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Article

Formation of Cellulose Nanofibers from Cellulose Diacetate via Electrospinning

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Abstract: The study explores the production of nanofibers from cellulose diacetate (CDA) dissolved in acetone-water mixtures via electrospinning, with acetone-to-water ratios of 95:5, 92.5:7.5, and 90:10. It demonstrates the saponification of CDA nanofibers in potassium hydroxide to obtain cellulose II nanofibers, analyzed using IR spectroscopy and X-ray diffraction. Optimal conditions for electrospinning were identified with a 10% CDA solution in acetone containing 10% water, producing uniform nanofibers with diameters of 90–550 nm. Alkaline hydrolysis of CDA nanofibers yielded cellulose II nanofibers with an average diameter of 350–400 nm and improved crystallinity. These cellulose II nanofibers, with high swelling capacity and potential for applications in air filters and biodegradable medical materials, were characterized by their large surface area and mechanical properties. The findings offer insights into the processing parameters and potential uses of cellulose nanofibers, filling a knowledge gap in the efficient production and application of biodegradable nanomaterials.

Keywords: Electrospinning, Nanofibers, Cellulose Diacetate, Cellulose II, IR Spectroscopy, X-Ray Diffraction Analysis.

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1. Introduction

In recent years, the electrospinning technique has been widely used in the production of nanofibers based on synthetic and natural polymers and their derivatives. Currently, based on nanofibers, the possibility of producing filter materials, composite materials, scaffolds for tissue engineering, biodegradable bactericidal coatings for surgery and medical products, protective clothing, and much more has been shown.

Among natural polymers, it is of great scientific and practical interest to study the possibility of obtaining nanofibers from ethers. Currently, there are known methods for producing nanofibers from di- and triacetyl cellulose and a number of other simple, complex, and mixed cellulose ethers.

Currently of particular interest is the study of the possibility of obtaining nanofibers based on cellulose. This is due to the fact that, due to the high hydrophilicity and large surface area of cellulose nanofibers, there is the possibility of their chemical modification as well as the possibility of their biodegradation.

This report presents the results of studies on the production of cellulose nanofibers based on cellulose diacetate (CDA).

It is known that CDA is highly soluble and forms stable, dilute, and concentrated

solutions in a number of organic solvents and their mixtures [1, 2].

2. Materials and Methods

For the electrospinning of nanofibers from CDA solutions, it is necessary to select an appropriate solvent that meets the requirements for the electrospinning of nanofibers from polymer solutions with at least the same volatility as water.

Cellulose diacetate with a degree of substitution or acetylation of 2,6 and a degree of polymerization of 400 from "Fergana Chemical Plant" LLC was selected as a research object. The main reagents used were purchased from Sigma-Aldrich: acetone (99,5%, cat. No. 179124); potassium hydroxide (KOH) (≥85%, cat. No. 1310-58-3); and to obtain distilled water, a DZ-10L11 distiller from "Huanghua Faithful Instrument Co" Ltd. was used.

Electroforming of CDA solutions of various concentrations containing different amounts of water was carried out on a NanoNC eS-robots device (NanoNC Co. Ltd., Korea) under the following the following conditions: voltage 22–25 kV, solution flow rate 10-15 μl/min, chamber temperature 25–40 °C, and distance between anode and cathode 10-15 cm.

The morphological characteristics of the surface of DAC nanofibers were studied using a scanning electron microscope (SEM) (SEM-EVO MA 10) (Germany). Experiments on a scanning electron microscope were carried out as follows: To carry out the sample preparation process, a round holder made of a metal alloy is glued, on top of which a carbon film with a double-sided adhesive surface is glued, onto which the sample is glued. During the measurement, an accelerating voltage (EHT, Extra High Tension) of 10.00 kV was applied, and the working distance (WD, working distance) was 8,5 mm. Images were acquired at various scales using Smart SEM software.

IR-Fourier spectroscopic studies of CDA nanofibers were carried out using an Inventio-S (Bruker) IR-Fourier spectrometer in the spectral range of 4000 ± 500 cm-1. X-ray diffraction analysis of CDA nanofibers was carried out on a Miniflex 600 device (Rigaku) at 40 kV and a current of 15 mA, range $2\theta = 5–44°$.

Based on the results of the studied solutions of CDA in their mixtures, acetone containing from 5% to 10% non-solvent water was chosen as a solvent.

3. Results and Discussion

It has been established that a high voltage is applied to a drop of a solution of CDA in acetone containing various amounts of non-solvent water, and the charge on the surface of the solution exceeds the surface tension of the solution drop; a thin stream is drawn out of the solution, which collects on a grounded electrode in the form of a plate after the solvent evaporates. It has been established that the diameter and morphology of the resulting CDA nanofiber are influenced by all variables of the electrospinning process, including the nature of the solvent and its composition, solution concentration, applied voltage, distance between the collector and its bip, as well as the rate of solvent evaporation [3].

It is known that in CDA solutions, macromolecules are never completely and perfectly molecularly dispersed but exist in the form of complex molecular associates, depending on the strength and quantity of intra- and intermolecular interactions [4–6].

Taking into account the above, we studied the rheological properties of CDA solutions of different concentrations in acetone containing different amounts of "non-

solvent" water. It is known that the structural viscosity of CDA depends on the degree of structuring and increases sharply with an increase in its molecular weight; the polarity of CDA depends on diacylation and the concentration of the solution in a given solvent, as well as the content of "non-solvent" water in the solvent-acetone. The value of structural viscosity (ηstr) also strongly depends on the nature of the solvent.

It has been established that with an increase in the concentration of CDA, the viscosity of the system increases significantly, and the dependence of the viscosity of solutions on the flow velocity gradient practically does not change and remains constant. The viscosity of CDA solutions, depending on the gradient of the viscous flow rate, changes with the water content in the solvent composition (acetone) and increases in the sequence 5:7,5:10%, regardless of the concentration of the CDA solution. Thus, for the electrospinning of CDA solutions of various concentrations dissolved in acetone containing "non-solvent" water in the range of 5–10%. Based on the results of a study of their rheological properties, a 10% solution prepared in acetone containing 10% water was selected. [7-9]

In Fig. 1, SEM micrographs of nanofibers obtained by electrospinning 10% CDA solutions dissolved in acetone-water mixtures of various volume ratios are presented.

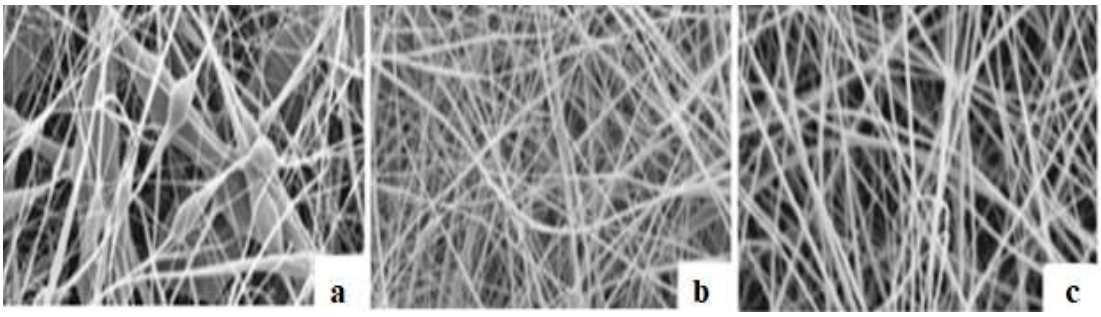

Figure 1. SEM micrographs of nanofibrous nonwoven fabrics obtained from 10% CDA solutions containing 5% (a), 7,5% (b) and 10% (c) water in acetone.

As can be seen from fig. 1(a), CDA nanofibers have a heterogeneous composition in diameter containing elongated beads at a water content of 5% in acetone, which is apparently explained by the resistance of the solution jet to the stretching flow during the electrospinning process. When the water content in acetone increases to 7,5% in a 10% CDA solution, more uniform nanofibers with a diameter of 90–430 nm are observed in SEM images of nanofibers. At the same time, almost 50% of the fibers had a diameter of 250 nm.

By increasing the water content to 10% in a 10% CDA solution, defect-free homogeneous nanofibers with a diameter of 90–550 nm were obtained by electrospinning.

Thus, optimal conditions have been established for the formation of nanofibers from 10% solutions of CDA dissolved in acetone containing 10% water with a smooth, relatively hydrophobic surface with an average diameter of 90–550 nm. [10-13]

Next, we investigated the possibility of obtaining cellulose nanofibers based on CDA nanofibers. It is known that to obtain cellulose nanofibers, it is necessary to select direct solvents that meet the requirements of electrospinning. Known direct solvents for cellulose often have a complex structure; their evaporation temperature is quite high, and solutions of cellulose in known complex solvents do not meet the basic requirements of electrospinning. Taking into account the above, we investigated the possibilities of obtaining cellulose nanofibers based on CDA nanofibers.

CDA was obtained by the partial alkaline hydrolysis of triacetylcellulose in an alkaline medium. Under heterogeneous conditions, CDA with a degree of acetylation of 2,4–2,6 were obtained. [14-15]

We have investigated the possibility of producing hydrated cellulose nanofibers by alkaline hydrolysis of non-woven CDA nanofibers in an alkaline medium. To obtain hydrated cellulose nanofibers, non-woven webs of CDA nanofibers were kept in water at a temperature of 25°C for 12 hours. Next, the canvases were subjected to diacetylation in a 0,1 M aqueous solution of potassium hydroxide at a temperature of 35°C for 1 hour. The diacetylation reaction of CDA nanofibers proceeds at a fairly high speed due to their large surface area, and at the end of the reaction, CDA nanofibers with an acetylation degree of 2,6 are formed into cellulose nanofibers containing 4-6 residual acetyl groups per 100 anhydroglucose units of the cellulose macromolecule. The resulting cellulose nanofibers with an average diameter of 600–650 nm swollen in a pure environment of 270–20%.

IR spectroscopic studies of nanofibers and their hydrolysis in an alkaline medium contribute to the study of the mechanisms and kinetics of the saponification reaction of acetyl groups and changes in the content of CDA ester bonds. Comparative studies of the IR spectra of CDA and cellulose obtained by hydrolysis of CDA nanofibers in an aqueous solution of potassium hydroxide were carried out on an Inventio-S (Bruker) IR Fourier spectrometer in the spectral range of 4000 ± 400 cm-1, which are presented in fig. 2.

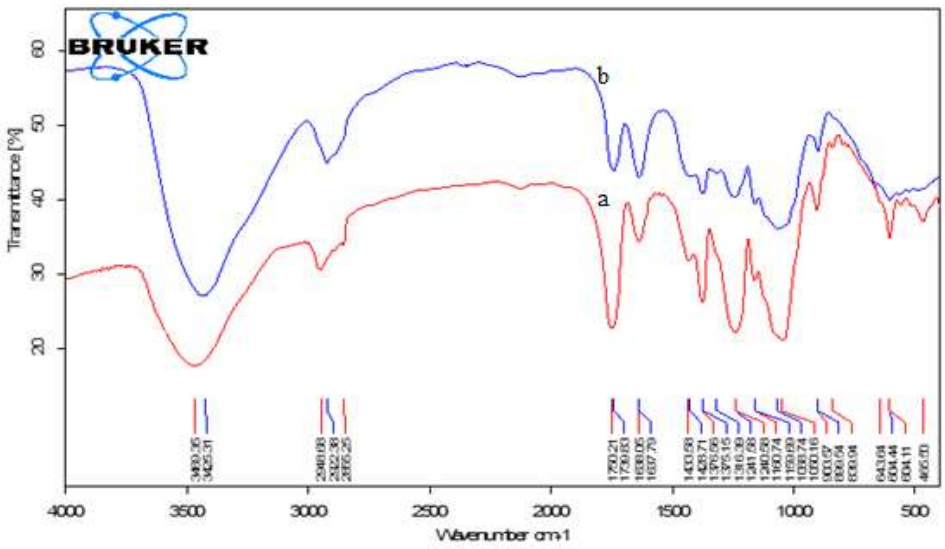

Figure 2. IR spectra of CDA nanofibers (a) and cellulose II nanofibers (b)

As can be seen from fig. 2 in the spectra of CDA nanofibers (a), there are intense bands at 3469, 2948, and 2855 cm-1 characterizing stretching vibrations of acetyl groups, bands at 1050 and 1240 cm-1 characterizing the ester bond, and bands at 1433 and 1376 cm-1 - deformation vibrations of acetyl groups are also visible groups. Intense bands at 1638–1750 cm1 are attributed to -C=O bonds of acetyl groups of CDA, and bands at 465.604 and 643 cm-1 are attributed to out-of-plane bending vibrations of -C-OH groups of CDA.

In the IR spectra of hydrated cellulose nanofibers obtained by alkaline hydrolysis of CDA nanofibers, fig. 2(b), less intense, in relation to the spectra of CDA, broad blurred bands at 2922, 1739, 1638, and 1428 cm-1 are observed, which are attributed to internal deformation vibrations of -CH2- in groups CH2-OH, at 1316 and 1375 cm-1 bending vibrations of -C-OH and -CH= groups, at 1241, 1159, and 1068 cm-1 stretching vibrations =C-O- and 604 and 899 cm-1 attributed to stretching vibrations of methylene groups and deformation vibrations of =CH- bonds of pyranose rings of elementary units of cellulose II.

Based on the results of the analysis of the IR spectra of CDA nanofibers and cellulose II, it was concluded that it is possible to study the mechanism and kinetics of the diacetylation reaction of CDA nanofibers to cellulose II nanofibers and to quantify the ester

bonds in the process of diacetylation of CDA nanofibers in an alkaline medium to cellulose II nanofibers.

Next, we carried out X-ray diffraction analysis of CDA nanofibers and hydrated cellulose nanofibers on a Miniflex600 device (Rigaku) at 40 kV and a current of 15 mA in the 2θ range of 3–40°.

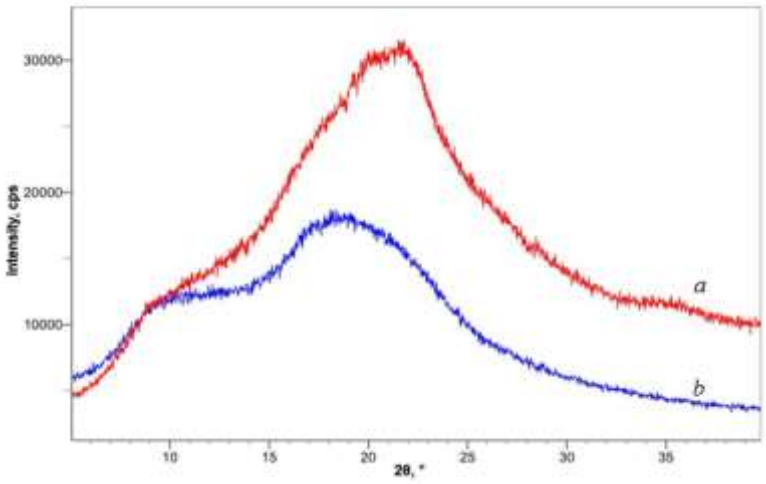

Figure 3. X-ray diffraction patterns of samples: a) CDA treated with KOH; b) CDA initial

A wide amorphous halo is observed in the diffraction patterns of the original CDA nanofibers, fig. 3 (b), which confirms the information about the absence of long-range order, which is apparently related to the values of the degree of substitution of acetyl groups in CDA macromolecules, which prevent the formation of oriented structures, and confirms the transition of CDA macromolecules to an amorphous form. As can be seen from the CDA diffraction pattern, the amorphous halo has a bimodal shape, and maxima are observed in the regions 2θ = 10° and 19°, which is apparently due to the formation of twisted amorphous structures in CDA nanofibers.

X-ray diffraction analysis of CDA nanofibers obtained by saponification in a 0.1 M solution of potassium hydroxide fig. 2 (a) shows that the occurrence of the diacetylation reaction leads to the formation of cellulose II nanofibers and the appearance of characteristic reflections of the crystalline structure of cellulose II, with a maximum at 2θ = 21°.

The increase in the degree of crystallinity of cellulose nanofibers compared to CDA nanofibers is apparently explained by their transition to an oriented state during the diacetylation of acetyl groups in CDA nanofibers.

Thus, the possibility of obtaining cellulose II nanofibers by diacetylation of CDA nanofibers in an alkaline medium has been demonstrated. The resulting samples of cellulose nanofibers had an average diameter of 350–400 nm and a residual content of 4-6 acetyl groups per 100 anhydroglucose units. The degree of swelling of cellulose II nanofibers in water was 270–20%. The resulting nanofiber nonwoven cellulose fabrics have unique properties due to their large surface area per unit volume and can be widely used in the creation of air filters and in the medical practice of biodegradable wound coverings with hemostatic and bactericidal properties. By chemically modifying cellulose nanofibrous webs, it is possible to significantly expand the range of their practical applications.

4. Conclusion

The conditions for obtaining cellulose diacetate nanofibers from acetone solutions containing 5, 7,5 and 10% water.

The possibility of obtaining cellulose II nanofibers from cellulose diacetate nanofibers by saponification of acetyl groups in an aqueous solution of potassium hydroxide has been demonstrated.

Comparative studies of the properties of cellulose diacetate and cellulose II nanofibers were carried out.

Possible areas of practical application of nanofibrous nonwovens made from cellulose II have been identified.

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