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PRODUCING OF NONWOVEN MATERIALS BY ELECTROSPINNING THE BIOCOMPATIBLE POLYMERS WITH CHITOSAN ADDITION

Об'єктом дослідження є біосумісні композиційні нановолокнисті неткані матеріали з антисептичними властивостями, отримані методом електроформування. Одним з найбільш проблемних місць є створення нетканого біосумісного композиційного матеріалу з бактерицидними властивостями, що раніше не перероблявся в волокна способом електроформування через високі енергетичні і фінансові витрати.

В ході дослідження використовувалися композиції біосумісних полімерів: хітозану, полівінілацетату (ПВА) та полівінілового спирту (ПВС). Запропоновано для отримання нетканих полімерних матеріалів метод електроформування на лабораторній установці капілярного типу, з подачею розчину «знизу-вгору».

Отримано біосумісні композиційні неткані матеріали з антисептичними властивостями. Це повязано з тим, что запропонований метод електроформування дозволяє отримати неткані матеріали з певними розмірними характеристиками волокон при введенні в композицію розчину хітозану в молочній кислоті. Зокрема, для композиції на основі ПВА частка волокон з діаметром 0,5–0,62 мкм зросла на 9 %, а для композицій з ПВС – зменшилася на 21 %. Встановлено оптимальну напругу електричного поля 30 кВ та відстань між електродами 9–11 см для отримання волокон із біосумісного ПВС та ПВА з додаванням хітозану.

В результаті досліджень морфологічних особливостей отриманих волокон методом оптичної поляризаційної мікроскопії доведено, що при визначених параметрах електроформування отримуються волокна з діаметром від 0,5 до 1,6 мкм. В результаті визначення статистичного розподілу полімерних волокон у нетканому матеріалі за діаметром встановлено, що 69–94 % волокон мають діаметр 0,5–0,72 мкм.

Частина волокон, отриманих на лабораторній установці капілярного електроформування, відповідають області нанорозмірів, що відкриває перспективи отримання біосумісних нановолокон з антисептичними та фунгіцидними властивостями. Тому виробництво полімерних біосумісних нетканих матеріалів методом електроформування можна використати при створенні терапевтичних систем.

Ключові слова: *метод електроформування, біосумісні волокна, неткані матеріали, полімерні волокна.*

1. Introduciton

Electrospinning of composite nonwoven materials is a progressive technology that allows to process solutions and melts of various polymers, allows for a wide variation of technological parameters of production, and also favorably differs by the flexibility and simplicity of instrumentation [1, 2]. Promising is the use of the electrospinning method for the production of materials for sanitary and hygienic, biomedical purposes and consumer goods [3]. In this regard, it is relevant to study the laws governing the production of nanofibers from various polymers and their mixtures by the electrospinning method and determining the areas of their application.

2. The object of research and its technological audit

The object of research is biocompatible composite nonwoven nanofiber materials with antiseptic properties, obtained by the electrospinning method.

Using the electrospinning method, nonwoven materials can be obtained for therapeutic systems with a large specific surface and air permeability.

And the addition of chitosan to the polymer composition for electrospinning will make it possible to obtain complexes with drugs and to increase the efficiency of treatment of infected wounds [4, 5]. Fig. 1 shows a schematic diagram of a capillary type laboratory device for performing electrospinning processes.

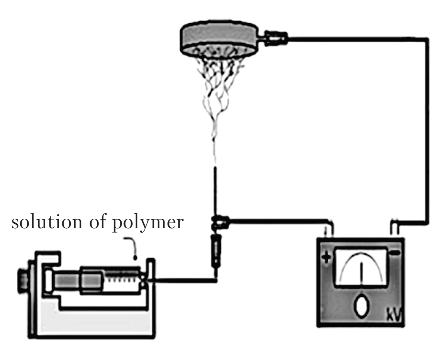

Fig. 1. Diagram of a capillary device for electrospinning processes

The advantage of fibrous materials obtained by electrospinning technology, lies in the narrow distribution of fibers in diameter. This ensures the production of products with predictable properties.

In contrast to all other methods of obtaining nano- and submicro-fibers, electrospinning is the most productive process, which has the potential on an industrial scale both

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in capillary and in non-capillary technology [6]. Although the theoretical rationale for these promising technologies is not enough.

It is of interest to study the possibility of using electrospinning for processing biocompatible polymers with the addition of bactericidal and fungicidal preparations. They were not processed by this method into fibers before, because they required very high energy and financial costs for such processing.

3. The aim and objectives of research

The aim of research is development of a technology for producing biocompatible composite polymer nanofiber nonwoven materials using the capillary type electrospinning method.

To achieve this aim it is necessary to solve the following tasks:

1. To determine the effect of the technological parameters of electrospinning for the compositions of chitosan with polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) to obtain nonwoven fibrous materials with predictable properties.
2. To investigate the morphological features of the fibers obtained by optical polarization microscopy.
3. To determine the statistical distribution of polymer fibers in nonwoven material in diameter.

4. Research of existing solutions of the problem

There are many ways to manufacture drugs and biologically active substances based on biocompatible polymers in the form of therapeutic systems. The use of nano-sized polymer fibers is also possible for drug delivery [3]. It is known that when administered orally, patients are forced to take much more than necessary, their number. Possible external use in the form of dressings applied to wounds or to open skin to protect them from possible adverse environmental effects with simultaneous continuous therapy with nanoparticles of a therapeutic substance [7].

A widely used approach is based on the placement of nano-sized drug particles in nonwovens from nanofibers during stenting. Stents are coated with several layers of nanofibers containing drug particles, resulting in its long-term release.

In this regard, the global trend of the production technology of innovative fibrous materials is reducing the diameter of the filaments to micro- and nano-dimensions [8, 9]. The following technologies are used to form ultrafine fibers: spraying, aerodynamic spraying of polymer melt and electrospinning.

Electrospinning technology allows to obtain new fibers with a controlled porous structure [10]. It is known that this method successfully processes synthetic polymers, polylactide (PLA), polyglycolic acid (PGA), polycaprolactone (PCL), polydioxanone (PDO), polyvinylpyrrolidone (PVP), polystyrene (PS) and others [11]. A wide range of natural polymers, including collagen, elastin, silk and fibrinogen, as well as mixtures of natural and biocompatible synthetic polymers, are also used for electrospinning [12].

Chitosan is soluble in acetic, formic and lactic acids. Lactic acid and its salts are widely used in the manufacture of various cosmetics due to their strong biological and antibacterial effects. It is able to penetrate the epidermal barrier and actively influence the physiological processes in all layers of the skin by stimulating reparative processes in response to damage by a bactericidal effect.

Chitosan has various physico-chemical and biological properties, leading to numerous applications in such areas as waste and water purification, agriculture, light industry as a dressing agent, cosmetics, food industry [13].

Biocompatibility, biological destructiveness and biological activity of chitosan, as well as the absence of toxicity and allergenicity make it a very attractive substance for various applications as a biomaterial in the pharmaceutical and medical fields [14].

Chitosan promotes wound healing, bone regeneration, has analgesic and antimicrobial effects, and is used for the delivery of drugs and vaccines in veterinary medicine [15].

Chitosan film with the addition of cumin oil is known, which have antimicrobial and antioxidant properties [16].

The results of the development [17] of the technological bases of non-spinneret electrospinning of chitosan-containing nanofiber materials for mixed solutions of chitosan and PVA in 30 % acetic acid containing ethanol are known.

PVA and PVAc are widely used in many areas, in particular in medicine and pharmacology [7, 10]. The choice of PVA and PVAc is due to their basic properties. These polymers are physiologically neutral substances, completely non-toxic, odorless, well tolerate exposure to solvents, fats and oils. They have high tensile strength and flexibility, exhibit film-forming properties.

Thus, the results of the analysis allow to conclude that chitosan, PVA, and PVAC can be used as part of a composition for electrospinning as the polymer and film-forming polymers. This will ensure the biological destruction, the sorption and hemostatic properties of fibrous materials for the therapeutic systems.

5. Methods of research

The use of chitosan (CAS No. 9012-76-4) with the addition of 8–10 % solution of polyvinyl alcohol (PVA) brand PVA-17-99 and PVA (CAS No. 9003-20-7) is investigated in the research.

A 10 % solution of chitosan in lactic acid (60 % CAS No. 50-21-5) was prepared and the compositions were examined in the ratio of chitosan:PVA (1:1), chitosan:PVAc (1:1). The rheological properties of the studied samples were studied using a Brookfield DV-III rheometer using the SC4-27 (USA) thermal platform of the block with a temperature interval of 20–22 °C.

Composite nonwoven materials were obtained by electrospinning on a bottom-up capillary installation with an electric field voltage of 30 kV and a capillary diameter of 0.7 mm.

To study the morphological features of the obtained fibers, let's the method of optical polarization microscopy (Biolam C-11 microscope, Russia) were used. To determine the dimensional characteristics of the fibers, a method of analyzing digital images was used followed by statistical processing of the obtained data.

6. Research results

Composite nonwoven materials from chitosan with the addition of polyvinyl acetate and polyvinyl alcohol are

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obtained using a laboratory unit for electrospinning. It is found that chitosan, as an independent polymer is not formed. Therefore, it is used as film-forming polymers of PVA and PVAc.

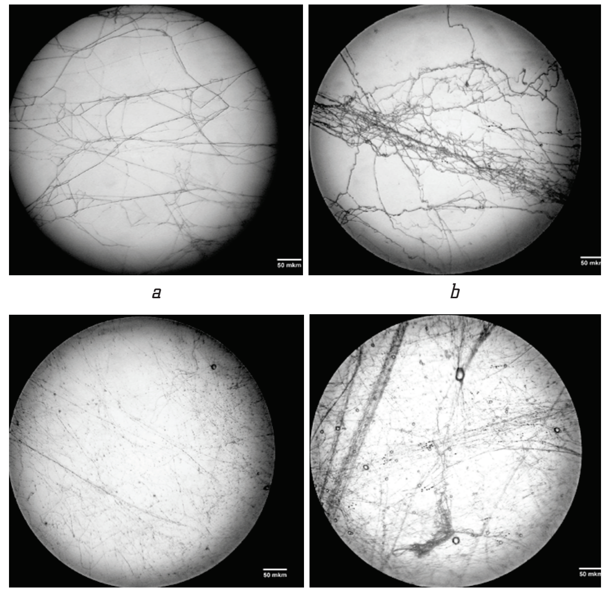
It is found that to obtain homogeneous materials, the viscosity of the solution of the composition should be in the range of 0.4 to 0.9 Pa·s. In the specified viscosity range of the solution, stable structures with dense weaves of fibers are formed. The optimal distance between the electrodes is 9–10 cm.

Fig. 2 shows the process of splitting the solution from the capillary into fibers and nonwoven material.

a *b*

Fig. 2. The process of splitting the solution from the capillary to: *a* – fibers by electrospinning; *b* – obtained fibers

Fig. 3 shows the micrographs obtained on an optical microscope «Biolam C-11» in polarizing light, fibers with PVA and PVAc and compositions based on them with the chitosan addition. The structure of the obtained materials is without noticeable defects.



a *b* *c* *d*

Fig. 3. Micrographs of nonwoven fibrous material obtained by the method of optical polarization microscopy (microscope «Biolam C-11»): *a* – polyvinyl acetate; *b* – polyvinyl acetate with chitosan; *c* – polyvinyl alcohol; *d* – polyvinyl alcohol with chitosan

Fig. 4 shows diagrams of the statistical distribution of the diameters of fibers with PVA and PVAc and compositions based on them with the chitosan addition.

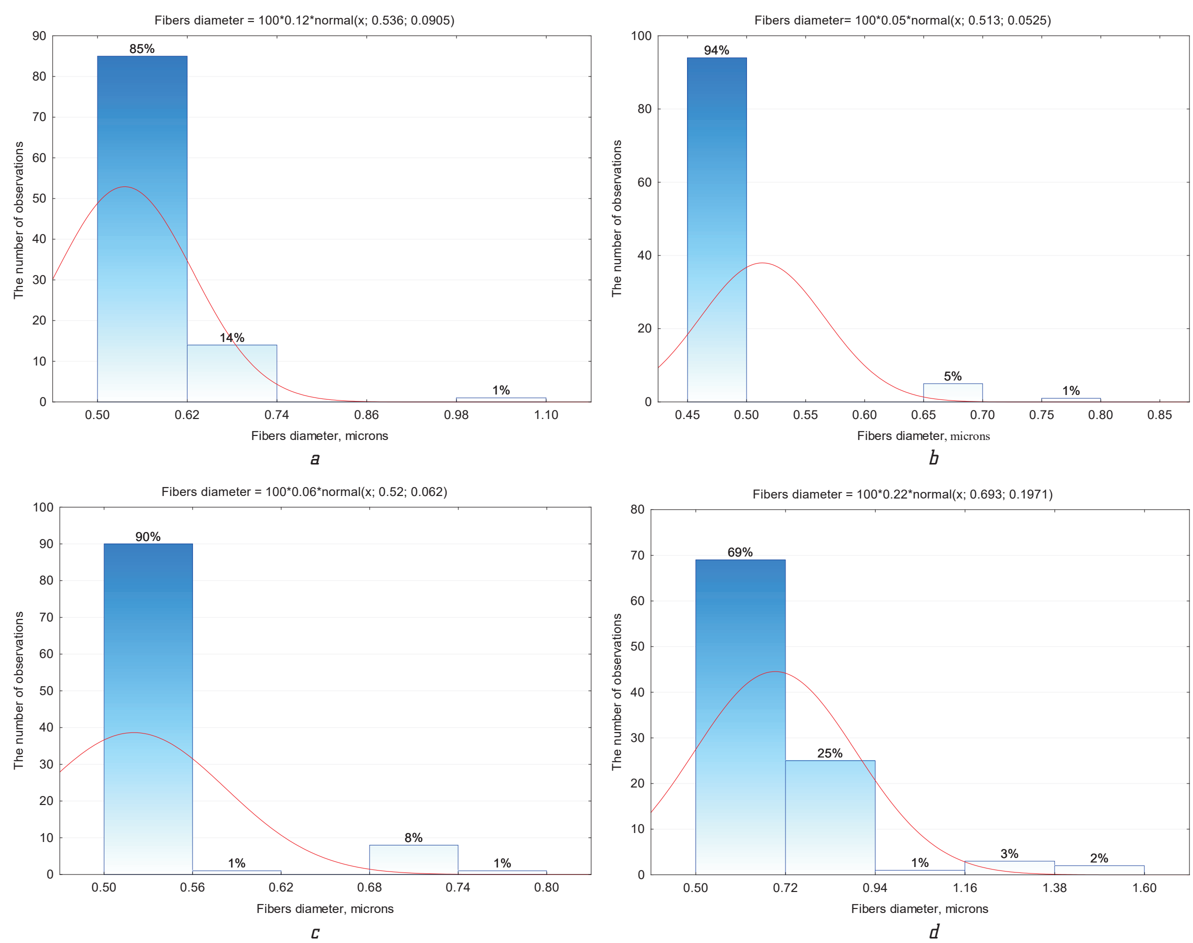


Fig. 4. Diagrams of statistical distribution of fiber diameters: *a* – polyvinyl acetate; *b* – polyvinyl acetate with chitosan; *c* – polyvinyl alcohol; *d* – polyvinyl alcohol with chitosan

As a result of determining the statistical distribution of polymer fibers in a nonwoven material by diameter, it is found that 69–94 % of the fibers have a diameter of 0.5–1.6 μm, depending on the composition of the solution.

As a result of the research, it is established that the composition of the polymer composition affects the fiber diameter and statistical distribution. For compositions based on:

– PVA 85 % of fibers with a diameter of 0.5–0.62 microns;

– PVA with the addition of chitosan 94 % of fibers with a diameter of 0.5 microns;

– PVAc – 90 % of fibers with diameters of 0.5–0.56 microns;

– PVAc with chitosan – 69 % of fibers 0.5–0.72 microns.

Part of the fibers obtained in the laboratory device of capillary electrospinning corresponds to the area of nano-dimensions, which opens up prospects for obtaining biocompatible nanofibers with antiseptic properties.

7. SWOT analysis of research results

Strengths. The strength of the developed electrospinning method is the possibility of obtaining nonwoven materials with nanoscale diameters of fibers with special properties.

Weaknesses. The disadvantages of the electrospinning method by the capillary method are low productivity. The use of a non-capillary formation can improve productivity.

Opportunities. A part of the fibers obtained in the laboratory installation of capillary electrospinning correspond to the area of nano-dimensions, which opens up prospects for obtaining biocompatible nanofibers with antiseptic and fungicidal properties. Therefore, the production of polymer biocompatible nonwovens by electrospinning can be used to create therapeutic systems.

Threats. The widespread introduction of developed technologies into production is hampered by the absence of Ukrainian equipment and at the same time the high cost of imported equipment. In addition, the specificity of the properties of the obtained materials requires additional conditions for their production and use, for example, the presence of a «clean room» in production or laboratory rooms.

8. Conclusions

1. The processes of obtaining nonwoven composite polymeric materials by the electrospinning method on a laboratory installation of capillary type are investigated. The parameters for obtaining fibers from biocompatible polyvinyl alcohol and polyvinyl acetate with the addition of chitosan are determined. The optimum voltage of the electric field is 30 kV and the distance between the electrodes is 9–11 cm.

2. As a result of research of the morphological features of the obtained fibers by the method of optical polarization microscopy, it is proved that with certain parameters of electrospinning, fibers with a diameter of 0.5 to 1.6 microns are obtained.

3. As a result of determining the statistical distribution of polymer fibers in nonwoven material by diameter, it is found that 69–94 % of fibers have a diameter of 0.5–0.72 microns, depending on the composition.

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