Scientific Nicolet FTIR spectrophotometer (IS-10) using a standard transmittance cell. The spectra were recorded in the wave number range ( $4000\text{--}400\text{ cm}^{-1}$ ) with a resolution of  $4\text{ cm}^{-1}$ .

$^1\text{H}$  liquid nuclear magnetic (NMR) spectra were acquired using Bruker Avance III 500 MHz Spectrometer. The powder and the coating material were dissolved in dimethylsulfoxid (DMSO) at a concentration of 5 mg. The morphology of the films was studied using Quanta 200 F scanning electron microscope (SEM).

Thermal treatment was analyzed by the pipe furnace (OTF-1200X-S), films were heat-treated in a vacuum (0.1 MPa) at a temperature of  $180\text{ }^\circ\text{C}$  for 0.5 h. The temperature range ( $120\text{--}220\text{ }^\circ\text{C}$ ) was used for thermal sterilization of medical devices, implants in particular.

*Staphylococcus aureus* (*S. aureus* ATCC12600) and *Escherichia coli* (*E. coli* ATCC 25922) were used for the microbiological studies. The activity was assessed using a standard agar technique [18, 19]. The coated titanium plates were previously cut into circles with a diameter of 6 mm.

The antibacterial activity of the films was judged by the inhibition zones of the growth of bacteria formed around the plates.

This paper also presents the results of studies on the changes in the antibacterial activity of the composite films after their stay in an aqueous medium. For this purpose, the coated titanium substrates were placed in a physiological solution and kept for the time required. Then the samples were washed in distilled water and dried by warm airflow at the temperature of 60 °C.

### 3. Results and discussion

#### 3.1. The results of FTIR spectroscopic analysis

The IR spectra of the composite films are shown in Fig. 1. They demonstrate not only the absence of intensive chemical interaction (the formation of new chemical bonds) between PLA and ciprofloxacin in the dispersion zone. They also indicate the absence of chemical interaction directly in the composite films. Thus, in the first approximation the composite films can be considered as mechanical mixtures of the initial components. Later, a comprehensive comparative analysis of the IR spectra of the films was carried out.

The IR spectrum of the ciprofloxacin is characterized by the presence of a broad absorption band in the range of (3600–3000)  $\text{cm}^{-1}$  caused by the stretching vibrations of OH groups. This is due to the ability of a thin layer of antibacterial chemotherapeutic drug to absorb intensively moisture from the air. The stretching vibrations of C=O bonds appear near 1720  $\text{cm}^{-1}$  while the C=C

stretching vibrations in the quinoline ring (in this range the optical density of deformation vibrations of NH bonds of secondary amines is very small) appear near 1600  $\text{cm}^{-1}$ . In the range of wave numbers (1500–1400)  $\text{cm}^{-1}$  the stretching vibrations of C–O groups appear as well as vibrations –COO– (ionized carboxyl group). The stretching vibrations of C–F bonds are manifested in the wave number range (1050–1000)  $\text{cm}^{-1}$ . The IR spectrum of the ciprofloxacin thin layer corresponds to the standard IR spectrum of the drug compound. The differences appear only in the displacement of a number of bands, carbonyl ones in particular. This explains the effect of the physical state of the material under study on the level of intermolecular interaction [20]. The IR results indicate the absence of a noticeable degradation of the chemotherapeutic drug under the electron beam action. This phenomenon is due to the low molecular weight of the ciprofloxacin that facilitates the transition of the drug into the gas phase in the absence of intense heating and radiation exposure.

In the IR spectrum of polylactide, the absorption bands responsible for the C=O stretching vibrations (1750  $\text{cm}^{-1}$ ) and C–O (1180, 1080, 1040  $\text{cm}^{-1}$ ) bonds are most pronounced. The absorption near 1455  $\text{cm}^{-1}$  is due to the asymmetric deformation vibrations –CH<sub>3</sub>. The appearance of the bands at 1382  $\text{cm}^{-1}$  and 1360  $\text{cm}^{-1}$  is due to symmetric and asymmetric vibrations –CH– [21, 22].

The IR spectrum of the PLA/Cip composite films is represented by all the bands characteristic of the IR spectra of PLA and ciprofloxacin powder. Neither the emergence of new bands nor the disappearance of the bands characteristic of single-component layers was recorded. A slight displacement of a number of absorption bands were due to the redistribution of hydrogen bonds between the components of the composite layer [20].

#### 3.2. The NMR spectroscopy results

The NMR spectrum of ciprofloxacin 1H is shown in Fig. 2. The quinolone ring system contains three isolated aromatic protons 3, 4 and 5. The aliphatic region consists of methylene protons (1 and 1'; 2 and 2') of the piperazine ring and methine protons (6) and methyl (7 and 8) of the cyclopropyl ring.

The comparative analysis of the NMR spectra of the ciprofloxacin films and the initial ciprofloxacin powder allows evaluating the effect of the electron beam on the destruction of the drug

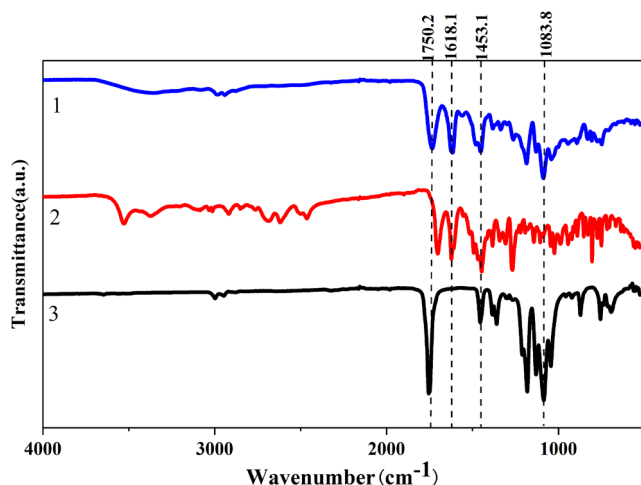


Fig. 1. FTIR spectra of films and powder: 1 – PLA/Cip films; 2 – ciprofloxacin; 3 – PLA.

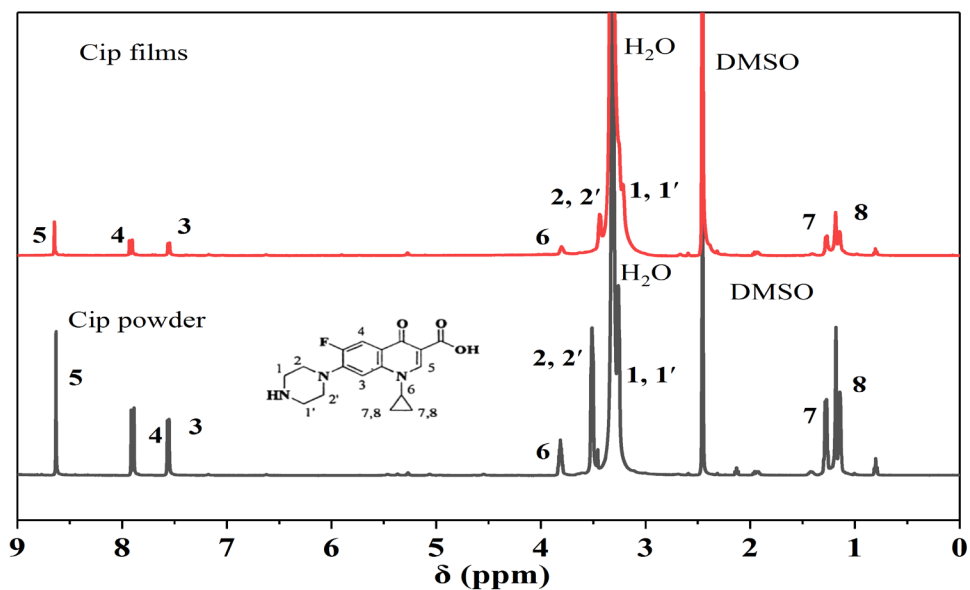


Fig. 2.  $^1\text{H}$  Liquid NMR spectra of ciprofloxacin powder and ciprofloxacin films.

compound structure. The analysis did not show any noticeable differences in the NMR spectrum of the films and the NMR spectrum of the original drug compound. This means that the resulting low molecular degradation products of ciprofloxacin are not able to condense on the substrate at room temperature.

### 3.3. XPS analysis results

The results of the XPS analysis of the composite films are shown in Fig. 3. The chemical composition of the films is represented by four elements – C, O, N, F. The composite peak of C1s was decomposed into composite peaks with centers at

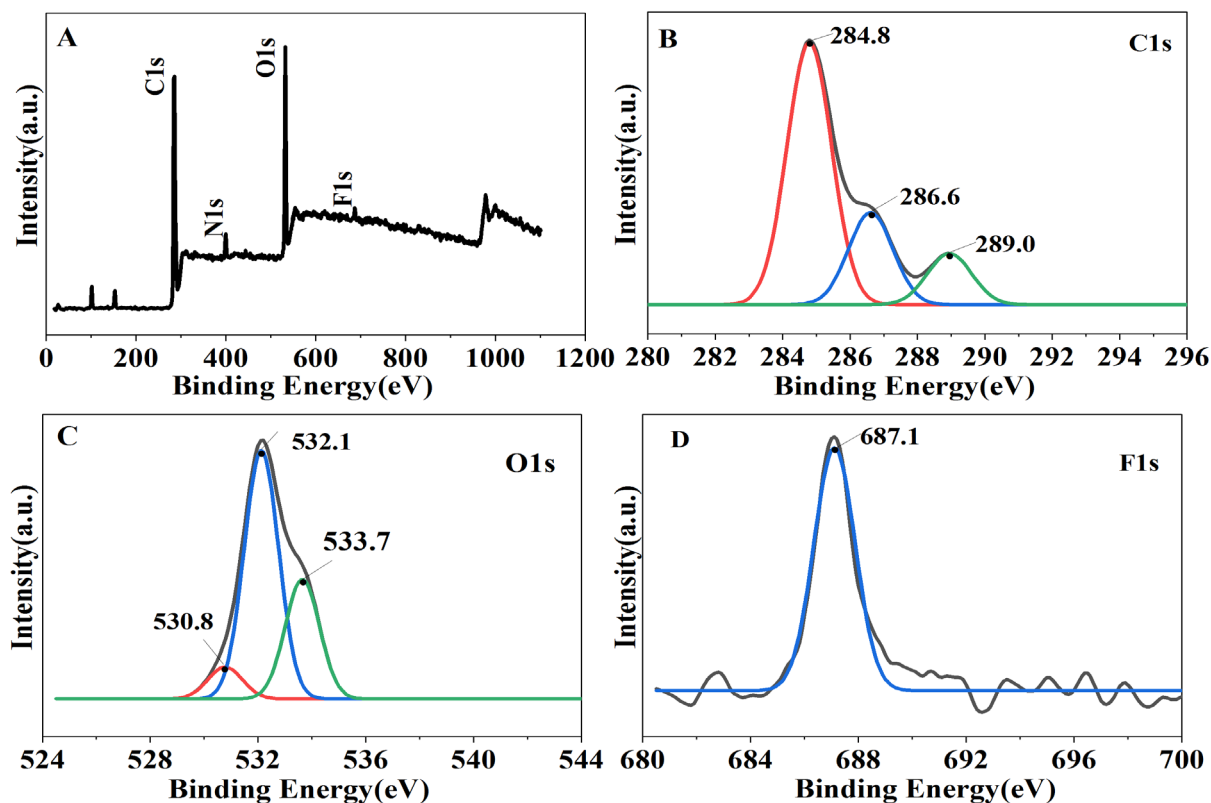


Fig. 3. XPS core spectrum and XPS spectrum of C1s and F1s: A – XPS core spectrum; B – XPS spectrum of C1s; C – XPS spectrum of O1s; D – XPS spectrum of F1s.

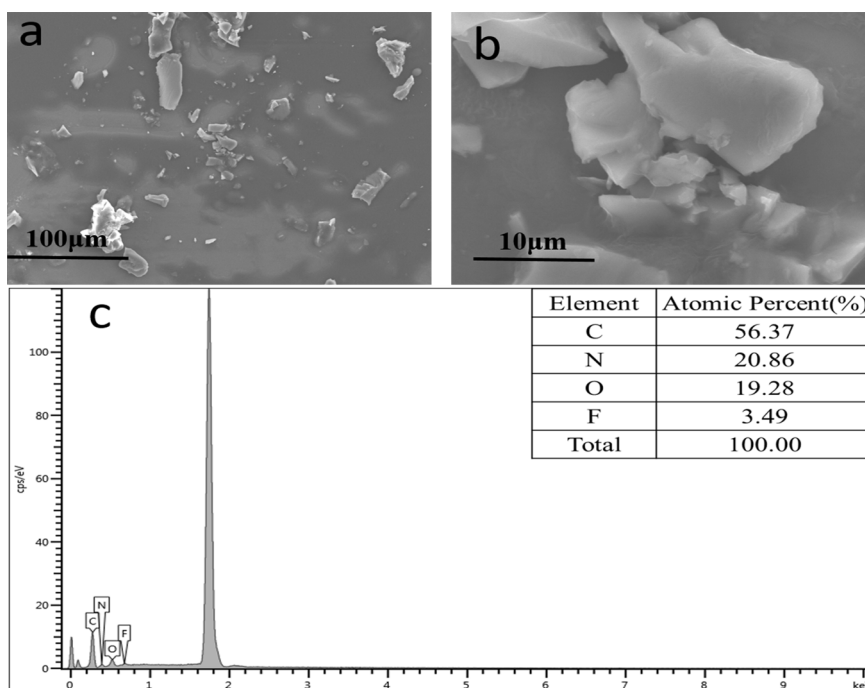


Fig. 4. SEM image and EDS spectrums of different elements of composite layers.

284.8 eV (corresponding to C–C bonds in PLA and ciprofloxacin), 286.6 eV (C–O bond) and 289.0 eV (C=O, C=C, C–F) [23, 24], accounting for 44.8%, 45.4% and 9.8%, respectively.

The XPS spectra of O1s can be deconvoluted into three peaks at 530.8, 532.1 and 533.7 eV peaks. The characteristic peaks of 530.8 eV correspond to the oxygen atoms on hydroxyl groups in ciprofloxacin molecules. The characteristic peaks at 532.1 and 533.7 eV correspond to C=O and C–O bonds in PLA molecules, which is consistent with the XPS analysis of C1s. Moreover, F1s has only one peak centered at 687.1 eV.

In conclusion, the characteristic functional groups of ciprofloxacin in PLA/Cip composite films still exist, which are consistent with NMR and FTIR analysis, and it can be inferred that the composite films possess good antibacterial properties.

### 3.4. The results of microscopic analysis

Large fragments are presented on the surface of the deposited films (Fig. 4). The chemical elemental analysis of the films made it possible to correlate such formations with the polymer microdroplets. The result is fully consistent with the visual control data of the process of electron-beam dispersion of mixed targets. The melting of the polymer component is accompanied by the intensive formation of a droplet phase. To produce a homogeneous layer,

it is necessary to monitor continuously the dispersion parameters, i.e. to reduce the heating current when the entire volume of the target is melted. It should be mentioned that the films formed at the mass ratio of the components PLA/Cip 1:1 are characterized by a solid defect-free structure.

It is known from the EDS images of Fig. 4(c) that the distribution of four elements C, O, N and F in the film materials, where the three elements of C, N and O are responsible for the largest proportion of the films.

### 3.5. The results of antibacterial analysis

The dimensions of inhibition zones of microorganisms provided by PLA/Cip films are presented in Fig. 5. It is obvious that the composite films are resistant to *S. aureus* and *E. coli* with good

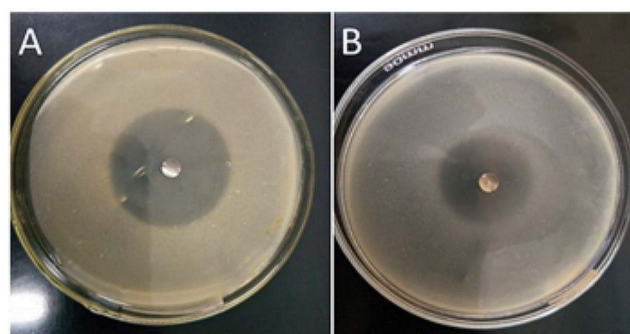


Fig. 5. Antibacterial effect of PLA-based ciprofloxacin films against *S. aureus* (A) and *E. coli* (B).

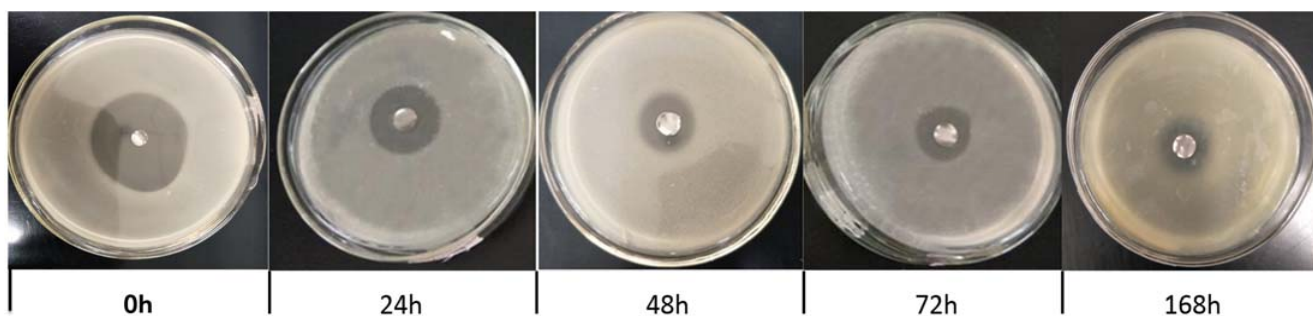


Fig. 6. The change in the diameter of the inhibition zone of *S. aureus* growth by the composite layer of PLA/Cip=1:1 with release times.

antibacterial effects. Ciprofloxacin is a broad-spectrum antibiotic, which has a selective inhibitory effect on bacterial DNA helicases, and it can impair the function of DNA helicase, thus preventing DNA from forming negative supercoiling and eventually causing bacterial reproductive disorders and death. Therefore, it has bactericidal effect on most Gram-positive and negative bacteria.

When the bacteria is *S. aureus*, the diameter of the antibacterial ring is 42 mm, and when it comes to *E. coli*, the diameter of the antibacterial ring is 34 mm. It indicates that the antibacterial films are resistant to *S. aureus* better.

The studies of the changes in the antibacterial activity of the deposited films during their exposure in the physiological solution were carried out (Fig. 6). The drug release rate of the composite films was moderate. It was established that there is no loss of antibacterial activity of the films even after 7 days of exposure in a physiological solution. There is a gradual decrease in the diameter of the inhibition zone and the blurring of its boundaries with an increase in the length of the films dipped in the physiological solution. The values of the inhibition zone diameter gradually decrease in the following order: 38 mm (0 h), 19 mm (24 h), 16 mm (48 h), 14 mm (72 h) and 12 mm (168 h). Even after 7 days exposing in an isotonic solution, the films still possess the antibacterial activity with regard to *S. aureus*. The diameter value of the inhibition zone compared to the same value after 1 day of leaching is reduced by no more than 37%.

### 3.6. Thermal treatment analysis

The main study of Figs. 7 and 8 is the effect of thermal treatment on the structure and morphology of the films. It is known from Fig. 7 that the transmittance at 1084.5  $\text{cm}^{-1}$  and 1745.6  $\text{cm}^{-1}$  of PLA-based ciprofloxacin composite films indi-

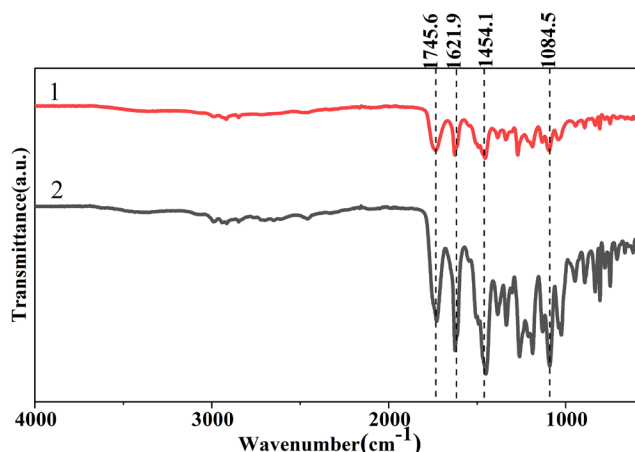


Fig. 7. FTIR spectra of PLA-based ciprofloxacin films: 1 – without thermal treatment; 2 – thermal treatment at 180 °C for 0.5 h in vacuum.

cated the C–O bonds and carbonyl C=O stretching in PLA, the composite films correspond to the transmittance of ciprofloxacin at 1454.1  $\text{cm}^{-1}$  and 1621.9  $\text{cm}^{-1}$ , which belong to  $\nu_{\text{C-O}}$  and quinolones, respectively. Each absorption peak of the films after annealing is consistent with the peaks of original films, which indicates that the structure of the films has not changed after annealing at 180 °C for 0.5 h. After annealing, the molecules are rearranged on the substrate by diffusion, and the large fragments become small masses under the action of thermal motion, but the overall morphology has not changed.

After thermal treatment, the structure and morphology of the PLA-based ciprofloxacin composite films have not changed indicating that if the films are used on the surface of medical devices, it will not damage the structure of the films after heat sterilization. It can be inferred that the PLA-based ciprofloxacin films can provide a simple and effective method for maintaining the antibacterial activity of medical devices.

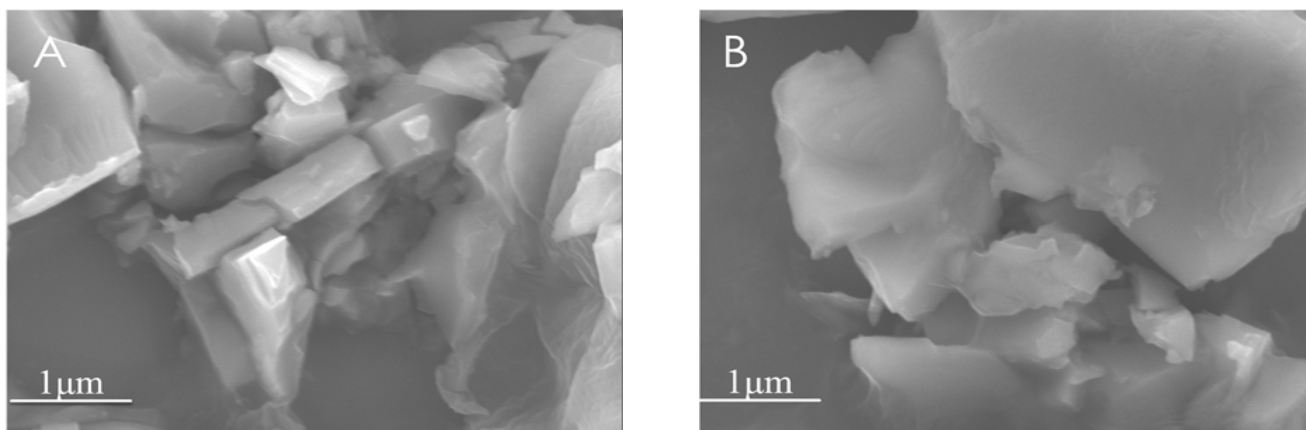


Fig. 8. SEM image of PLA-based ciprofloxacin films: A – thermal treatment at 180 °C for 0.5 h in vacuum; B – without thermal treatment.

#### 4. Conclusions

PLA/Cip films with mass ratios (1:1) were successfully prepared by low-electron beam dispersion. The antibiotics were carried by PLA deposited on different substrates, which was confirmed by FTIR and XPS. Composite films based on PLA and ciprofloxacin can be considered as highly dispersed mechanical mixtures of the initial compounds. No chemical bonds between the components of the different natures have been established. The studies have shown that there is no difference in the molecular structure of the ciprofloxacin films compared with the structure of the initial powder of the drug compound. It was found by SEM that the ciprofloxacin and PLA were uniformly deposited on the substrate, with the existence of polymers, the coating is continuous because there is no significant microcracks in the films. Even after 7 days of exposure in an isotonic solution, the films still preserve antibacterial activity with regard to *S. aureus*. In particular, the diameter value of the inhibition zone compared to the same value after 1 day of leaching is reduced by no more than 37%. The films have good thermal stability, their structure and morphology aren't changed after thermal treatment at 180 °C for 0.5 h.

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