



Surface properties and antimicrobial activity of composite nanofibers of polycaprolactone with silver precipitations

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ABSTRACT

Purpose: The purpose of the article is to investigate the structure and antimicrobial properties of composite nanofibers with silver particles precipitated onto the nanofibers surface.

Design/methodology/approach: A solution was prepared in the first place made of the following solvents to fabricate antimicrobial composite nanofibers of polycaprolactone with silver precipitations: formic acid and acetic acid at a rate of 70:30. Then, silver nitrate was introduced into the fabricated solution of the solvents and it was subjected to the interaction of ultrasounds, and after 10 minutes polycaprolactone was added to the solution, and then the solution was mixed for 12 hours and a solution was obtained with a 10% concentration and the mass fraction of 0, 1, 3 and 5% of silver nitrate additives. The solution was forced into a positive voltage electrode placed above a negative voltage electrode; the solution was then subjected to the activity of a strong electrostatic field transforming the solution into micro- and nanofibers. After electrospinning, the fibers obtained underwent the activity of a 2% ascorbic acid solution, by means of which silver was precipitated on the nanofibers surface. Viscosity and electrical conductivity tests were performed of single-component and double-component solutions, of the fibers' structure in a transmission electron microscope, of the BET, Langmuir specific surface area and DTF porosity with the method of gas adsorption and antimicrobial activity of the nanocomposites produced on the nanocomposites on following bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans*.

Findings: The use of a formic acid and acetic acid solution at a rate of 70:30 for preparation of a polycaprolactone solution for its electrospinning enables to obtain a non-toxic and fully biodegradable polymer nanofibers of polycaprolactone with PCL/Ag silver precipitations possessing high antimicrobial performance against Gram+, Gram- bacteria and fungi.

Practical implications: Antimicrobial composite nanofibers with silver nanoparticles precipitated onto the nanofibers surface can be applied in biodegradable antiseptic dressings in the form of mats or other textiles containing polymer nanofibers of polycaprolactone with PCL/Ag silver precipitations obtained as a result of electrospinning.

Originality/value: The research outcomes confirm that it is feasible to manufacture polycaprolactone nanofibers with PCL/Ag silver precipitations possessing high antimicrobial performance against Gram+, Gram- bacteria and fungi.

Keywords: Nanofibers; Nanosilver; Electrospinning; Antimicrobial properties; *Staphylococcus aureus*; *Escherichia coli*; *Candida albicans*

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PROPERTIES

1. Introduction

The purpose of this article is to obtain and examine the structure and properties of polycaprolactone PCL micro- and nanofibers manufactured in an electrostatic field containing silver nanofibers on the PCL/Ag surface. The essential aspect is to investigate surface properties and antimicrobial activity of the created polycaprolactone composite nanofibers with PCL/Ag silver precipitations.

An exudation is often formed in the wound healing process which, in chemical terms, contains a mixture of cytokines, growth factors and proteolytic enzymes destroying growth factors. The presence of microorganisms is leading to excessive production of protease, while the excess of protease produced by cells is inhibiting the regeneration process at the stage of inflammatory condition. If microorganisms are not removed from the wound environment, an exudation continues to be formed, and this phenomenon causes excessive production of protease in the cells, the presence of which may lead to wounds that may heal from several days to several months and even years. For this reason, it is so important to modify a material being in contact with a living organism to include chemical compounds or particles eliminating microorganisms from the wound environment [1-3]. This is not an easy task as wounds subjected to surgical operations are especially prone to infections, and also wounds containing impurities, ulcerations, decubitus and such with extensive and deep tissue destruction caused by burning [4-7].

An ability to acquire antibiotic drug resistance is an additional impediment in combating microorganisms [3,8,9]. This is an aftermath of numerous errors committed for the last 60 years. The excessive usage of antibiotics by patients and antibiotics excessively added to the fodder given to farm animals, which are consumed by humans in the form of ready-made meat products, should be highlighted here [10]. Bacteria in organisms of animals, subjected to the continuous activity of the antibiotics introduced, acquire resistance to the given drug, which is due to the fact that a bacterium is able to produce an

enzyme decomposing an antibiotic, or to synthesise a new type of protein binding the given antibiotic, which prevents its intended antimicrobial performance. Such activity is making it largely difficult to fight microorganisms [10]. It should also be noted that we are more and more often witnessing loss in efficiency of the antibiotics used for the last 60 years. A commonly occurring *Staphylococcus aureus* bacterium can be given as an example. The bacterium poses a serious threat, often leading even to death [11-12]. In addition, *Staphylococcus aureus* bacterium causes numerous out-of-hospital and MRSA (methicilin-resistant *Staphylococcus aureus*) infections causing high mortality [13-16].

For this reason, the solutions offered by modern nanotechnology are becoming more widespread apart from, or even in lieu of, antibiotic treatment [17-22]. A useful solution in this case is to apply polymer nanofibers with a varied diameter, which can be manufactured by several methods [23-27]. A method, which has experienced the greatest advancement, is polymer nanofiber electrospinning in an electrostatic field [28,29] using molten polymers and from solutions [25,30-32]. Nanofibers with various morphology can be fabricated according to the manufacturing conditions of electrospinning, including hollow, porous, flat, directed, branched, co-axial nanofibres and ones with different composition [33-35]. Electrospinning enables to obtain polymer nanofibres in an electrostatic field, including nanofibres with full and empty section, core-shell nanofibres consisting of two parts [22], porous nanofibres [36], dual- and multicomponent nanofibres, composite nanofibres [37] containing metal particles or ceramics, as well as organic materials [1,2,38-42].

This article concentrates on polycaprolactone (PCL), i.e. a semi-crystalline, linear, aliphatic and biocompatible polyester with good mechanical properties, widely used in medicine [17,26]. The article pinpoints technological methods of fabricating polycaprolactone polymer PCL nanofibers and scrutinises the antimicrobial force of silver nanoparticles connected with a developed specific area of polycaprolactone polymer PCL nanofibers, which are next tested on Gram+, Gram- bacteria and fungi to demonstrate their suitability in medical applications.

2. Experimental procedure

Polycaprolactone with the molecular mass $M_w = 105000$ g/mol, by Sigma Aldrich, was employed for manufacturing polycaprolactone nanofibers with PCL/Ag silver precipitations. A 99.9% mixture of formic acid by Sigma Aldrich with 99.9% acetic acid by Sigma Aldrich was used as a solvent. AgNO₃ silver nitrate by Tantal was used as an antimicrobial material. Silver was precipitated onto the surface of PCL fibers using a 2% ascorbic acid solution.

A solution was prepared in the first place made of the following solvents: formic acid and acetic acid at a rate of 70:30. Then, silver nitrate was introduced into the fabricated solution of the solvents. The so combined components underwent ultrasounds' activity with a Ut 200 device with a Labindex titanium probe. After 10 minutes, polycaprolactone was added to the solution, and then the solution was mixed for 12 hours and a solution was obtained with a 10% concentration and the mass fraction of 0, 1, 3 and 5% of silver nitrate additives. The solution obtained was placed into a container of the Yflow device where it was pumped into a working chamber by means of an infusion pump. When the solution was forced into a positive voltage electrode placed above a negative voltage electrode, the solution was then subjected to the activity of a strong electrostatic field (Table 1) transforming the solution into micro- and nanofibers. The solution was pumped at 30°C, which permitted to maintain its constant viscosity for the entire duration of electrospinning. After electrospinning, the fibers obtained underwent the activity of a 2% ascorbic acid solution, by means of which silver was precipitated on the nanofibers surface.

Viscosity tests of single-component and double-component solutions were performed by means of an Alpha L rotational viscometer by Labindex. An APM attachment was used for the measurement, dedicated to solutions

with the volume of 8-13 ml, additionally equipped with a cooling flange enabling to measure viscosity at 25°C. A TL6 spindle with its speed adjustable within the range of 0.3 to 100 rev./min was used for the test.

An electrical conductivity (EC) test was undertaken for single-component solutions and double-component solutions using an MM41 multimeter by Labindex. Calibration in a water solution of Crysolyt KCl 3M with the conductivity of 1413 μ S/cm was made before a conductivity measurement. An electrical conductivity measurement according to stability over the time of 4 seconds at the temperature of 25°C was employed in the tests.

The structure of fibers was examined with a transmission electron microscope (TEM) TITAN 80-300 by FEI.

The BET¹, Langmuir specific surface area and DTF porosity² was assessed with the gas adsorption method. A Gemini VII 2390t specific surface area analyser by Micrometrics was used for the examinations. The samples for the examinations were prepared as follows: the samples were weighed, dried in vacuum for 24 hours at the temperature of 30°C to remove moisture and the adsorbed gases. The samples were then dried in the device's flasks and measurement conditions were defined, and a correlation was made after making the measurement. Pressure within the range of 0.1 to 0.65 P/P_0 was assumed for adsorption and desorption. Nitrogen with the purity of 5.0 was used as measuring gas, all measurements were correlated after making the measurements for all the samples.

The tests of antimicrobial activity of the nanocomposites produced were carried out with the following bacteria: *Staphylococcus aureus* ATCC 25923, *Escherichia coli* ATCC 25922, *Candida albicans* ATCC 10231 and on the reference fungal strains of *Candida albicans*.

The samples of each of the examined composite sized 10×10mm were plasma sterilised and placed in 4 ml of the suspension of the reference fungal strain with the final density of 1.5×10^5 CFU/ml (the units forming bacterial colonies in 1 ml) in tryptone water. A sample of UG material in 4 ml of tryptone water and 4 ml of tryptone water was used as a negative control and 4 ml of suspension of the reference microbial strain with the density of 1.5×10^5 CFU/ml was used as a positive control. The (examined and control) tests were made in 2 repetitions. After 17 hours of incubation at the temperature of 37°C in oxygen conditions, the volume of 20 μ l was sifted from each test onto the permanent substrate for cultivating the fungi of Sabouraud agar. After 48 hours of

Table 1.

Fabrication conditions of double-component nanofibers

Type of nozzle applied	standard nozzle
Process type	single-stream process
Flow rate, ml/h	1.00
Type of collector applied	flat 40x40 cm
Electrostatic voltage, kV/cm	0.95-1.63
Solution temperature, °C	25
Gas temperature in working chamber, °C	23
Gas humidity in working chamber, %	20-30

¹ BET isotherm, i.e. Brunauer, Emmett and Teller isotherm – a simple model of multilayer adsorption from gas phase.

² Density functional theory – DFT.

incubation at the temperature of 37°C in oxygen conditions, the quantity of the cultivated fungus colonies was assessed to identify anti-fungal efficacy (AFE). The AFE of the examined samples was calculated according to the following dependency (1):

$$AFE [\%] = \frac{V_c - V_t}{V_c} \times 100 \% \quad (1)$$

where: V_c – microbial suspension density in the positive control (blanc),

V_t – density of the tested microbial suspension

The reference strains *Staphylococcus aureus* and *Escherichia coli* were used in the tests of antibacterial activity. The plasma-sterilised samples of each of the examined nanocomposites and UG material were placed in 4 ml of the suspension of the reference fungal strain with the final density of 1.5×10^5 CFU/ml in tryptone water. A sample of UG material in 4 ml of tryptone water and 4 ml of tryptone water was a negative control and 4 ml of suspension of the reference microbial strain with the density of 1.5×10^5 CFU/ml was a positive control. The tested and control sample was made in 2 repetitions. After 17 hours of incubation at the temperature of 37°C in microaerophilic conditions, the volume of 20 µl was sifted from each of the tested and control sample onto the permanent substrate for cultivating the bacteria of Columbia agar with a 5% addition of sheep blood. After 48 hours of incubation at the temperature of 37°C in microaerophilic conditions, the number of the cultivated bacteria colonies was evaluated to determine anti-bacterial efficacy. The AFE of the examined samples was calculated according to the following dependency (2):

$$ABE[\%] = \frac{V_c - V_t}{V_c} \times 100\% \quad (2)$$

where: V_c – microbial suspension density in the positive control (blanc),

V_t – density of the tested microbial suspension.

3. Results

The viscosity of the suspensions employed is essential in the fabrication process of micro- and nanofibers in an electrostatic field. The viscosity of the solutions obtained is changed by introducing the additives of silver nitrate into the initial polycaprolactone solution. The higher viscosity of the solution along with a higher fraction of the additive introduced was identified in all the cases based on the viscosity tests of polycaprolactone solutions containing silver nitrate additives with the fraction of 0, 1, 3 and 5%

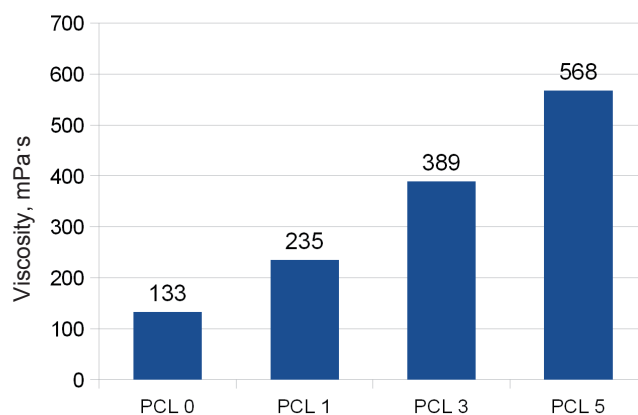


Fig. 1. Growth of polycaprolactone solution viscosity along with growth of silver nitrate fraction; PCL 0 without AgNO_3 , PCL 1 with 1% addition of AgNO_3 , PCL 3 with 3% AgNO_3 , PCL 5 with 5% AgNO_3

performed using a rotational viscometer (Fig. 1). Solution viscosity is rising for polycaprolactone solutions from 133 mPa·s for a solution not containing the additives up to 568 mPa·s for a solution containing 5% of silver nitrate.

A very important property of a solution, apart from viscosity, is electrical conductivity. The conductivity tests of polycaprolactone solutions containing silver nitrate additives with the fraction of 0, 1, 3 and 5% using a conductometer indicate higher electrical conductivity of the solution along with the growing fraction of silver nitrate additives in relation to the initial solution (Fig. 2). The conductivity of solutions after adding silver nitrate is rising from 28 µS·cm, for a polycaprolactone sample not containing silver nitrate, to 840 µS·cm, for a sample containing 5% of silver nitrate.

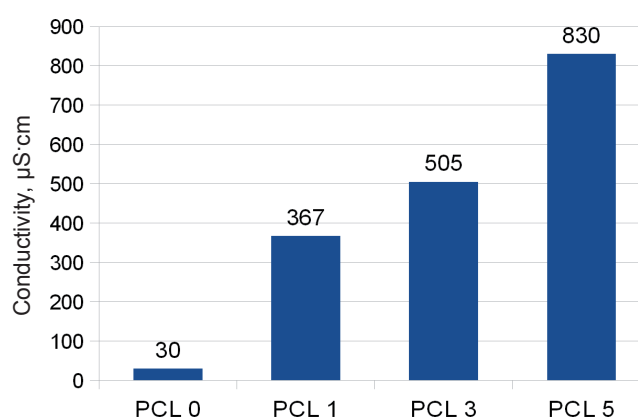


Fig. 2. Growth of polycaprolactone solution conductivity along with the higher concentration of silver nitrate; PCL 0 without AgNO_3 , PCL 1 with 1% addition of AgNO_3 , PCL 3 with 3% AgNO_3 , PCL 5 with 5% AgNO_3

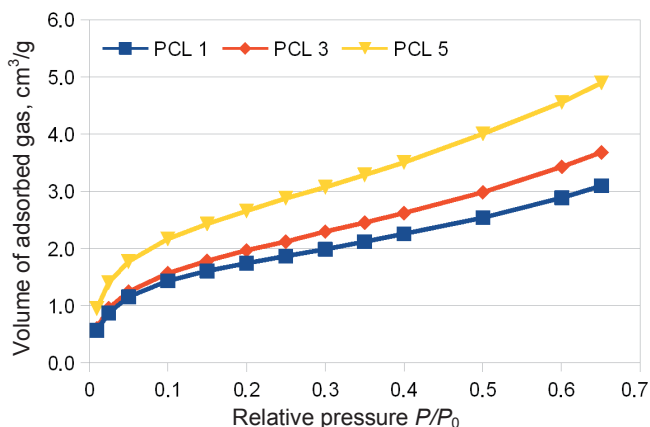


Fig. 3. Adsorption isotherms for the samples of fibers obtained from a mixture of formic acid and acetic acid with: 1% addition of AgNO_3 (PCL 1), 3% addition of AgNO_3 (PCL 3), 5% addition of AgNO_3 (PCL 5)

The tests of the BET, Langmuir specific surface area and of porosity with the DTF method (Figs. 3-5) with the nitrogen adsorption method indicate varied impact of the introduced additives on the specific surface of the examined samples. A larger specific surface area of composite fibers containing silver may be linked to the formation of silver aggregates on the surface of nanofibers. The highest porosity in the tests into the porosity of samples containing silver nitrates investigated with the DFT method within the porosity range of 1.4-5.4 nm is seen for samples containing 5% of silver nitrate, and the total area of pores larger than 1.4 nm is occupying the area of $5.21 \text{ m}^2/\text{g}$, whilst in the

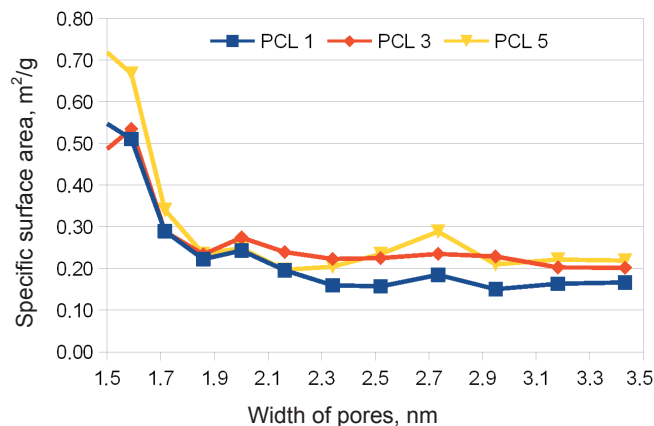


Fig. 4. The specific surface area of pores determined with the FTF method in an incremental way for the samples of fibers obtained from a mixture of formic acid and acetic acid with: 1% addition of AgNO_3 (PCL 1), 3% addition of AgNO_3 (PCL 3), 5% addition of AgNO_3 (PCL 5)

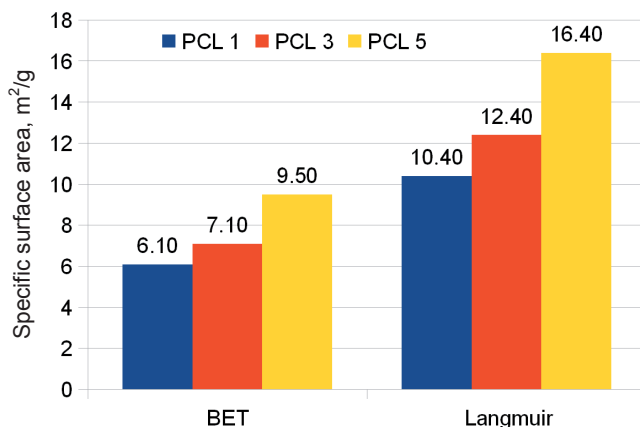


Fig. 5. The specific surface area calculated with BET method and Langmuir method for the samples of fibers obtained from a mixture of formic acid and acetic acid with: 1% addition of AgNO_3 (PCL 1), 3% addition of AgNO_3 (PCL 3), 5% addition of AgNO_3 (PCL 5)

largest samples, the area of $0.76 \text{ m}^2/\text{g}$ s occupied by pores with the diameter of 1.57 nm.

As the fraction of silver nitrate is growing, so is growing the BET and Langmuir specific surface area, due to the presence of silver and its aggregates on the surface of samples (Figs. 6-8).

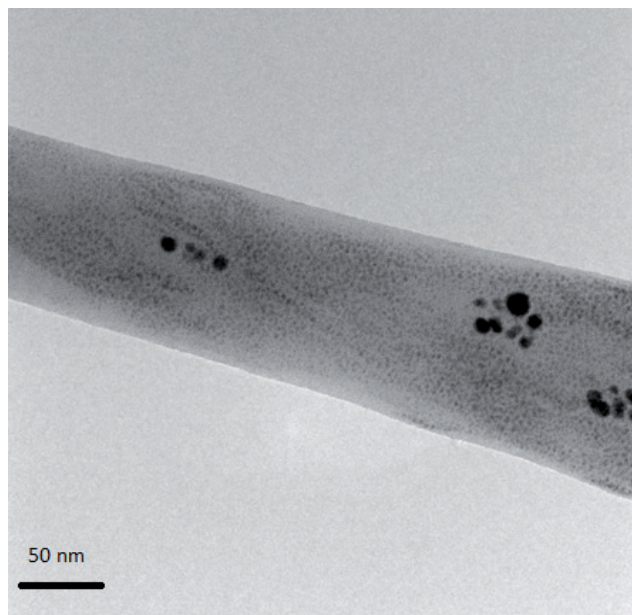


Fig. 6. Geometrical characteristics of composite fibers with 1% addition of silver nitrate; a photograph taken after precipitation of silver with a 2% ascorbic acid solution (TEM)

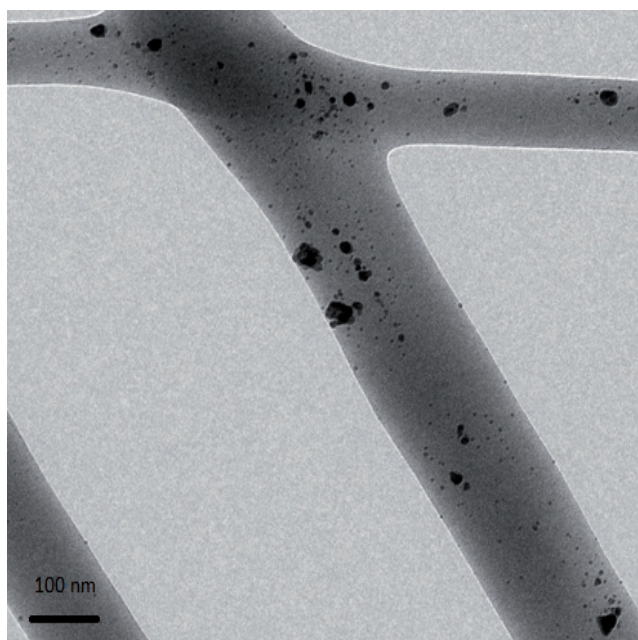


Fig. 7. Geometrical characteristics of composite fibers with 5% addition of silver nitrate; a photograph taken after precipitation of silver with a 2% ascorbic acid solution (TEM)

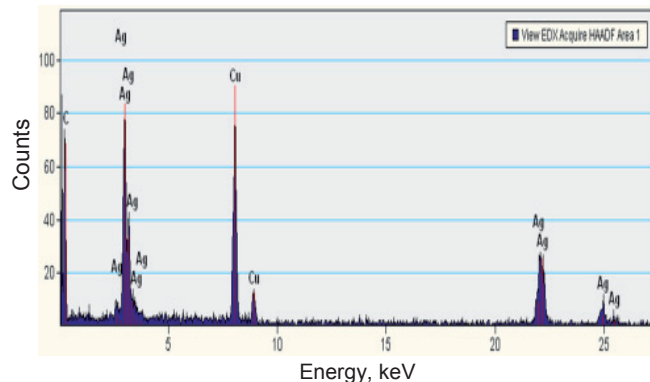


Fig. 8. EDX for composite nanofibers containing silver on the surface, peaks for copper derive from the copper support mesh applied

The investigations into antimicrobial properties of nanofibers with a 0-5% fraction of silver nitrate additives undertaken using Gram+ bacteria (*Staphylococcus aureus*), Gram- (*Escherichia coli*) and fungi (*Candida albicans*) show increased efficiency of antimicrobial activity of the nanofibers achieved as the fraction of the introduced silver nitrate additives is growing (Fig. 9). Positive and negative controls yielded expected results.

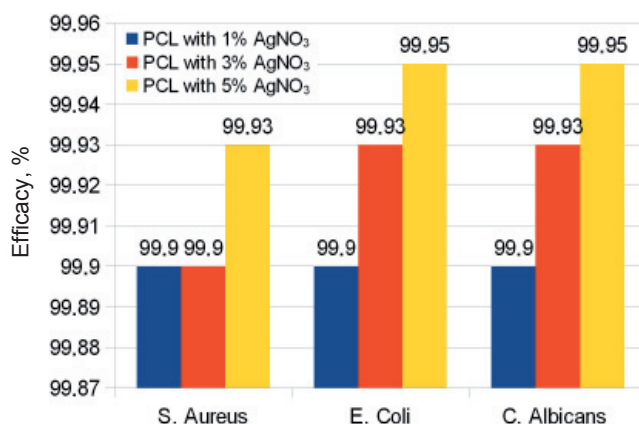


Fig. 9. Average efficiency of antimicrobial activity of nanofibers with 1-5% addition of silver nitrate in relation to Gram+ bacteria (*Staphylococcus aureus*), Gram- bacteria (*Escherichia coli*), and fungi (*Candida albicans*), after 17 hours of incubation

4. Conclusions

It was demonstrated based on the investigations conducted that the use of a formic acid and acetic acid solution at a rate of 70:30 for preparation of a polycaprolactone solution for its electrospinning enables to obtain a non-toxic and fully biodegradable polymer nanofibers of polycaprolactone with PCL/Ag silver precipitations. As the fraction of silver nitrate precipitated as silver on the surface of polycaprolactone nanofibers is growing, so is growing the surface area of the nanofibers obtained. Polycaprolactone nanofibers with PCL/Ag silver precipitations possess high antimicrobial performance against Gram+, Gram- bacteria and fungi. The combination of high electrospinning efficiency, intoxicity of the solvents employed and a broad spectrum of antimicrobial activity of the examined additive of silver nitrate points out it is feasible to employ composite materials in the field of medicine. For this reason, they can be applied in biodegradable antiseptic dressings in the form of mats or other textiles containing polymer polycaprolactone nanofibers with PCL/Ag silver precipitations obtained as a result of electrospinning.

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