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Obtaining New Biopolymer Materials by Electrospinning

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Abstract
The paper covers aspects of the technology of fibre electrospinning for the production of nonwoven fabrics for various application areas. The conditions of forming nano- and microfibres from solutions of collagen hydrolyzate and dibutyrylchitine were studied as well as polymer-polymer complexes based on polyacrylic acid, polyvinyl alcohol and polyethylene oxide. A comparative analysis of different methods of electrospinning – electrocapillary, electric and Nanospider™, was conducted. Promising application areas of non-woven fabrics in medicine sanitation as well as for clothing and footwear production are shown.

Key words: *fibres electrospinning, collagen hydrolyzate, biopolymer materials, chitosan.*

Introduction

In the modern world there has been a steady trend towards an increase in the production and consumption of products and materials that contain natural biodegradable polymers.

Over the last five years, the largest producers and consumers of biopolymers have been such Western European companies as NatureWorks (Cargill), Novamont, Innovia Films and Arkema. They accounted for 53% of the total global demand, which in 2015 reached approximately one million tons (the profit from production reached USD 2.9 billion) [1].

The increase in demand will occur due to consumers' preferences for more environmentally friendly materials, a gradual decrease in the cost of biopolymer production, as well as a simultaneous increase in the cost of traditional synthetic material manufacture. According to some researchers, starting from 2015, the dominance of biopolymers on the world market has been moving from the United States and Western Europe to the Asia-Pacific Rim. By 2020, in the Asia-Pacific Rim countries, the demand will be 875 thousand tons per year. [2].

Large-tonnage biodegradables materials include polymeric materials based on starch and its derivatives, collagen, modified polyvinyl alcohol, polyacrylic acid, polydioxanone, chitosan and its derivatives.

According to experts in 2005, the estimated global production of chitosan only from marine organisms amounted to 109 tons per year. This fact shows the high importance of this oceanic fauna as an industrial source of chitin. Global industrial production of chitosan, the most examined derivative of chitin, amounts to thousands tons per year [3].

The original method of synthesis of dibutyrilchitin (DBC), the soluble derivative of chitin, was developed by the Engineering Institute of Polymer Materials and Dyes (Torun City, Poland) in cooperation with Lodz University of Technology (Poland) [4, 5]. The suggested method is used for chitin of different origin (crabs, shrimps, krill, insect chitin), which makes it possible to manufacture products with a specific chemical structure and degree of esterification. Dibutyrilchitin is easily soluble in common organic solvents, and these solutions have good fibre- and film-forming properties [6]. Such properties of dibutyrilchitin enable the production of a wide range of biomaterials suitable for medical use: films, fibres, fibre-bonded materials and knitted fabrics. In accordance with the European Standards EN ISO 10993, studies of the biological properties of dibutyrilchitin-based products have shown their good biocompatibility and ability to accelerate wound healing [7-9].

One of the natural polymers is collagen (collagen dissolution products). Collagen combines the positive qualities of a synthetic polymer and biological tissues, and at the same time, it is deprived of a number of their negative properties. The complete absence of toxicity and carcinogenicity, weak antigenic properties, the ability of this biopolymer to stimulate reparative processes in the tissue and to form stable complexes with a wide range of medicinal substances, as well as its sorption and plastic properties define the wide usage in various fields of medicine [10].

The first attempts of scientists – biotechnologists and chemists of Gdansk University to obtain a collagen extract from marine fish go back to the mid 70-ies of the XX century. The joint work of Polish scientists and research of a team of experts in biotechnology from the Inventia company led to the patenting of a unique

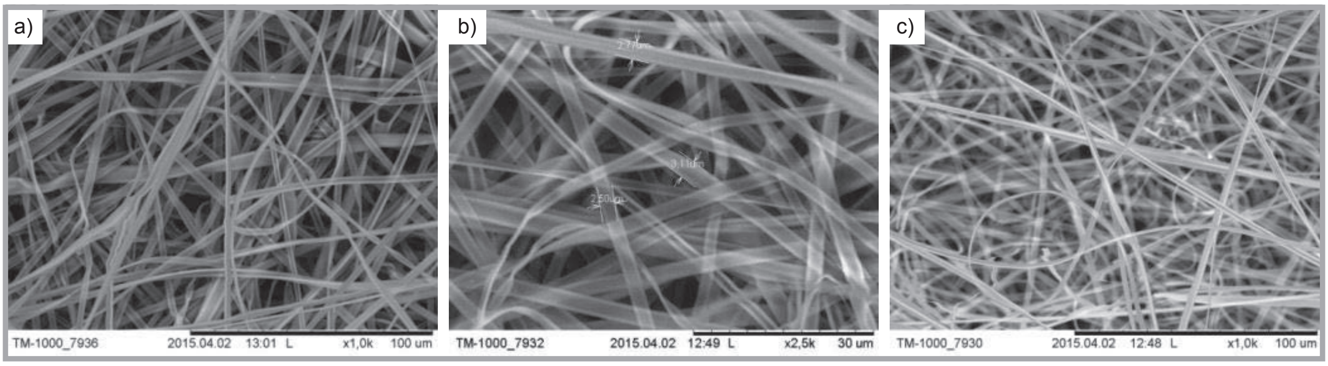

Figure 1. *Photomicrographs of fibres obtained by the FME method made from 8% ethanol solution of DBC: a) by electrocapillary method (magnification 1,000 times), b) by electric centrifugal method (magnification 2,500 times), c) by Nanospider™ technology (magnification 1,000 times).*

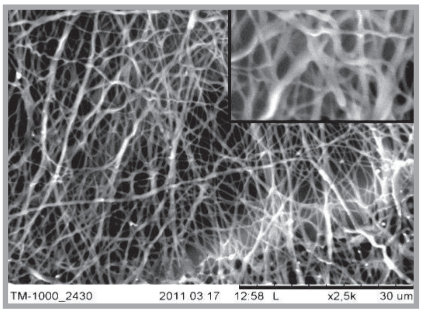

Figure 2. *Photomicrographs of fibres obtained by the Nanospider™ method from PVA – PCD – PEO solution mixture (exaggeration in 2,500 times).*

innovative technology for obtaining raw materials with a molecular mass of the native 3D-collagen molecule which is equal to about 340 kDa [11].

All of the aforesaid allows for the conclusion that the partial replacement of synthetic biopolymers by natural polymers (compostable and biodegradable) enables to obtain materials with a specific structure and properties, and further create products working in close contact with the human body.

One of the most advanced technologies for the above-mentioned material's production is the process of fibrous material electrospinning (FME) from polymer solutions and melts. Nowadays this method is one of the most promising for obtaining unique nano- and microfibrous structures to create so-called "smart textiles" – or "smart" materials in general.

Recently the issue of expanding the spheres of application of fibre-bonded fibrous materials obtained by the electrospinning method has become urgent. As a consequence new polymers (polymeric pairs): chitosan, ester chitin derivatives (dibutyrilchitin), collagen dissolution products, polyether, polyacrylic acid, interpolymer complexes of different composition and structure, and others are involved in the manufacturing process.

The aim of the work was to obtain fibre-bonded fibrous materials from biopolymers solutions and their mixtures with complex-creating water-soluble polymers by the electrospinning method in order to create products for sanitary purposes.

Experimental

Materials

The objects of study in this paper were dibutyrilchitin with a molecular weight of 132×10^3, the product of collagen dissolution in acetic acid (PCD) with a molecular weight of 3×10^5, polyvinyl alcohol (PVA) with a molecular weight of 7×10^4 and degree of hydrolysis of 87%, and polyethylene oxide (PEO) with a molecular weight of 1×10^6.

Methods

The dynamic viscosity of the spinning solution was determined by means of a viscometer – Brookfield DV-II-Pro (USA), the specific volumetric electrical conductivity – using a conductivity meter – Expert-002 (Russian Federation). Studies of the structure of fibre-bonded and individual fibres were carried out on a scanning electron microscope – Hitachi TM 1000 (USA). The electrospinning of biopolymers solutions was carried out at the Research Institute of Physical Chemistry n.a. L.Ya. Karpov.

Electrospinning was composed of 8% solution of dibutyrilchitin with an ethanol and n-propanol mixture (viscosity of the spinning solution – 0.4-0.8 Pa × s, electrical conductivity – 20-25 μS/cm, surface tension – 20-22 mN/m).

The process was carried out both by capillary, electro aerodynamic, electric-centrifugal and non spunbonded methods on a Nanospider™ unit.

Results and discussion

The work confirmed previous results [12, 13] for the good fibre-forming ability of DBC in a wide range of volume flow from 1 to 50 ml/hour, and the possibility of obtaining materials based on its fibres with a diameter from 150 to 300 nm.

For the first time attempts at dibutyrilchitin solution electrospinning in different ways were made. The possibility of obtaining fibres with all the known methods of the FME process was shown. It was proved that both the solvent composition and the way the process is implemented affect electrospinning productivity as well as the fibre diameter and the structure of the fibre-bonded materials (***Figure 1***).

From the literature data it is known that solutions of rigid-chain biopolymers such as chitosan, cellulose and collagen cannot be formed using FME technology without adding high molecular additive promoting fibreising. When forming nanofibres from collagen solution products, mixture compositions PCD – PVA – PEO were used, where PVA was a high molecular collagen plasticiser [14], and PEO – additive improving electrospinning.

While forming a mixture of 7.5% solution of PVA with 2.3% solution of PCD, a ratio of 50:50 was used. The number of polyethylene oxide was 10% by weight of the mixture of PVA – PCD. The process of electrospinning was carried out with Nanospider™ technology under the following conditions: viscosity of the solution – 0.6 Pa × s, electrical conductivity – 60 mS/m, and surface tension – 45 mN/m. Photomicrographs of the nanofibres are shown on ***Figure 2***.

The diameter of fibres obtained from collagen solutions was on average from 300 to 500 nm.

Comparing dibutyrilchitin with the collagen dissolution product, from the point of view of the ability to fibreize as well as the technological features of the electrospinning process, it is possible to note that DBC is capable of fibreizing by any method using FME technology, and there are practically no defects in the structure of nanofibres (drops, thickenings). Blend compositions containing collagen are rather difficult to recycle by the electrocapillary method because of the poor degree of solution dispersion, which leads to capillary aperture "plugging".

Preliminary experiments showed the possibility of combining the two technological spinning solutions of collagen and dibutyrilchitin. It was established that during the processing of blend compositions by Nanospider™ technology, it is possible to obtain fibres with higher capacity as well as with different diameters (from nano- to submicro- and microfibres). The use of blend compositions represents significant scientific interest and opens up broad prospects for the development of materials combining the wound healing (reparative) properties of dibutyrilchitin and the sorption plastic properties of collagen, including its ability to form stable complexes with a wide range of drugs.

Conslusions

In general, the studies conducted have shown the potential of electrospinning technology for biopolymers and blend composition processing. Using different methods of electrospinning (capillary, electro-aerodynamic, electric centrifugal and non-spunbonded) allows to directionally regulate the structure and properties of nano- and microfibres in order to produce fibre-bonded fabrics for hygiene and sanitary products and medical devices.

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