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Research paper

PLLA scaffold modification using magnetron sputtering of the copper target to provide antibacterial properties

A.D. Badaraev[a], A.L. Nemoykina[b], E.N. Bolbasov[a], S.I. Tverdokhlebov[a,*]

[a] Department of Experimental Physics, Tomsk Polytechnic University, Tomsk 634050, Russia
[b] Laboratory of Biopolymers and Biotechnology, Tomsk State University, Tomsk 634050, Russia

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ABSTRACT

Using the electrospinning method, we produced biodegradable scaffolds from poly-L-lactide acid polymer (PLLA – poly-L-lactide acid). Using DC magnetron sputtering of the copper target we modified the surface of the scaffolds. For investigate scaffolds morphology, structure and elemental composition were used scanning electron microscopy, X-ray diffraction and X-ray fluorescence analysis. The results of scanning electron microscopy reveal that scaffolds consist of chaotically located fibres. The diameters of fibres range from 0.8 to 2 μm. Initially amorphous scaffold after modification has crystalline structure. The count of oxygen and copper with modification is increased, but count of carbon decreased. For the investigation of the scaffolds wetting ability were used glycerol and water. The wetting angles for the both liquids were similarly comparable. The values for the wetting angles range from 114 ± 5° to 125 ± 5°, what indicated that scaffolds had hydrophobic properties. Testing for antibacterial features indicated that the modified scaffolds are capable to have a bacteriostatic effect. Compared to the number of bacteria cultured without scaffold (11.8 ± 1.26 CFU × 10^4/ml), two modified samples have bacteriostatic properties (reducing the number of bacteria on 30 and 50%). Economically effective method PLLA scaffolds modification could be used for creating low-cost wound dressings with antibacterial properties.

1. Introduction

Biodegradable polymers, based on polyethers, such as polycaprolactone (PCL), polylactic acid (PLLA), polyglycolic acid (PGL) are used in the food, medical and chemical industries [1]. The best known biodegradable polymers material is polylactic acid [2]. Destruction of polylactic acid polymer does not have a negative effect on the human organism [3]. Thanks to biocompatibility and the absence of toxicity, polylactic acid polymers can be used to make biomedical equipment [4,5], implants [6] and wound dressing material [7]. In tissue engineering, biodegradable polymer materials are commonly used to encourage the healing of wound surfaces [8].

Nonwoven biodegradable materials (scaffold), applying to encourage the wound healing, can be produced using method of electrospinning, which is relatively simple [9]. When formed in this manner, the polymers scaffold is highly porous and has a high surface-to-volume ratio, close to that of living human tissue [10].

Where non-antibacterial dressing material is used, there is a possibility of microbial contamination of the wound surface, leading to deterioration patient overall condition. Furthermore, non-antibacterial dressing material imposes the need for antiseptics and antibacterial substances, which tend to complicate the healing. Hence the interest for modified dressings which have antibacterial properties.

Research is currently being conducted, aimed at developing polymers with antiseptic qualities, based on metal nanoparticles [11–13]. The interest of metal nanoparticles linked with development of antibiotic resistance [14]. Such resistance partially linked with the forming of biofilms on the organic surfaces. Nevertheless, biofilms don't help bacteria be protected from the nanoparticles [11]. However, process of forming nanoparticles has a range of problems, including the high cost of synthesis and consequent storage in nano form [15]. Consequently, research continues for new, resource-efficient methods of producing polymers with antiseptic qualities.

One alternative method is based on modification of materials, adding the required properties to them, by using DC magnetron sputtering to apply different types of functional coating, which

* Corresponding author.
E-mail address: tverd@tpu.ru (S.I. Tverdokhlebov).

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could be consist of metals, alloys and different compounds [16]. This modification method is commonly used in various technical domains. DC magnetron sputtering requires relatively not lot amounts of energy and time. By method magnetron sputtering can be produced a thin metal film with antiseptic qualities [17].

Copper coatings and nanopowder act as bacteriostatics and bactericides [18,19]. Copper is considerably cheaper than silver, which makes this material more economically effective. In the work of Svetlichnyi et al. [20] were obtained that Cu_2O nanocomposite has more bacteriostatic properties compare with nano-ZnO/fabric composite [21].

Materials used in medicine must be sterilised. This requirement applies to antibacterial polymers destined to be used in wound dressings. Typically, biodegradable polymers are sterilised by gas, such as ethylene oxide [22]. Such sterilization process is quite long, and there is a need to remove the residual ethylene oxide, which can take up overnight [23]. The most sufficient problem related with ethylene oxide sterilization is that after this process remain toxic residues [24]. That is why obtained scaffolds don't may be applied in medicine such as material for wound dressings. This underlines the importance of finding an alternative, resource-efficient sterilisation method for polymer-based dressing materials, which could also be used in the field.

One of the most commonly used low-cost methods (in terms of energy and time) is autoclaving. This method is based on a high-temperature steam treatment, the duration of which is measured in dozens of minutes, allowing for considerable reductions in the cost of the materials produced for medical use.

The use of such resource-efficient processes of manufacture and sterilization may reduce cost on the scaffolds for biomedical applications. The aim of this work is obtaining modified PLLA scaffold with copper using DC magnetron sputtering, investigation the morphology of surface, elemental composition and antibacterial activity.

2. Materials and methods

2.1. Scaffold fabrication

Nonwoven scaffold was formed by electrospinning method using the installation «NANON-01A», from 3% solution of the polymer (Poly-L-lactide PURASORB PL 38) in the dichloromethane (CH_2Cl_2) [25]. The sedimentation of scaffold occurred on the cylindrical collector surface (diameter 100 mm, length 210 mm) at the following technological parameters: the collector rotation speed 50 r/min, the solution supply rate 6 ml/h, the voltage between the collector and the needle 27 kV, the distance between the needle tips and the collector 190 mm.

2.2. Scaffold modification

Scaffold was modified on a sputtering system, which was created in Dr. Tverdokhlebov's lab [26], using the DC magnetron sputtering method of copper target. The copper target with 99.99% purity was used for sputtering. The following parameters were set for modification: the power discharge 40 W; the current 0.2 A; the operating pressure of 99.99% Ar in the chamber 0.7 Pa; the distance between magnetron and target 40 mm; the magnetron area 240 cm^2; the modification time 10, 20, 30 s.

2.3. Autoclaving

Autoclaving was performed using a Tuttnauer 2340 MK autoclave, set as follows: pressure 1.5 MPa; temperature 121 °C; time 30 min. In the work of Tapalskiy et al. [27] such parameters are some of the most suitable for autoclaving polymer coating, particularly in the case of polylactic acid, since they are not hampered by deformation and changes in molecular structure of the polymer coatings containing metal nanoparticles.

2.4. Testing the molecular structure and elemental composition

The examination of the scaffold morphology was performed using the Quanta 200 3D scanning electron microscope (SEM). SEM images were obtained with 2000× and 20,000× magnifications. Images with less magnification served to create distribution histograms, based on fibre diameter, which were then used as the basis for calculation of normal distribution; the measurements were made by the Image 1.38 software package, which measured up to 200 diameters for each image. In order to evaluate the dependence of fibre diameter on the modification time and the effect of autoclaving, we used the ANOVA dispersion analysis.

The analysis of elemental composition was conducted using the X-ray fluorescence method (XRF) and a Shimadzu XRF 1800 setup, with the following channels: carbon (C), oxygen (O), copper (Cu). The scanning angle for each element was: carbon 23–43°; oxygen 43–47°; copper 130–136°. The scanning speed 8°/min, scanning step 0.1°. The instrument was calibrated for alloy steel, for the all elements, result did not exceed the range in ±5%.

Material structure was analysed based on X-ray diffraction analysis (XRD) using the Shimadzu XRD 6000 with following parameters: the wavelength of monochromatic Cu Kα radiation 1,54 Å; the voltage of X-ray tube 40 kV; the current of X-ray beam 30 mA; scanning angle range 10–80°; scanning speed 2°/min; scanning step 0.02°. The scaffold crystal size was calculated by Debye–Scherrer equation [28]:

$$l_c = \frac{k\lambda}{cos\theta\sqrt{\beta^2 - \beta_r^2}},$$

where k is Scherrer's constant (for spherical particles −0,9); λ is the wavelength of the incident radiation; θ is the diffraction angle; β full width at half maximum; β_r is the apparatus broadening reflex.

The analysis of wetting ability was conducted using the «sitting drop» method, and a DSA-25 KRUSS setup. Two types of liquid were used: water and glycerol. All wetting angles were measured after 1 min interaction drops with scaffold surface.

2.5. Antibacterial analysis

Antibacterial analysis was carried out using an Escherichia Coli (E.Coli) culture, obtained from the ALL-Russian Collection of Microorganisms. The one-day bacterial culture was cultivated on meat-and-peptone agar (GRM broth 15 g/l, agar 15 g/l), and then transferred to the meat-and-peptone broth. The culture was cultivated at 37°C in a shaker, at 200 r/min for 18 h. The culture was spun at 8000 r/min for 10 min. The residue was rinsed twice with NaCl 0.9% physiological solution and then spun again. The rinsed residue was introduced with a physiological solution in order to make a suspension. All milieus and solutions had been prepared in accordance with ISO 22196:2011. 1 ml of bacterial suspension with a 10 × 10 mm sample of scaffold was added to the test tube. One part of the samples was tested immediately. The other part of the samples was placed in a thermostat for 24 h at 37 °C.

For more visual display of results, the quantity of bacteria was normed based on the average of their initial volume. The average quantity of bacteria was 2.15 CFU × 10^4/ml (Colony Forming Units × 10^4/ml).

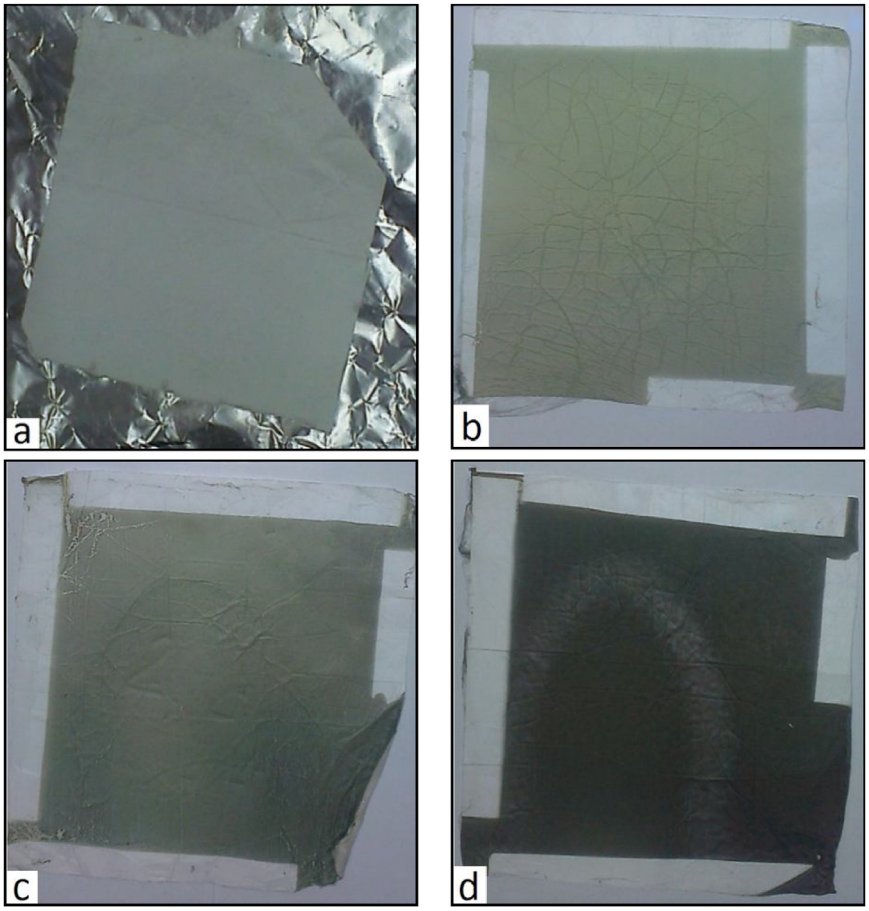

Fig. 1. The first group of samples. The unmodified (original) scaffold (a), modified by DC sputtering of the copper target during different time periods: b) 10 s; c) 20 s; d) 30 s.

3. Results and discussion

3.1. Fabricated and modified scaffold

The first group of samples is indicated in Fig. 1a–PLLA scaffold, formed by electrospinning, whilst Fig. 1b, c and d show scaffolds modified at different times in plasma, using DC sputtering of the copper target.

On visual inspection, the polymer scaffolds had a uniform surface without visible deformations, bubbles or stratification.

The colour of the initial PLLA scaffold is white. As indicated in Fig. 1, the PLLA scaffold becomes darker as the time of modification gets longer. After 10 s, the modified scaffold becomes greyish-yellow. After 20 s, the modified sample becomes grey, and after 30 s it becomes black-grey.

Such colour changing of initial scaffold, probably due to the formation of a copper oxide (II) [29]. We believe that copper oxide could be formed from the interaction of copper, which located on the scaffolds surface, with ambient air [30,31]. Modification using DC magnetron sputtering with Ar-plasma allow to create AgO from metallic silver: after sputtering of Ag target on the cotton plate, were revealed by method X-ray photoelectron microscopy the presence of AgO after modification [32].

Fig. 2 shows the scaffolds after autoclaving (the second group of samples).

It was observed after autoclaving that the surface of the samples presented corrugations and their linear dimension was reduced, which indicates certain thermal shrinkage. The unmodified PLLA scaffold preserved its initial white colour, while that of other samples was changed. Following autoclaving, the colour of scaffolds that had been modified for 10 s changed from grey-yellow to white-yellow, whilst in those modified for 20 s, it changed from grey to white-yellow. The biggest change in colour was observed in samples modified for 30 s, which had changed from black-grey to light-yellow.

Since yellow and red shading is typical for metallic copper, it can be assumed that the thermal processing in autoclaving had resulted in the chemical bonds between copper and oxygen being ruptured, purifying the copper:

$$CuO + CO \rightarrow Cu + CO_2, \quad (1)$$

We believe, that carbon monoxide is obtain as a result of bond scission PLLA chains by Ar-plasma modification, after consecutive conversions chain reactions [33]. Molecules of CO could be trapped from the chemically active surface of PLLA scaffold [34].

The temperature of the reaction (1) depended from the crystal structure CuO. Amorphous CuO can interact with CO at room temperature $< 30\,^{\circ}C$ [35]. For the CuO with crystals size 16 nm, the reaction temperature $\sim 100\,^{\circ}C$, for the crystals with size 115 nm, the temperature $\sim 200\,^{\circ}C$ [35]. Highly crystalline CuO could be react with CO at a temperature $\sim 200\,^{\circ}C$ [36]. For example, in the work of Gerasimov et al. [37] described that temperature of the reaction between CO and CuO are different and varying from 68 °C to 265 °C.

We can assume that on surface, after Ar-plasma modification, were formed nano crystal structure of CuO. This structure has allowed us to produce the reaction (1) under appropriate conditions of autoclaving (see caption “Autoclaving”).

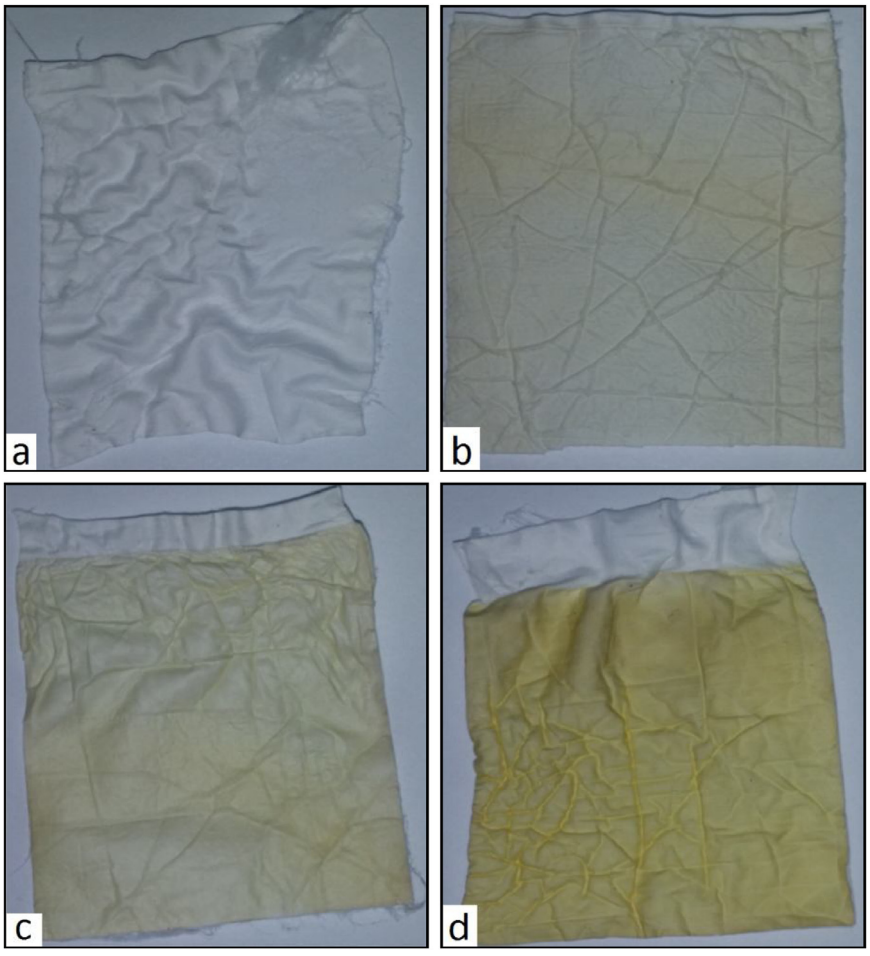

Fig. 2. The second group of samples. The unmodified (original) scaffold (a), modified by sputtering of the copper target during different time periods: b) 10 s; c) 20 s; d) 30 s.

Table 1
Elemental composition.

Sample/modification time in seconds	Element, % (1st group)			Element, % (2nd group)		
	C	O	Cu	C	O	Cu
PLLA scaffold/0 (initial sample)	66.54 ± 3.32	33.46 ± 1.71	–	64.80 ± 3.24	35.20 ± 1.76	–
PLLA scaffold/10	62.38 ± 2.98	37.59 ± 1.88	0.03 ± 0.01	63.84 ± 3.19	36.13 ± 1.81	0.03 ± 0.01
PLLA scaffold/20	61.99 ± 3.11	37.95 ± 1.92	0.06 ± 0.03	62.47 ± 3.12	37.47 ± 1.87	0.06 ± 0.03
PLLA scaffold/30	62.90 ± 3.21	37.01 ± 1.85	0.09 ± 0.05	59.28 ± 2.96	40.61 ± 2.03	0.11 ± 0.06

3.2. XRF readings

Table 1 illustrates the elemental composition of the scaffolds.

In the 1st group of samples, the change in carbon percentage content was comparable and changed in range of error.

The oxygen content was increased after modification. The concentration of oxygen in modified scaffolds was increased in comparison with their initial state, irrespective of the processing time in magnetron-charged plasma. This is due to the interaction between the atmospheric air and the chemically active polymer surface, which formed as a result of plasma surface treatment of the PLLA scaffold [38]. With increasing of modification time, the copper content is increase. The increase of oxygen and copper contents in modified scaffolds (1st group) is hypothetically linked to the formation of copper oxide.

Autoclaving does not effect on the elemental composition. All values for 2nd group samples were in range of errors.

3.3. SEM results

Fig. 3 shows the scaffold surface with small (2000×) and large (20,000×) magnifications and a distribution histogram based on fibre diameter.

It is noted that the structure of these polymer scaffolds presents a chaotic fibres distribution with various diameter, which is characteristic of polymer scaffolds formed by electrospinning method. The typical fibre structure found in the both scaffolds groups was preserved after modification, which indicates the correct selection of the parameters copper target sputtering. Scaffolds from the 2nd group (after autoclaving) also preserved their initial closely-interwoven surface structure.

Fibre diameters ranged from 0.8 to 2 μm for all samples. Using the ANOVA dispersion analysis method, we found that no considerable difference could be established between sample groups 1 and 2, and that the diameter of fibres does not appear to be dependent on modification time. Consequently, the fibre diameter does

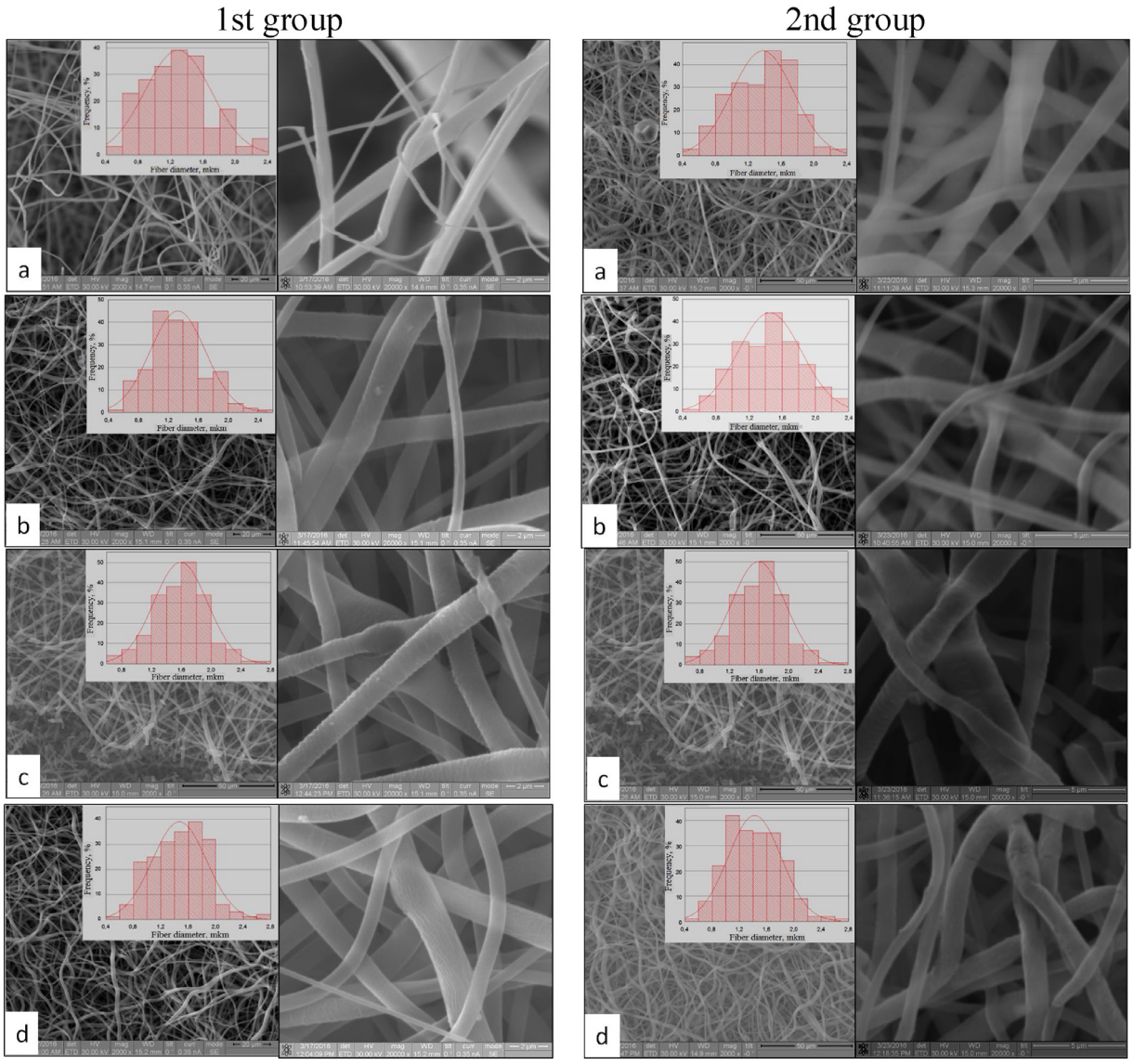

Fig. 3. Images of the scaffold with small and large magnification and the distribution histogram with different modification times: a) 0 s, b) 10 s, c) 20 s, d) 30 s.

not change by either modification or autoclaving. The analysis was carried out with the statistic value being set at $p = 0.05$.

3.4. XRD readings

Fig. 4 shows scaffold diffractograms. To ensure that peak values can be determined for copper, its oxides and polymer, we used a wide range of diffraction angles 10–80°.

Regardless of the large diffraction angle ranges, from 10–80°, the characteristic peaks of copper crystallographic areas were not observed, that is why it was not possibility to calculate the crystal size of copper and its oxide. This was possibly due to insufficient sensitivity of the test.

Crystallographic areas of PLLA scaffolds (200/110) and (203) were clearly visible at 16.5° and 19° respectively. The growth of this peaks indicates the formation of phase α' from the amorphous state [39].

In the initial PLLA scaffold the amorphous structure was found to be dominant. Modified scaffolds had predominantly crystalline structure. When autoclaving, the degree of modified samples crystallinity was increased, an amorphous scaffold has become a crystalline structure. The initial PLLA scaffolds also had a crystalline structure after autoclaving. Samples from the second group presented a higher degree of crystallinity in comparison to the first group.

Table 2
Crystals size of PLLA scaffolds.

Sample/modification time in seconds	Crystals size, nm (1 group)	Crystals size, nm (2 group)
PLLA scaffold/0	–	18 ± 0.8
PLLA scaffold/10	23.1 ± 1.6	24.7 ± 1.5
PLLA scaffold/20	24.5 ± 2.2	23.2 ± 1.4
PLLA scaffold/30	21.3 ± 1	25.4 ± 1.7

One knows that crystalline structures in polymers tend to appear at temperatures higher than the vitrification temperature (for PLLA scaffold 54–58 °C) [40]. Autoclaving was occurring at high vapour temperatures, which also lead to a high degree of crystallization. By autoclaving the phase of α' mostly changed onto α crystalline structure [41].

Table 2 shows the crystallite size of scaffolds.

From the data table, we can see that from the modification time, the size of crystals from the 1st group are changing non-

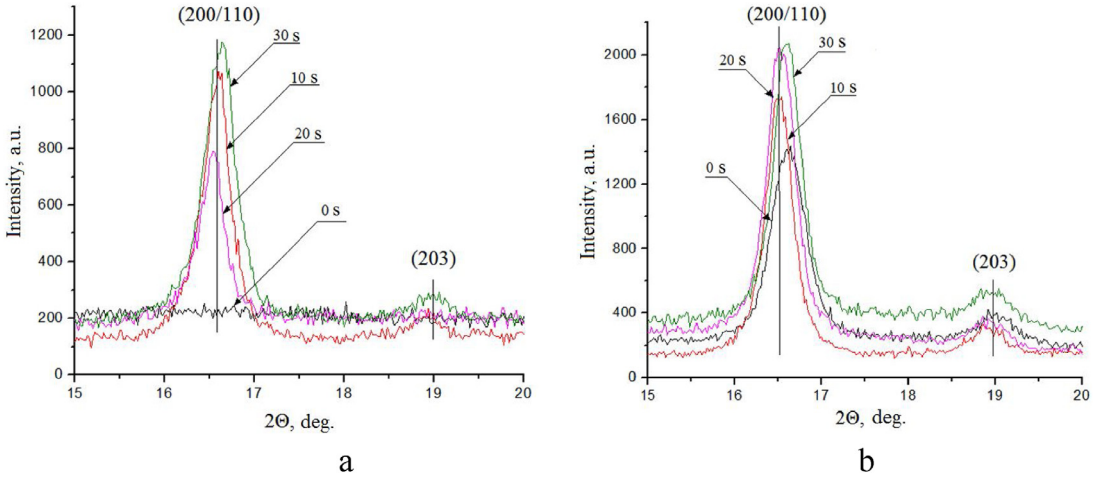

Fig. 4. Diffractograms for the 1st group of samples (a) were different from those for the 2nd group (b) with different modification times (results obtained relate to PLLA scaffolds).

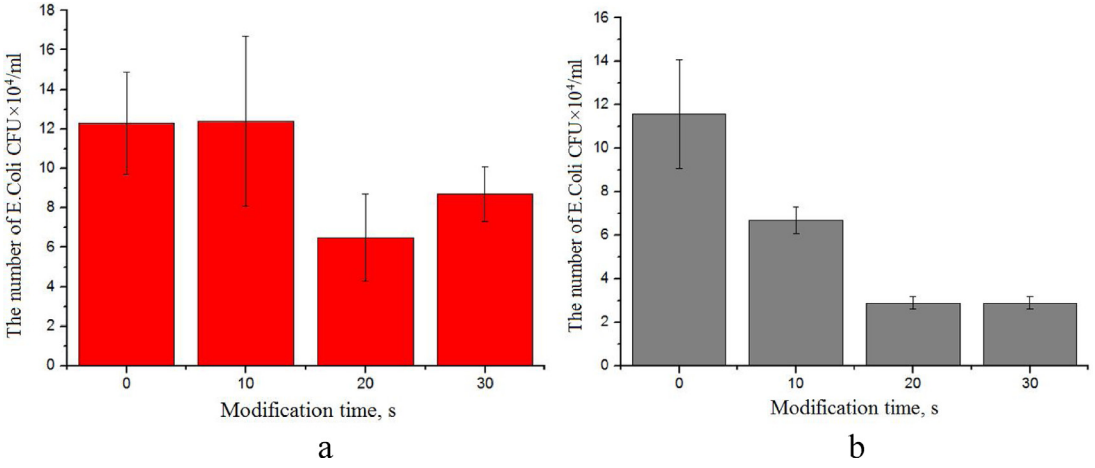

Fig. 5. The amount of E.Coli CFU in the solution used in the 1st (a) and 2nd (b) sample groups, with different modification times.

Table 3
The measurements of wetting angle.

Sample/modification time in seconds	The angle of water wetting, °	The angle of glycerol wetting, °
PLLA scaffold/0	114 ± 5	119 ± 2
PLLA scaffold/10	125 ± 6	123 ± 1
PLLA scaffold/20	118 ± 2	125 ± 5
PLLA scaffold/30	115 ± 10	123 ± 3

linear. The unmodified (original) sample from the 1st group don't have a crystalline structure, that is why it's not calculated the size of crystals for him. The sizes of crystals for modified samples from the second group are roughly comparable and varies from 23.2 nm to 25.4 nm. For the second group scaffolds, exist a marked difference in size between initial sample (18 ± 0.8 nm) and the modified samples.

The crystals appearance indicates the formation a crystalline phase from amorphous.

3.5. The test results for wetting ability

The measurements of the wetting angle are indicated in Table 3.

Analysis was only conducted on scaffolds from the first group, since it was not possible to accurately measure the wetting angles of autoclaved samples due to thermal shrinking.

The analysis of wetting ability indicated that the initial PLLA scaffold has a water wetting angle of 114°, which makes this scaffold hydrophobic. All modified samples were found to be hydrophobic, their wetting angles being almost identical to those measured on initial samples. The wetting angle for glycerine was not significantly different to that of water. The hydrophobic properties of the scaffolds are preserved after modification, this is due to the formation on the surface of discontinuous copper metallic clusters on the material surface [42] that retains it hydrophobic properties [19].

To improve the properties of the scaffolds, it is advisable to make their surface more hydrophilic. Higher wetting ability would make the surface much more effective in the absorption of wound exudate, making it more suitable for dressing material [43].

3.6. Test results for antibacterial properties

Fig. 5 indicates the analysis result of the antibacterial properties when exposed to E.Coli bacterial cultures cultivated for 24 h on the scaffolds.

In the solution without scaffold, the number of bacteria was 11.8 ± 1.39 CFU × 10^4/ml, similar to that found in the solution exposed to unmodified PLLA scaffold: in the 1st sample group, the composition was 12.3 ± 2.62·10^4 CFU × 10^4/ml, whilst in the 2nd group, it was 11.7 ± 2.52·10^4 CFU × 10^4/ml. These results indicate the absence of any antibacterial effect of the initial scaffold as well

as the absence of any infection of the samples by the bacteria present in the ambient air during the experiment.

In the solution exposed to modified scaffolds from the first and second group, especially where the time of modification was 20 s and 30 s, the amount of bacteria relatively low, which indicates on the antibacterial effect of the samples.

The 2nd group of samples had a more prominent bacteriostatic effect, which was most certainly due to the formation of metallic copper from copper oxide (II) during autoclaving. This assumption is consistent with other works [44,45] which showed that metallic copper nanopowders have stronger antibacterial effects compared to copper oxide nanopowders.

4. Conclusions

The results of our research showed that modified PLLA scaffolds in copper plasma that has been charged with a DC magnetron current of 0.2 A and modified up 10–30 s have unaffected linear dimensions. Autoclaving at a temperature of 121 °C for 30 min tends to lead to a reduction of the sample's linear dimensions due to thermal shrinking. Modification and autoclaving do not affect scaffold morphology, maintaining its complexly interwoven fibre structure. Modification and autoclaving both changed amorphous structure of PLLA scaffolds on the crystal, autoclaving increasing their crystallinity. The scaffolds are hydrophobic, and their modification by charged magnetron plasma does not change their wetting angle.

Increase of oxygen concentration and copper in scaffolds following modification indicates the formation of copper oxide. The process of autoclaving leads to formation of metallic copper from copper oxide (II). Such oxide could be formed from the interaction between copper on the scaffolds surface and ambient air. Scaffolds modified by magnetron-charged copper plasma have bacteriostatic properties. Autoclaving intensifies PLLA scaffolds bacteriostatic features. The proposed methods for modification and sterilisation by autoclaving are cheap and relatively simple, which makes application of such PLLA scaffolds in the production of wound dressing material more desirable. Further enhancements of this product may be possible by increasing its wetting ability.

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