

NANOFIBER OF CELLULOSE AND ITS ACETATES

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Abstract

The properties of cellulose diacetate (CDA) solutions in solvent-acetone and acetone-water mixtures in the ratios 9.5:5, 93.5:7.5, and 90:10 were studied. Optimal concentrations of CDA solution were found at which the insoluble water content in acetone is 7.5%, exhibiting properties close to those of Newtonian solutions. CDA nanofibers were obtained in the form of nonwovens with an average diameter of 350–10 nm nanofibers. To obtain cellulose nanofibers, CDA nanofibers were hydrolyzed in a 0.1 M potassium hydroxide solution, and nanocellulose webs with a thread diameter of 350–400 nm and a degree of swelling in the water of 270% were obtained.

Keywords: cellulose diacetate, nanofibres, electrospinning, rheological properties, viscosity, thermodynamic properties, non-Newtonian liquids..

Introduction

Cellulose esters - diacetate (CDA) and cellulose triacetate (CTA) belong to the class of large-scale artificial polymers obtained from a renewable source of raw materials - wood and cotton cellulose. CDA and CTA are widely used to obtain a wide range of polymeric materials such as fibers, threads, textile materials, films, membranes, plastics, and other products for various purposes, and in the last decade - in the production of microfibers, proto membranes for biochemical chemical purposes, nanocomposite materials for microelectronics, specific optical elements. Despite this diversity, the possibility of creating new materials with unique properties based on cellulose acetates is not fully implemented. For example,

Products based on CDA and CTA are obtained from solutions or melts of cellulose acetates since their melting temperature is much higher than the temperature of intense thermal decomposition.

Phase analysis of systems CDA and CTA - a low molecular weight solvent makes it possible to predict its behaviour when one or another parameter changes, and knowledge of the mechanism of phase separation kinetics opens the way to a directed influence on the morphology of the system and, accordingly, to the creation of materials with desired properties [1, 2].

The research aimed to study the rheological properties of solutions and the possibility of forming nanofibers from CDA solutions by electroforming.

It is known that CDA is highly soluble and forms stable solutions in several organic solvents and their mixtures. [3,4] Unlike cellulose and its derivatives, CDA, considering its solubility in various organic solvents, can be used in electrospinning processes.

For electrospinning fibers from CDA solutions, it is necessary to choose an appropriate good solvent, at least as volatile as water. In this work, acetone was chosen as the solvent. When a high voltage is applied to a drop of a solution of CDA in acetone, and the charge on the surface of the solution exceeds the surface tension of the drop of the solution, a thin stream is drawn out of the solution, which is collected on a grounded electrode. It has been established that the diameter and morphology of the resulting fiber are affected by all the variable processes of electrospinning, including the nature of the solvent and its composition, and the concentration of the solution. the applied voltage, the distance between the collector and its type, as well as the rate of evaporation of the solvent [5].

There are works on the electroporation of CDA solutions in acetone containing a non-solvent, water [6-8], which mixes well with acetone but is not a solvent for CDA. The introduction of a solution of CDA + water helps to reduce the overall rate of evaporation of the solvent in the air gap of electrospinning, which positively affects the drawing of nanofibers and reduces the clogging of the “die”. Since the viscosity of CDA is determined by the nature of the polymer, the degree of polymerization and the degree of its deacetylation, the size, and shape of the macromolecule, the quality of the solvent, in this case, the content of water in acetone. The effects of the composition of the spinning solution on the change in their rheological characteristics were determined. CDA macromolecules are rarely completely molecularly dispersed in solution but exist in the form of complex molecular associates.

The aim of this study is to investigate the rheological properties of CDA solutions of various concentrations in acetone containing various amounts of “non-solvent” water for the formation of nanofiber by the method of electrospinning.

EXPERIMENTAL PART

Cellulose diacetate with a degree of substitution or acetylation of 2.6 and a degree of polymerization of 400 000 Ferghana Chemical Plant was chosen as the objects of research. The main reagents used were purchased from Sigma-Aldrich: acetone (99.5%, Cat. No. 179124); To obtain distilled water, a DZ-10L11 distiller from Huanghua Faithful Instrument Co., LTD was used.

In order to study the rheological properties and formation of nanofibers by electrospinning, a 5%, 10%, and 15% solution of DAC was prepared with a mixture of acetone-distilled water at a ratio of 95:5%, 92.5:7.5% and 90:10%. The behaviour of the solutions was studied in a shear flow generated in a system of coaxial cylinders on an MCR 92 Rheometer (Anton Paar, Austria) at a temperature of 25°C. The rheological data were processed using the RheoCompass software.

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

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 was made of a metal alloy, on top of which a carbon film with a double-sided adhesive surface was glued, on which the sample was 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. The image was acquired at various scales using the SmartSEM software.

RESULTS AND DISCUSSION

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 detailing and the concentration of the solution in a given solvent, as well as the content of “non-solvent” water in the acetone solvent. The value of structural viscosity η_{str} also strongly depends on the nature of the solvent. In all cases, the structural viscosity Increases with an increase in the energy of intermolecular interaction E_2 where:

$$E_2 \propto f(K, E, SP)$$

TO -structural factor which ranges from 1 code single crystal and 0- when highly dilute solution.

E - the energy of interaction of one unit of CDA with a solvent SP-degree of polymerization DAC.

When the solution is diluted, the flexibility of CDA macromolecules increases, since their vibrational and rotational movements are facilitated.

With an increase in the flexibility of the chains of CDA macromolecules, the structural factor K decreases, which leads to a decrease in the energy of intermolecular interaction E_2 . Factor K depends not only on the flexibility of CDA macromolecules but also on their packing density: it decreases in amorphous and increases in crystalline regions. The structure of the CDA macromolecule itself also has a great influence on the value of the K factor, primarily the regularity of the arrangement of acetate groups along the length of the macromolecular chain.

The process of transition of CDA to a viscous-flowing state as a result of its dissolution should not differ from the dissolution of low-molecular compounds. The dissolution of CDA can occur spontaneously only when the free energy of the system decreases, that is, ΔG_0 . This is achieved when ΔH and ΔS increase.

It is known that the structural viscosity of polymers depends on the degree of structuring and increases sharply with an increase in the molecular weight, the polarity of the polymer, and its concentration in solution, as well as with the addition of a "non-solvent", in the case of CDA water, acetone.

The value of structural viscosity η_{str} also depends on the nature of the solvent. Thus, in all cases, η_{str} increases with an increase in the value of E_2 since the structural viscosity itself is due to the intermolecular interaction of macromolecules in solution.

At $E_2 = 0$ the value $\eta_{str} = 0$.

When forming nanofibers from CDA solutions by electrospinning, it is necessary to study the rheological properties of the solutions, namely, the dependence of its viscosity on the nature of the solvent, the concentration of CDA in the solution, the molecular weight and molecular weight distribution of macromolecules in the solution, the change in the viscosity of CDA solutions over time, and the study of its viscosity from temperature.

An analysis of the rheological properties of CDA solutions depending on the specified parameters contributes to the choice of a CDA solution, based on which it is possible to form nanofibers with the necessary structures, physicochemical and physic mechanical parameters.

This report presents the results of a study of the rheological properties of CDA solutions with a degree of deacetylation of 2.6 and a degree of polymerization of 400 in acetone with a concentration of 5%, 10%, and 15%, where the content of "non-solvent" water in the solvent ranged from 5%, 7.5%, and 10%.

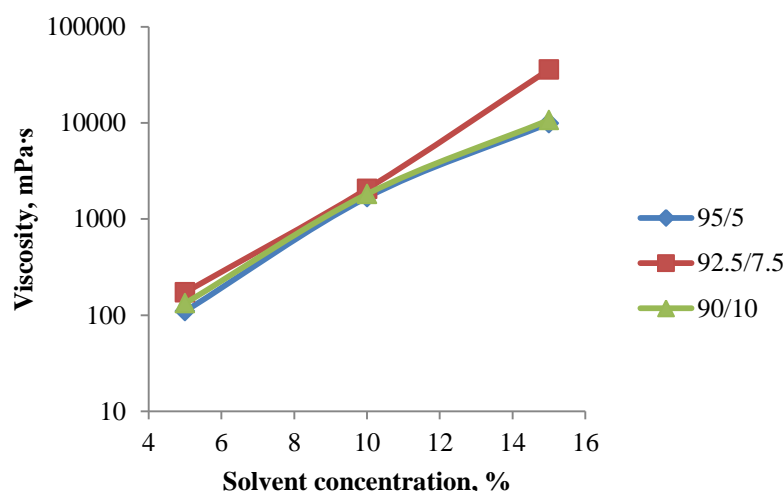


Figure 1. The dependence of the viscosity of DAC solutions on the concentration at different thermodynamic properties of the solvent (acetone/water percentage).

Figure 1 shows changes in the viscosity of solutions in acetone containing 5-10% of the "non-solvent" - water, depending on the concentration of CDA. As can be seen from Figure 1, with an increase in the concentration of CDA in a solution within 5-15%, an increase in the viscosity of the system is observed. At the same time, starting from the concentration of CDA in a solution of 10%, the solution where the concentration of water in acetone is 5 and 10% exhibits the properties of non-Newtonian liquids, and at a water concentration of 7.5%, an increase in viscosity with an increase in the concentration of CDA, the solution exhibits the properties of Newtonian liquids.

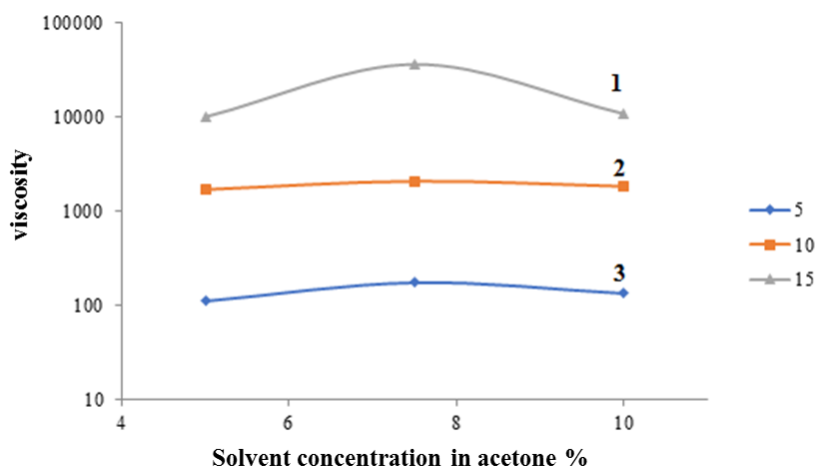


Figure 2. Dependence of the viscosity of CDA solutions of various concentrations on the thermodynamic properties of the solvent.

This fact is explained by the fact that in CDA solutions where the solvent is acetone contains 7.5% water, the distance between dissolved CDA macromolecules is quite large due to fluctuation and the probability of intermolecular interactions between them and the formation of associates is low. Further, studies were carried out on changes in the viscosity of CDA solutions depending on the water content in the acetone solvent.

As can be seen from Fig. 2, with an increase in the water content in acetone from 5 to 10%, the solution has the lowest viscosity, where the CDA concentration is 5% and the character of the curve slightly changes towards non-Newtonian liquids. (Fig. 2. *curve-1*)

In 10% CDA solutions, with an increase in the water content in acetone from 5 to 10%, the viscosity of the system changes slightly but is significantly higher than in a 5% CDA solution. Curve 3 characterizes the change in the viscosity of a 15% CDA solution with a change in the water content in acetone. The nature of curve 3 shows that when the water content in acetone is 7.5%, the solution has the highest viscosity and is typical for non-Newtonian solutions.

Further, we carried out studies of changes in the viscosity of CDA solutions depending on the gradient of the solution flow velocity.

It is known that at low shear stresses, the solution flow velocity gradient is proportional to the shear force, and only under these conditions do viscous polymer systems behave like Newtonian fluids.

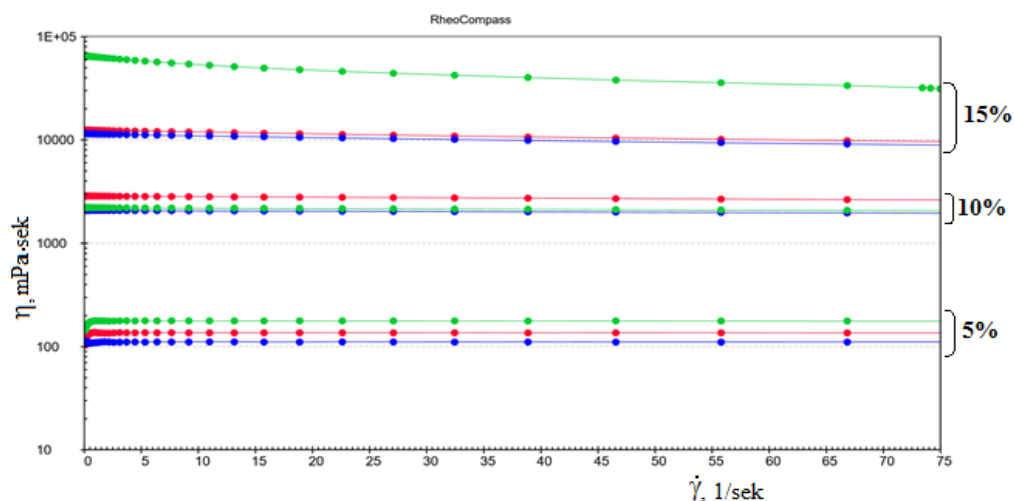
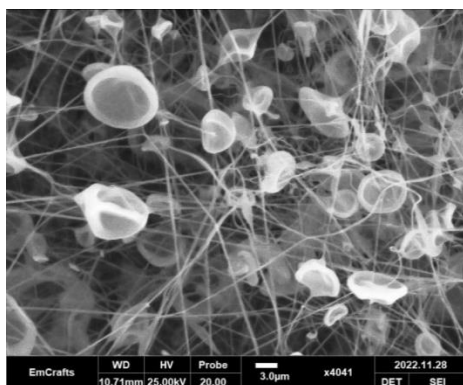


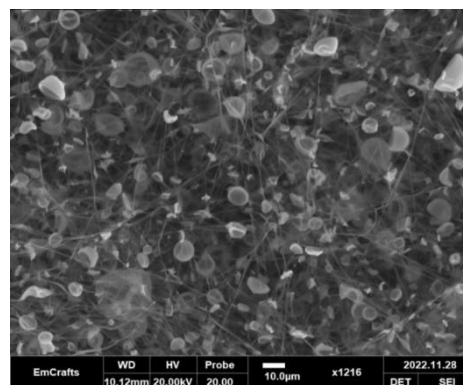
Figure 3. Rheograms of CDA samples at different concentrations dissolved in acetone/water mass ratios: Blue 95/5; Green 92.5/7.5; Red 90/10.

As can be seen from the results of the studies shown in Figure 3, 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 gradient of the flow rate of solutions practically does not change and remains constant.

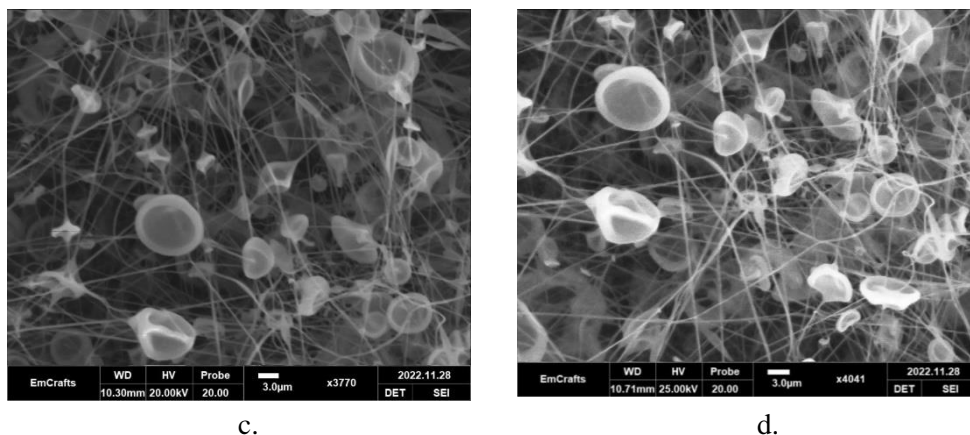
The viscosity of CDA solutions depends on the viscous flow velocity gradient depending on the water content in the composition of the solvent - acetone and increases in the sequence 5: 10: 7.5%, regardless of the concentration of the CDA solution. Thus, for the electroporation of CDA solutions of various concentrations dissolved in acetone containing “non-solvent” water in the range of 5-10%, based on the results of studying their rheological properties, a 10% solution prepared in acetone containing 10% water was chosen.



a.



b.



c.

d.

a) 1200x; b) 3700 times; c) 1000 times; d) 15000 times

Figure 4. SEM images of nanofibers obtained from 5% DAC solutions

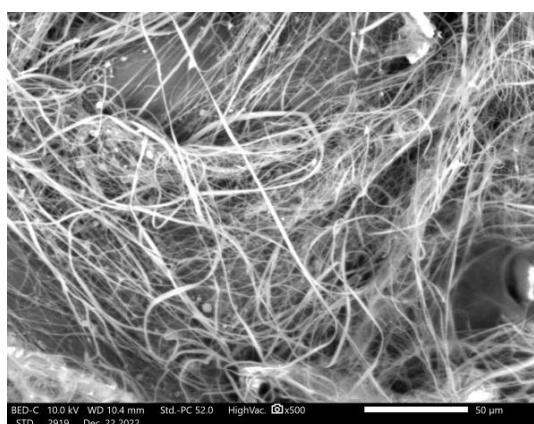
Electrospinning of CDA solutions of various concentrations containing various amounts of water was carried out on a NanoNC eS-robots device (NanoNC Co. Ltd, Korea) under the following conditions: voltage 22–25 kV, solution flow rate 10–15 $\mu\text{l}/\text{min}$, chamber temperature from 25–40 $^{\circ}\text{C}$, the distance between anode and cathode 10–15 cm.

The results of electron microscopic studies of the obtained nanofibers showed that the thickness of the CDA nanofibers was directly dependent on the composition of the solvent in the first place, as well as on the spinning conditions, and fluctuated in the range of 100–800 nm.

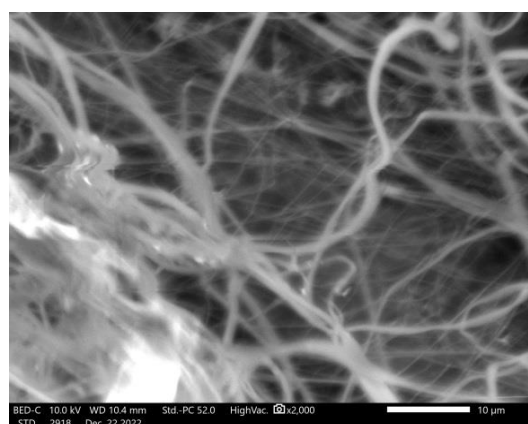
As can be seen from the SEM images in Fig. 5, the presence of knots and beads is related to the electrospinning conditions and the water content in the CDA solution.

Further studies were carried out to optimize the compositions of solutions in CDA by changing the concentration of CDA solutions, varying the water content in the CDA solution in acetone, and varying the modes of electrospinning of CDA solutions in acetone-containing water. beads (Fig. 5).

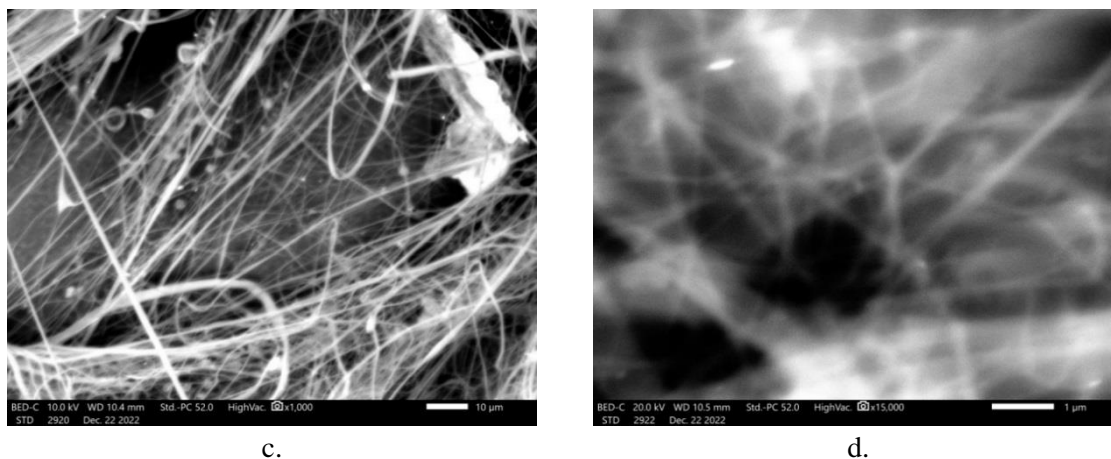
Based on the results of a preliminary assessment of the possibility of forming nanofibrous non-woven materials from CDA with a degree of deacetylation (acetylation) of 2.6 and a degree of polymerization of 400 dissolved in acetone containing 5% non-solvent water at the above installation. It was shown that the CDA solution has fibre-forming properties under electrospinning conditions. The formation of 5% solutions of CDA in acetone containing 5% water at a voltage of 25 kV ensured the jet-resistant formation and subsequent curing of the formed nanofibers with a diameter of 500 nm.



a.



b.



c.

d.

a) 500x; b) 2000 times; a) 1000 times; b) 15000 times

Figure 5. SEM images of nanofibers obtained from 5% CDA solutions.

It is known that the presence of three hydrophilic hydroxyl groups in the anhydrous glucose unit of cellulose makes it possible to obtain its derivatives with different properties. Unlike cellulose fibers, nanofibers, and their esters, due to their branched surface and the availability of hydroxyl groups, can easily enter into functionalization reactions. However, the direct preparation of cellulose nanofibers from its solutions is difficult because direct cellulose solvents have a complex composition and are often not volatile.

Considering the foregoing, we have investigated the possibility of obtaining cellulose nanofibers from nonwoven cellulose diacetate nanofibers. To obtain nonwoven nano cellulose webs of cellulose, nonwoven CDA nanofibers were kept in an aqueous medium at 25°C for 12 hours.

Next, and subjected to deacetylation in a 0.1 m aqueous solution of potassium hydroxide at a modulus of 1:10, at a temperature of 35°C for 1 hour.

Thus, from CDA nanofibers containing 40–42 free hydroxyl groups per 100 anhydrous glucose units, nonwoven nano cellulose fabrics with high hydrophilicity were obtained containing 6 ± 2 free hydroxyl groups per 100 anhydrous glucose units. The resulting nano cellulose fibers had an average diameter of 350–400 nm and swelled up to 270% in water.

The resulting hydrophilic nano cellulose nonwoven materials are of interest in the production of chemically modified nanomaterials for various purposes.

CONCLUSIONS

The rheological properties of CDA solutions of various concentrations in acetone containing various amounts of water were studied and the optimal composition of the solvent was selected.

The conditions of electrospinning of 5% solutions of CDA in acetone containing 5% water were studied and non-woven fabrics with a nanofiber diameter of 500:20 nm were obtained.

Cellulose nanofibers with a diameter of 350–400 nm and a degree of swelling in water of 270% with a residual content of 6 ± 2 acetone groups per 100 anhydrous glucose units of the cellulose macromolecule were obtained by hydrolysis of the acetate groups of CDA in a 0.1 potassium hydroxide solution.

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