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Flax Noils as a Source of Cellulose for the Production of Lyocell Fibers

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Abstract: The production of long flax fiber for the subsequent production of textile yarn is accompanied by the formation of a significant amount of waste—noils, which is a mechanical mixture of long and short flax fibers and shives. Comparative studies of the structure and chemical composition of the fibrous fraction of noils and shives were carried out using IR spectroscopy. The solubility of shives and flax noils in N-methylmorpholine-N-oxide (NMMO) was studied, a comparative analysis of the rheological behavior of solutions of flax and wood cellulose was carried out and the optimal temperature–concentration conditions for obtaining flax fibers from noils were determined. It was shown for the first time that using the method of solid-phase activation of the cellulose-solvent system makes it possible to obtain fibers in a short period of time (no more than 10 min). The structure of both the raw material and the resulting fibers was studied by X-ray diffraction analysis. The thermal properties of a new type of cellulose fibers was evaluated. The complex of the conducted studies allows us to consider flax fibers from noils along with flax fibers from long-staple flax, as a real alternative to fibers from wood pulp.

Keywords: noils; flax; annual plants; cellulose; N-methylmorpholine-N-oxide; fibers; Lyocell

1. Introduction

As it is known, the vast areas of Russia occupied by forests are an almost inexhaustible source of raw materials for the production of wood pulp. The produced cellulose is further used for making paper and packaging, molding of cardboard products, production of films, membranes, cellulose fibers, etc. To obtain cellulose materials, polymer purification from impurities is required. Such cellulose is often called soluble or viscose pulp. Unfortunately, for a number of reasons, plants that produced dissolving wood pulp, including those with a high proportion of α-fraction, gradually lost their competitiveness and were closed in Russia. This led to an increase in dependence on foreign raw materials. In addition, in recent years there has been a shortage of wood resources all over the world [1]. The main reasons for the reduction of forest areas are harvesting of wood, deforestation and forest degradation [2]. The last two factors account for about 10% of global CO_2 emissions [3]. Therefore, in order to conserve forests and preserve the environment, it is necessary to partially or completely replace them with renewable plant biomass.

Another source of high-quality cellulose is a fully imported product—cotton [4]. Unlike wood, for which the yield of cellulose does not exceed 50%, its content in cotton reaches 95% [5–8]. At present, the maximum capacity for growing cotton has been reached. In the main cotton growing regions, a decrease in sown areas has been observed due to a decrease in water supplies, and depletion and pollution of soil with chemicals [9]. These

factors, as well as the high demand for cotton, have stimulated the growth of prices for it: in 2021, its cost increased by more than 30%.

The total volume of cellulose produced in the world from annual plants is 12% [10]. Besides cotton, cellulose is obtained from hemp, flax, miscanthus, etc. [11–14]. All of these crops have great potential for cellulose production. However, as is well known, in Russia and Europe only flax and hemp are grown on an industrial scale. As reported in [15–17], depending on the method of processing flax, it is possible to achieve a significant yield of cellulose (up to 87%). The proposed methods for isolating cellulose make it possible to achieve high purity of the product and the polymerization degree (1000–2100) of the alpha fraction reached 98% [15,18–20].

The indisputable advantages of flax are the relatively high productivity of the crop and its chemical composition. At present, up to eight tons of tow straw can be harvested from one hectare (2.3 tons of which are flax fibers). Depending on the type of flax processing, not only the physical and mechanical characteristics of the resulting product are formed, but the ratio of the useful yield of the product to the amount of byproduct also changes. So, in the process of obtaining high-purity flax wadding, about 12% of noils are formed, which are a mixture of short-fiber cellulose and shives (Table 1).

Table 1. Composition of linen noils.

Composition of Noils	% wt
Shives and weed impurities	3 ± 1.5
Cellulose fibers up to 5 mm	17 ± 9
Cellulose fibers 5–15 mm	57 ± 3
Cellulose fibers 15–30 mm	18 ± 5
Cellulose fibers 30–50 mm	3 ± 2.5
Cellulose fibers 50–70 mm	2 ± 0.5

The largest proportion of flax noils is cellulose fibers with the length of 5 to 15 mm. It is important that such fibers are practically not used for processing into textiles. The proportion of long fibers with a length of more than 3 cm is 5%. Long fibers are more in demand than short ones, but their small proportion and high energy intensity for their isolation make this fraction inaccessible for further processing into textiles. Along with short and long fibers, there is a small amount of shives in the noils. As in the case of long fibers, the removal of shives from noils is associated with a number of technological difficulties. Photos of the original flax, flax wadding, noils and shives are shown in Figure 1.
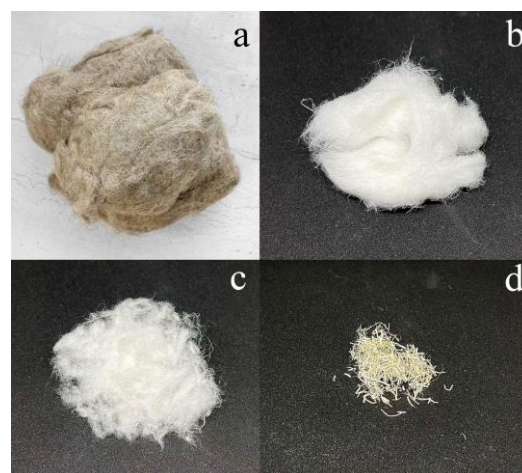

Figure 1. Photos of the original flax fibers (**a**), linen wadding (**b**), noils (**c**) and shives (**d**).

The main difference between the original flax fibers, noils and shives from flax wadding is their chemical composition, namely the proportion of cellulose, hemicellulose

and lignin. Note that lignin is currently practically a non-recyclable waste and accumulates in large quantities at specialized landfills. Unlike wood, in which the lignin content reaches 40%, in flax its fraction does not exceed 32% [21,22]. At the same time, the main part of lignin is concentrated in the shives, and in the fibrous part its content varies from 1 to 5%.

Thus, the process of obtaining cellulose and cellulose-containing by-products from flax can be considered as an alternative to the traditional method of pulping, which is accompanied by large emissions of lignin into the environment.

The structural features of cellulose are associated with the high energy of the network, which is formed by systems of inter- and intramolecular hydrogen bonds [22,23]. They limit the solubility of cellulose in water and in a number of traditional solvents. Direct complex solvents include DMAA/LiCl [24], aqueous solutions of zinc chloride [25], ionic liquids [26], N_2O_4/DMF [27,28], aqueous solutions of NaOH [29] and orthophosphoric acid [30,31]. In the 1930s, another class of cellulose solvents, amine oxides, was found [32]. Subsequently, N-methylmorpholine-N-oxide (NMMO) turned out to be the most suitable solvent [33,34]. The use of this solvent made it possible to implement the industrial production of cellulose fibers as an alternative to environmentally harmful viscose production [35]. For NMMO, a high degree of its regeneration has been also proven [36].

The literature presents a number of methods for processing the initial linen raw materials in order to remove impurities and increase the content of the cellulose alpha fraction [15,17,37,38]. Many of them require multi-stage and complex processing of linen raw materials using sodium hydroxide, acids, hydrogen peroxide, etc. However, such purity of cellulose is not always necessary to obtain cellulose fibers. Thus, in [39], it was shown that cardboard, paper, secondary raw materials obtained from textiles, etc. can be used as source of cellulose for the fiber production.

A comparison of the mechanical properties of fibers spun from cellulose with different contents of lignin and hemicellulose revealed that an increase in their content leads to a decrease in the strength characteristics of the fibers. The presence of hemicellulose in fibers increases their resistance to fibrillation and dyeability, which is associated with a less organized structure and a smaller size of fibrils aggregation [40]. Based on this, it is important to determine whether it is possible to use waste from the flax industry, for example, noils, as a cellulose source for the production of cellulose (Lyocell) fibers.

Hence, the aim of this work is to study the potential for obtaining flax cellulose fibers from flax production waste—linen noils containing shives, with mechanical properties at the level of industrial analogues. This can be established by studying the solubility of shives in NMMO, in order to obtain solutions based on flax noils, to evaluate their rheological behavior, to select fiber spinning conditions, to obtain experimental batches of fiber samples by dry-jet wet spinning and to study the structure and properties of spun cellulose fibers.

2. Experimental Section

2.1. Materials

To obtain spinning solutions, we used flax noils (short fibers containing a small amount of shives) (LenOm LLC, Kalachinsk, Russia) (DP = 1500, with moisture content of ~2–3% mass, content of alpha-cellulose in dry residue ~92%, fiber length < 5 cm). The noil milling was performed on a pilot twin-screw extruder (Berstorff ZE-40, (Krauss Maffei Berstorff, Munich, Germany) with a screw diameter of 40 mm and a temperature control system. To obtain the solutions, a fraction with a particle size of less than 250 μm was used. Sulfate cellulose (Baikal Pulp and Paper Mill, Siberia, Baykalsk, Russia) (DP = 600, moisture content ~8%, α-cellulose content ~94%) was used as a comparative cellulose. The resulting powdered cellulose was dissolved in a direct solvent, N-methylmorpholine-N-oxide (Demochem, Shanghai, China) with a water content of ~8–10% (T_m ~ 120 °C). Thermal oxidative degradation was suppressed by introducing 0.5% propyl gallate (Sigma-Aldrich, St. Louis, MO, USA).

2.2. Methods

2.2.1. Preparation of Solutions

The dissolution of cellulose was preceded by a stage of solid-phase activation of a polymer–solvent system according to a procedure previously described [41–43]. The activated pre-solutions were heated in a Rheoscope 1000 capillary viscometer chamber (CEAST, Torino, Italy) and passed through a capillary channel with a diameter (d) of 0.5 mm and a length (l) of 5 mm (aspect ratio l/d = 10) at temperatures of 120–135 °C. The quality of the spinning solution was evaluated using optical microscopy (microscope "Boetius", VEB Kombinat Nadema, Ruhla, Germany, former GDR).

2.2.2. Rheological Measurements

The rheological properties of cellulose solutions were studied on a HAAKE MARS 60 (Thermo Scientific, Karlsruhe, Germany) rotational rheometer. For measurements, a cone–plate operating unit with a diameter of 20 mm was used (the angle between the generatrix of the cone and the plate was 1°). The tests were carried out under steady flow conditions in the controlled shear rate mode in the range of 0.001–10 s^{-1}. The tests were carried out at 120 °C. Oscillatory tests were carried out in a mode corresponding to the range of linear viscoelasticity, in the frequency range (ω) 0.1–100 Hz at a constant specified stress (τ) 10 Pa.

2.2.3. Fiber Spinning

Spinning (production) of enlarged batches of flax cellulose-based fibers was carried out on a laboratory dry-jet wet stand (Figure 2), constructed on the basis of the single-screw extruder (SCAMIA, Saumur, France).
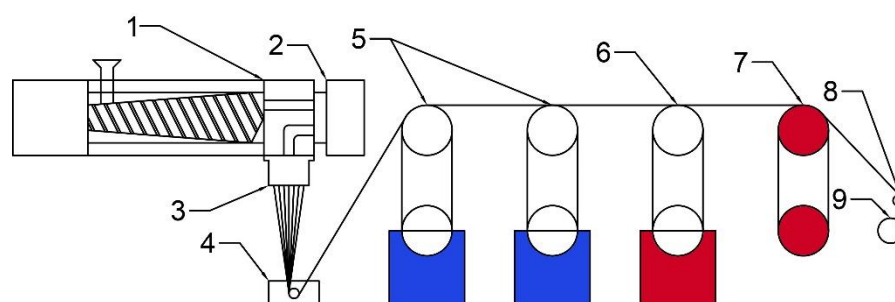

Figure 2. Schematic of laboratory equipment for dry-jet wet spinning of fibers (1—extruder, 2—spinning pump with an engine, 3—spinneret, 4—coagulation bath, 5—washing baths (T = 20–22 °C), 6—heated washing bath (T = 50 °C), 7—drying drums, 8—fiber spreader, 9—bobbin).

The spinneret used had 17 holes with a channel diameter of 250 μm. After exiting the spinneret, the jets of solution after bypassing the air gap enter the precipitation bath. Next, the fibers enter the water washing baths of different temperatures. After complete removal of the solvent, the fibers are dried and wound on bobbins.

2.2.4. Mechanical Testing

The mechanical properties of the fibers were determined on an Instron 1122 (Instron, Norwood, MA, USA) tensile testing machine at a rate of 10 mm/min with a base of 10 mm according to GOST 10213.4–2002.

2.2.5. Structural and Morphological Characterization

The fiber structure was studied using X-ray diffractometry on a Rigaku Rotaflex RU-200 (Rigaku Corporation, Tokyo, Japan) setup equipped with a rotating copper anode (CuKα radiation, wavelength is λ = 1.542 Å), a D-Max/B horizontal goniometer and a scintillation detector. X-ray survey was carried out in the "transmission" mode according to the Bragg–Brentano scheme in the continuous θ-2θ scanning mode in the angular range

of 5–45°, speed 2°/min and a scanning step of 0.04°. The measurements were carried out at room temperature. As objects, we used bundles of 100–150 monofilaments, which were fixed on a flat square aluminum frame perpendicular to the plane of rotation of the detector (equatorial position). The structure of the original powdered cellulose was studied when scanning in the "reflection" mode.

The crystallinity index (*CI*) was evaluated according to Segal's method [44], according to Equation (1).

$$CI = (I_{002} - I_{am})/I_{002} * 100, \tag{1}$$

where I_{002} is the intensity of the 002 peak and I_{am} is the amorphous intensity between the 110 and the 200 at 2θ = 18°.

The crystallite size was estimated according to the Scherrer method [45], Equation (2):

$$D = 0.89\lambda/B \cos \theta, \tag{2}$$

where *D* is the size of crystallite, *λ* is X-ray wavelength, and *B* is the full width half maximum (FWHM, in radian) and *θ* and is the corresponding Bragg angle.

The IR spectra of the fibers were recorded on a HYPERION-2000 IR (Bruker Optics, Ettlingen, Germany) microscope coupled with an IFS-66 v/s Bruker IR-Fourier spectrometer (crystal-Ge, scan 50, resolution 2 cm^{-1}, wavelength range 4000–600 cm^{-1}).

The morphology of cellulose fibers was studied by low-voltage scanning electron microscopy (SEM) using a FEI Scios microscope (Hillsboro, OR, USA) at an accelerating voltage of less than 1 kV in the secondary electron mode. To obtain SEM microphotographs of cross-sections, cellulose fibers were preliminarily cooled in liquid nitrogen and then, using a simple mechanical action on the fibers with a scalpel, cleavages were obtained.

2.2.6. Thermal Characterization

The thermal behavior of the fibers was studied on a thermal analysis device TGA/DSC1 (Mettler Toledo, Greifensee, Switzerland). The measurements were carried out in alumina crucibles with a volume of 70 μL in a temperature range from 30 to 1000 °C at a heating rate of 10 °C/min. The inert gas (argon) flow rate was 50 cm^3/min.

3. Results and Discussion
3.1. Structural Analysis

Figure 3 shows the IR spectra of flax noils and shives in comparison with the spectra of Baikal wood cellulose and lignin.
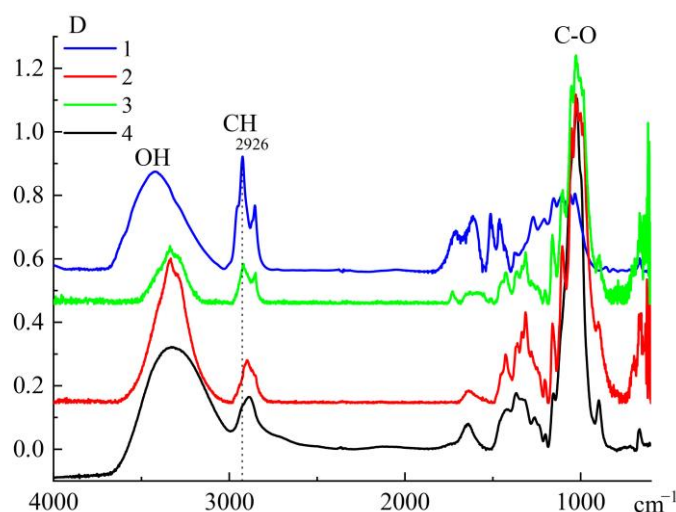

Figure 3. IR spectra of lignin (1), shives (2), noils (3) and Baikal wood cellulose (4).

Despite the fact that the studied cellulose-containing samples have similar spectral patterns, the spectra of noils and, especially, shives show certain differences when compared to the spectra of Baikal cellulose. Instead of the characteristic band of cellulose 2900 cm^{-1} (νCH) (deformation vibrations of -CH and -CH$_2$ groups), two bands at 2926 and 2850 cm^{-1} of lignin are clearly visible in the spectrum of the shives, corresponding to C-H stretching vibrations in the methyl and methylene groups [46,47].

In the noils spectrum, lignin is present in a significantly smaller amount, since the bands are not completely resolvable and the 2850 cm^{-1} band appears only as the right shoulder on the 2926 cm^{-1} band. Detailing of the spectra in the region of 1800–800 cm^{-1} did not reveal the aromatics of lignin either in the shives or in the noils. Apparently, the studied samples contain only fragments of the lignin destroyed during the deep processing of the flax pulp. However, along with the lignin fragments, the 1730 cm^{-1} band (νC = O in the ester group) clearly appears in the spectrum of the shives, indicating the presence of hemicellulose (uronic acid) [48].

Attention is drawn to a significant change in the spectral pattern of the noils and shives samples in the region of 1450–1200 cm^{-1} in comparison with the spectrum of Baikal cellulose. In the spectrum of Baikal cellulose this region is poorly resolvable, however clear bands appear at 1426, 1365, 1333 and 1314 cm^{-1} which are the deformation vibrations of the -OH, -CH and -CH$_2$ groups in the shives and especially in the noils (Figure 4).
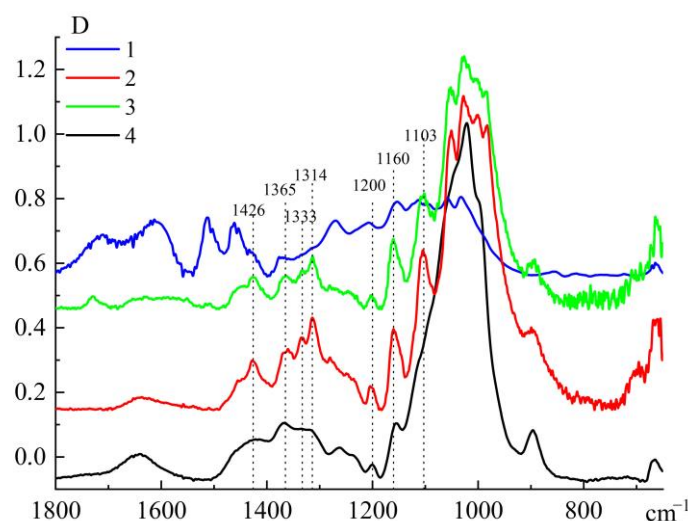

Figure 4. Detailing the spectra of shives (2) and noils (3) with the spectra of lignin (1) and wood cellulose (4).

The 2900 cm^{-1} (νCH), 1426 and 1370 cm^{-1} bands are used as internal standard bands to assess the degree of order in cellulose chains. The most sensitive to determining the degree of cellulose crystallinity is the relative intensity of the bands 1370 cm^{-1}/2900 cm^{-1} and 1426 cm^{-1}/900 cm^{-1} [49]. Our previous work [8] on the comparative evaluation of the crystallinity of long-fiber flax and wood pulp by the relative intensity of the 1430 cm^{-1}/900 cm^{-1} bands (O'Connor criterion) and by the relative intensity of the 1370 cm^{-1}/2900 cm^{-1} bands indicates that in flax cellulose, compared to wood pulp, both the intrachain and the interchain structural ordering are more highly expressed.

The results of the structure study of flax noils by the X-ray diffraction method confirm the data of IR spectroscopy (Figure 5).
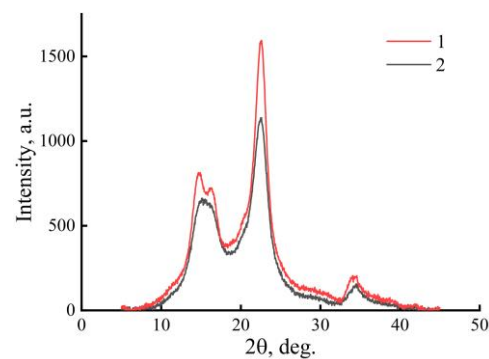
Figure 5. Powder diffraction patterns of flax noils (1) and wood (2) cellulose.

Native cellulose, regardless of its source, has a structure characteristic of polymorph I. The characteristic peaks of cellulose in the XRD patterns are in the regions 2θ ~14.6°, ~16.6° and ~22.7° [50]. As seen in Figure 5, the angular positions of the peaks of the diffraction patterns of flax noils and wood pulp, characterizing the intra- and interlayer periodicity, completely coincide in the presented diffraction patterns, which indicates the identity of the crystalline cells of the cellulose samples.

However, the sizes of the crystallites of flax noils and wood pulp, determined by the Scherrer equation, are different in size and equal to 5.6 and 4.2 nm, respectively. The crystallinity index for flax noils is higher compared with wood cellulose by almost 10%. Consequently, flax noils, despite the presence of impurities, are characterized by a higher content of an ordered crystalline phase compared with wood cellulose.

As shown in [8], despite the high regular structural organization of flax cellulose, it easily dissolves in NMMO. In order to identify the effect of changes in the chemical composition of flax cellulose in noils, namely, the presence of shives particles containing lignin and pentosans decomposition products, the solubility of shives particles in NMMO was studied. Figure 6 shows photographs of the evolution of the shives particle when kept in NMMO at T = 120 °C.
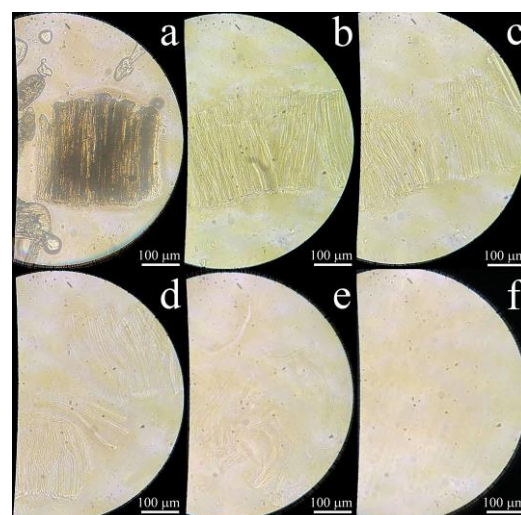

Figure 6. Dissolution of shives in NMMO, after 10 (**a**), 140 (**b**), 200 (**c**), 270 (**d**), 320 (**e**) and 540 (**f**) sec, T = 120 °C.

The first photo in the series shows a shives particle in a partially molten solvent. A couple of minutes after the beginning of the experiment, the entire solvent melted and the particle swelled; its transverse size almost doubled. The fibrillar nature of the shives particle is clearly manifested. Next, the evolution of local splitting of the particle occurs, while the longitudinal dimensions of the fibrils change insignificantly.

Apparently, fibrils with a more ordered structure interact with the solvent at a lower rate than the interfibrillar regions, in which low molecular weight compounds can be concentrated. After 5 min, the distance between the fibrils increases significantly. Further, this distance continues to increase, and the longitudinal size of the fibrils decreases. Complete dissolution of the particle under static conditions, between two glasses, occurs after 9–10 min. The dissolution of the shives in NMMO under conditions of active deformation allows us to hope for a significant decrease in the dissolution time. Grinding the noils to a powder with a particle size of less than 250 μm will also contribute to reducing the preparation time of the solutions.

Thus, despite of the presence of low molecular weight impurities of hemicellulose, as well as traces of lignin in the flax shives, their dissolution in NMMO was shown. For the preparation of spinning solutions, flax noils containing a small fraction of the shives were preliminarily crushed to a powder state in a twin-screw extruder.

3.2. Rheology

Structural features of flax noils, namely the large size of crystallites, high crystallinity and degree of polymerization, should determine the nature of the rheological behavior of the resulting solutions. The flow curves of solutions of flax noils and wood pulp are shown in Figure 7.
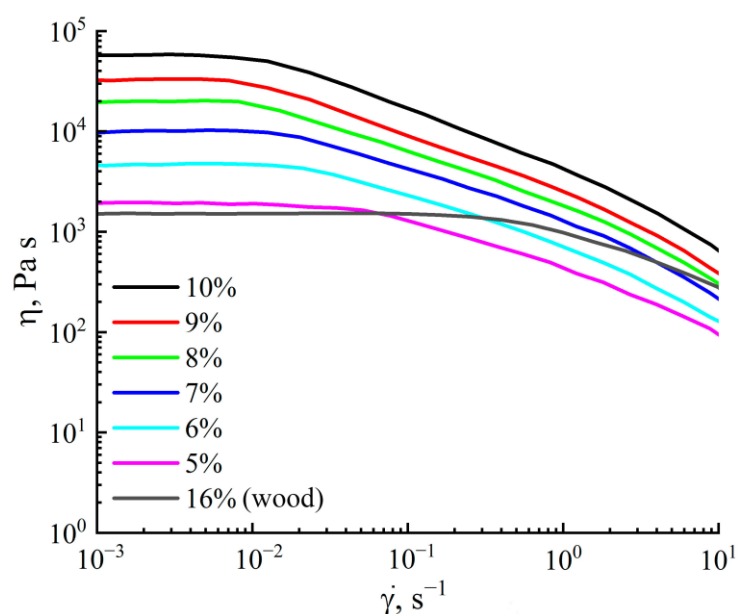

Figure 7. Flow curves of flax noils and wood cellulose solutions with different polymer concentration, T = 120 °C.

As seen in the figure, the structural features, presence of impurities and the high DP of flax noils lead to a significant increase in the viscosity of the resulting solutions compared with the viscosity of wood pulp solutions. Thus, the viscosity values for a 16% solution of wood cellulose practically coincide with the viscosity of a 5% solution of flax cellulose.

The character of the flow curves of solutions of various concentrations from flax noils changes insignificantly. With an increase in the cellulose content in the solution, the area of the Newtonian flow decreases, and the structural branch appears at lower shear rates. With an increase in shear stress, a decrease in viscosity values is observed on all flow curves. More clearly, the change in viscosity with an increase in the concentration of noils in the solution can be observed in the concentration dependence of viscosity (Figure 8).
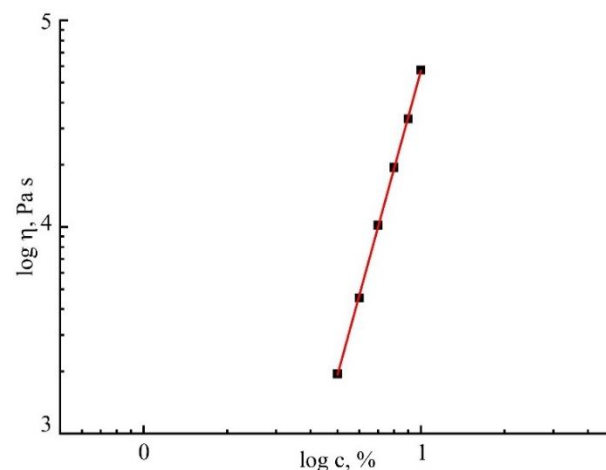
Figure 8. Concentration dependence of the viscosity cellulose solutions of flax noils in NMMO.

It can be seen from the figure that an increase in the content of noils in the system from 5 to 10% is accompanied by an increase in viscosity by more than 1.5 orders of magnitude.

The viscoelastic properties of the solutions were studied in a frequency range from 0.1 to 100 Hz and at a shear stress amplitude of 10 Pa, which corresponds to the area of linear viscoelasticity in the same frequency range (oscillatory amplitude sweeps in the range of shear stress of 0.1–100 Pa were performed at four frequencies—100, 10, 1 and 0.1 Hz.) (Figure 9).
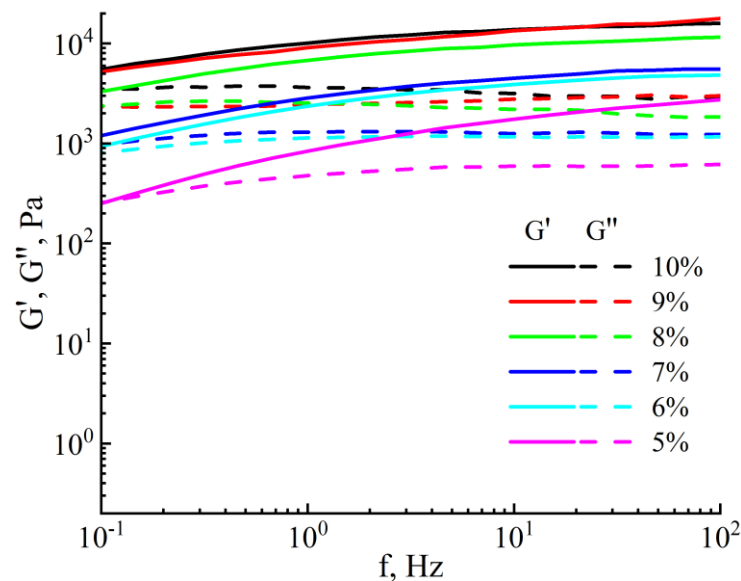

Figure 9. Frequency dependences of elastic (G′) and loss (G″) moduli of systems based on flax noils cellulose and NMMO. The concentration of solutions is indicated on the graph.

With a decrease in the concentration of noils cellulose in the system, a decrease in the elasticity of the solution is observed. Despite this, the elastic properties remain dominant. The crossover point in the studied frequency range appears only for 5% solutions. With an increase in the concentration of flax cellulose in the solution, the crossover migrates to the region of lower frequencies, which are not considered in this work.

Thus, to obtain spinning systems, the concentration of flax noils cellulose in the system should not exceed 7%.

The revealed temperature–concentration ranges of the features of the rheological behavior of the spinning solutions were used to assess the spinnability of flax noils cellulose solutions with different concentrations on a capillary viscometer. As the optimal content of

the polymer in the system, a concentration of 7% was chosen; the solution showed the best formability at a temperature of 120 °C.

3.3. Fiber Spinning

On a laboratory stand an enlarged batch of flax noils fibers was spun by a dry-wet method. The extruded jet, leaving the die, was drawn out in the air gap, passed through the water precipitation bath, the washing baths, and was taken onto the bobbin at a speed up to 100 m/min.

It is important to note that the use of the method of preliminary solid-phase activation of the flax noils cellulose-solvent system makes it possible to obtain a finished fiber within 7–10 min. This time includes both the solution preparation process and the formation of the fiber itself (Figure 10).

Figure 10. Photograph of a filament bobbin made from 7% solutions of flax noils cellulose in NMMO.

There is no alternative method for obtaining cellulose fibers in such a short time currently. In all external parameters, the resulting fibers do not differ from analogues spun via the viscose or traditional MMO process using a 50% aqueous solution of NMMO [35]. In that case the preparation time for spinning solutions is in the range of several hours.

3.4. Structure and Morphology of Fibers

The structure of the formed fibers was studied by X-ray diffraction analysis and scanning electron microscopy. The diffraction patterns of the obtained fibers, spun from 7% solutions of flax noils cellulose in NMMO, are shown in Figure 11.
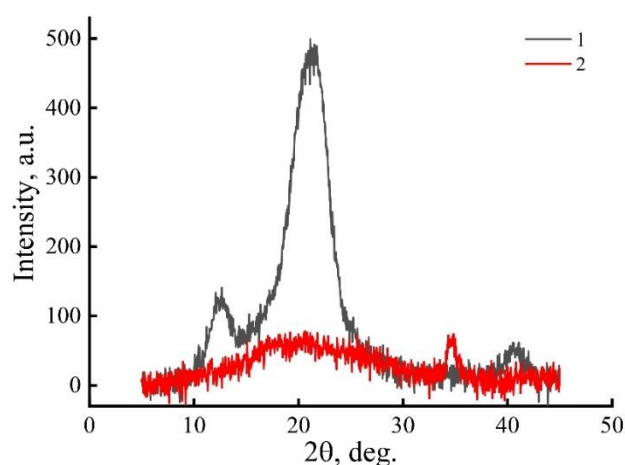

Figure 11. Equatorial (1) and meridional (2) diffraction patterns of fibers spun from 7% solutions of flax noils cellulose in NMMO (transmission mode).

The main peaks in the equatorial diffraction patterns appear in the regions 2θ ~12.1°, ~20.1° and ~21.5° (planes (101), (101) and (002)) and are close to the angular positions for wood-based regenerated cellulose fibers [51–53].

The observed structure is attributed to the cellulose polymorph II. It can be seen from the presented diffraction patterns that the main reflections of cellulose appear in the equatorial diffraction pattern. Such a redistribution of intensities between the equatorial and meridional diffraction patterns may indicate that the formation of a structural order proceeds in the plane perpendicular to the fiber axis.

The 2θ ~20.1° reflex in the diffraction pattern compared with the original flax noils cellulose (Figure 5) becomes wider. The sizes of crystallites were calculated from the half-width of the reflection using the Scherrer equation. Compared with the crystallites of the original sample, equal to 5.6 nm, they decreased to 4 nm, i.e., in the process of dissolution and spinning a certain worsening of the structural ordering of the macromolecules of flax noils cellulose takes place.

The morphological features of the obtained fibers were studied as well. Natural long-fiber flax has a smooth fiber surface and in the cross section the monofilaments are hollow and have the shape of a polygon [54]. The fibers spun from noils cellulose in NNMO have a round cross section and a smooth surface closer to Lyocell fibers obtained from wood pulp (Figure 12).
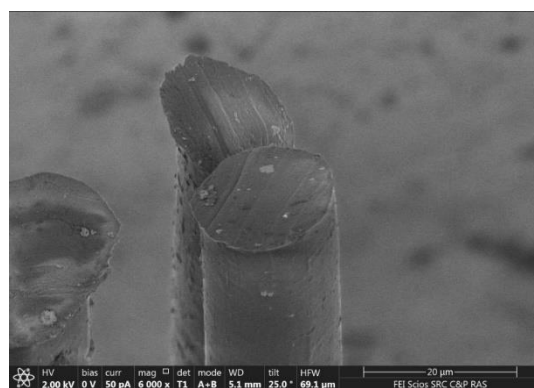

Figure 12. Micrographs of fibers spun from flax noils cellulose.

As can be seen from the photographs, the surface of the monofilaments is smooth and even. The average fiber diameter is 16–18 microns. The cross section of the filaments is round with a dense texture.

3.5. Mechanical Properties

The revealed structural and morphological features of flax noils fibers determine their mechanical properties. Table 2 shows the comparative mechanical properties of fibers formed from flax noils cellulose and wood pulp.

Table 2. Mechanical properties of fibers spun from flax noils cellulose and wood pulp.

C$_{solution}$, %	Diameter, μm	Strength, MPa	Modulus, GPa	Elongation, %
7 (flax noils)	16–18	950–1070	9–15	6–9
16 (wood pulp)	16–20	610–730	14–20	6–9

As can be seen from Table 2, flax noils fibers have high deformation and strength characteristics. The tensile strength for flax noils fibers is more than 30% higher compared with wood pulp fibers. Apparently, this is achieved due to the high orientation of longer macromolecules of flax cellulose and the formation of a system of hydrogen bonds, distinctive from the native one, including those between cellulose and impurities. The structure reformation that occurred in flax noils during their dissolution in NMMO and spinning,

which, as shown by X-ray diffraction studies, led to some loss of regular ordering of the macromolecules of the initial samples and, accordingly, increased their mobility and ability to deform. As is seen in Table 2, the values of elongation at break of fibers from plant and wood cellulose have the same level and are equal to 6–9%. This indicator is extremely important for flax fibers, since natural flax fibers have a low elongation, not exceeding 2–3% [55], which complicates the process of textile processing. The modulus of elasticity for fibers based on the wood pulp slightly exceeds one observed for fibers from flax noils cellulose. Thus, the data obtained allow us to consider the high mechanical characteristics inherent to the flax noils fibers.

3.6. Thermal Behavior

The revealed structural features and high mechanical properties of the obtained fibers create good prerequisites for their use as special fibers, for example, precursors of carbon fibers. The TGA and DSC curves for such fibers are shown in Figure 13.
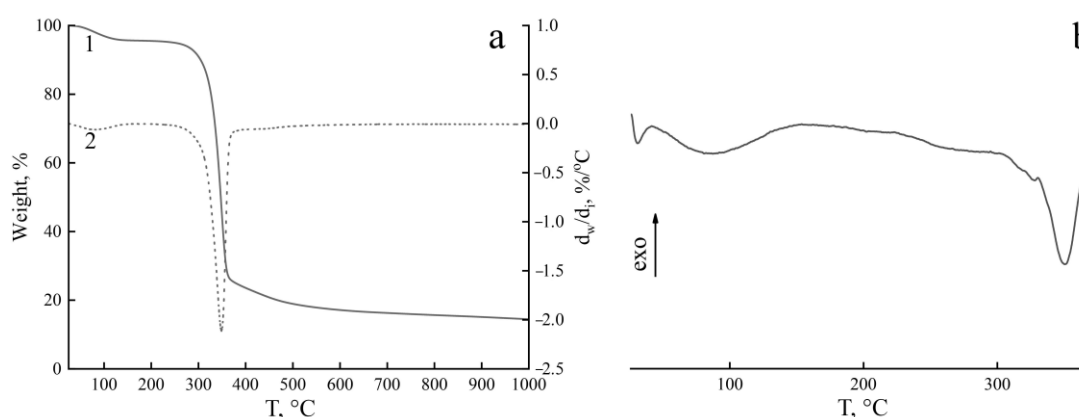

Figure 13. TGA ((**a**), 1), DTG ((**a**), 2) and DSC (**b**) data of fibers spun from 7% solutions of flax noils cellulose in NMMO. Atmosphere: argon 50 cm^3/min. Linear heating at 10 K/min.

The TG curve (a1) for flax noils fibers has a shape traditional for cellulose fibers: three areas of weight loss at heating to 1000 °C [56]. These areas correspond to the removal of adsorbed water (1), pyrolysis of cellulose (2) and a high temperature step at approximately 380 °C, where a decrease in mass is observed due to loss of oxygen and hydrogen (3). Upon reaching the maximum temperature, the residual char yield of the fibers is 14.5%.

The DTG curves (a2) make it possible to determine the temperatures at which the maximum weight losses are observed: at 76.3 °C (water loss) and at 353.4 °C (thermal decomposition of cellulose).

As for the DSC curves, thermal endo effects traditional for cellulose are observed.

4. Conclusions

The use of flax noils for deep processing for the first time was proposed. Flax noils are waste products from the process of producing long flax fibers. Their dimensions rarely exceed 2.5 cm, which makes them practically unclaimed in the textile industry (for producing threads, etc.). Together with long-staple flax fibers, a small amount of shives presents in the noils, which can contain, together with cellulose, hemicellulose and lignin. Despite the presence of impurities, shives are soluble in NMMO and dopes can be obtained from flax noils and processed into fibers.

The spinning of cellulose fibers is carried out by a dry-jet wet method. For the obtained fibers, the mechanical characteristics are determined and it is shown that their strength and strain characteristics are not inferior to known analogues obtained from wood pulp and other spinning methods.

For the first time, the duration for obtaining solutions of flax cellulose by the solid-phase method in NMMO and for the fibers spinning are estimated, which are tens of times

shorter in comparison with all known methods for obtaining spinning solutions and their processing into fibers.

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References

1. Taurbekov, A.T.; Mansurov, Z.A.; Chernoglazova, T.V. Obtaining Cellulose Fibers from the Fallen Leaves of the Elm. *Ann. Chem. Sci. Res.* **2021**, *2*, 1–5.
2. Krasovskii, A.; Maus, V.; Yowargana, P.; Pietsch, S.; Rautiainen, M. Monitoring Deforestation in Rainforests Using Satellite Data: A Pilot Study from Kalimantan, Indonesia. *Forests* **2018**, *9*, 389. [CrossRef]
3. Baccini, A.; Goetz, S.J.; Walker, W.S.; Laporte, N.T.; Sun, M.; Sulla-Menashe, D.; Hackler, J.; Beck, P.S.A.; Dubayah, R.; Friedl, M.A.; et al. Estimated carbon dioxide emissions from tropical deforestation improved by carbon-density maps. *Nat. Clim. Chang.* **2012**, *3*, 182–185. [CrossRef]
4. Gukezheva, M.K. Prospects of cotton import substitution in the national textile industry. *Eurasian Sci. J.* **2020**, *1*, 1–9. Available online: https://esj.today/PDF/80ECVN120.pdf (accessed on 10 April 2022).
5. Christie, R.M. *Colour Chemistry*; Royal Society of Chemistry: Cambridge, UK, 2001; p. 205. [CrossRef]
6. Zhang, Q.; Wei, F. *Advanced Hierarchical Nanostructured Materials*; John Wiley & Sons: Hoboken, NJ, USA, 2014; p. 512. [CrossRef]
7. Kudela, J.; Kurjatko, S. *Wood Structure and Properties '02*; Arbora Publishers: Zvolen, Slovakia, 2002; p. 221.
8. Makarov, I.S.; Golova, L.K.; Vinogradov, M.I.; Egorov, Y.A.; Kulichikhin, V.G.; Mikhailov, Y.M. New Hydrated Cellulose Fiber Based on Flax Cellulose. *Russ. J. Gen. Chem.* **2021**, *91*, 1807–1815. [CrossRef]
9. Dai, J.; Dong, H. Intensive cotton farming technologies in China: Achievements, challenges and countermeasures. *Field Crops Res.* **2014**, *155*, 99–110. [CrossRef]
10. Bowyer, J.L.; Stockmann, V.E. An exciting bio-based raw material for the global panels industry. *For. Prod. J.* **2001**, *49*, 10–21.
11. Gismatulina, Y.A. Obtaining cellulose by the nitrate method directly from flax straw. *Polzunov. Vestn.* **2014**, *3*, 160–163.
12. Ainullov, R.K.; Kostochko, A.V.; Valishina, Z.T.; Popov, D.V.; Aleksandrov, A.A. Method for Obtaining Bleached Hemp. Pulp. Patent RF 2735263, 3 April 2020.
13. Shulzhenko, D.V.; Bessonova, I.Y.; Azanov, M.V.; Dyachenko, L.R.; Fadeev, B.A.; Tyurin, E.T.; Zuykov, A.A. Method for Obtaining Cellulose from Miscanthus for Chemical. Processing. Patent RF 2763880C1, 11 January 2022.
14. Izgorodin, A.K.; Konoplev, Y.V.; Zakharov, A.G.; Prusov, A.N.; Voronova, M.I.; Volkova, I. Study of the possible use of intermediate flax as raw material for production of cellulose. *Fibre Chem.* **2004**, *36*, 343–347. [CrossRef]
15. Levdansky, V.A.; Levdansky, A.V.; Kuznetsov, B.N. A method for obtaining a cellulose product from flax with a high content of alpha cellulose. *J. Sib. Fed. Univ. Chem.* **2014**, *7*, 63–70.
16. Wiener, J.; Kovacic, V.; Dejlova, P. Differences between flax and hemp. *AUTEX Res. J.* **2003**, *3*, 58–63.
17. Lukanin, E.A.; Egorov, D.A. Cellulosic Product with an alpha-Cellulose Content of 98.5% or More and an Industrial Method for Its. Production. Patent RF 2703250, 15 October 2019.
18. Galashina, V.N.; Moryganov, A.P.; Zakharov, A.G.; Danilov, A.R.; Gataulin, A.M. Method for Obtaining Purified Flax. Fiber. Patent RF 2347862, 27 February 2009.
19. Prusov, A.N.; Prusova, S.M.; Zakharov, A.G.; Bazanov, A.V.; Smirnov, P.R.; Radugin, M.V. Chemical transformation of technical fiber of flax, hemp and jute to cellulose and their pyrolysis. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **2016**, *59*, 97–104. [CrossRef]
20. Veselov, V.M.; Abramov, Y.K.; Zalevsky, V.M.; Tamurka, V.G.; Volodin, V.S.; Evdokimov, V.D.; Mironov, B.I.; Vatueva, O.B.; Gukasov, N.A.; Marshannikova, L.M.; et al. Method for Obtaining. Cellulose. Patent RF 2574958, 10 February 2016.
21. Sjostrom, E. *Wood Chemistry: Fundamentals and Applications*; Elsevier: London, UK, 2013; p. 293.
22. Bochek, A.M.; Shevchuk, I.L.; Lavrent'ev, V.N. Fabrication of Microcrystalline and Powdered Cellulose from Short Flax Fiber and Flax Straw. *Russ. J. Appl. Chem.* **2003**, *76*, 1679–1682. [CrossRef]

23. Makarov, I.S.; Golova, L.K.; Vinogradov, M.I.; Mironova, M.V.; Arkharova, N.A.; Klechkovskaya, V.V.; Kulichikhin, V.G. Morphological Transformations in the Process of Coagulation of Cellulose Solution in N-Methylmorpholine N-Oxide with Isobutanol. *Polym. Sci. Ser. C* **2021**, *63*, 161–169. [CrossRef]

24. Yudianti, R.; Syampurwadi, A.; Onggo, H.; Karina, M.; Uyama, H.; Azuma, J. Properties of bacterial cellulose transparent film regenerated from dimethylacetamide–LiCl solution. *Polym. Adv. Technol.* **2016**, *27*, 1102. [CrossRef]

25. Lu, X.; Shen, X. Solubility of bacteria cellulose in zinc chloride aqueous solutions. *Carbohydr. Polym.* **2011**, *86*, 239–244. [CrossRef]

26. Gericke, M.; Schlufter, K.; Liebert, T.; Heinze, T.; Budtova, T. Rheological properties of cellulose/ionic liquid solutions: From dilute to concentrated states. *Biomacromolecules* **2009**, *10*, 1188–1194. [CrossRef]

27. Pavlyuchenko, M.M.; Kaputsky, F.N.; Grinshpan, D.D. Effect of organic solvent nature on the interaction of cellulose with nitrogen tetroxide. *J. Appl. Chem.* **1975**, *48*, 1822–1825.

28. Hammer, R.B.; Turbak, A.F. *Production of Rayon from Solutions of Cellulose in N2O4-DMF in Solvent Spun Rayon, Modified Cellulose Fibers and Derivatives*; American Chemical Society: Washington, DC, USA, 1977; Chapter 4.

29. Budtova, T.; Navard, P. Cellul. *NaOH-Water Based Solvents A Rev. Cellul.* **2016**, *23*, 5–55.

30. Grinshpan, D.D.; Gonchar, A.N.; Tsygankova, N.G.; Makarevich, S.E.; Savitskaya, T.A.; Sheimo, E.V. Реологические свойства концентрированных растворов целлюлозы и ее смесей с другими полимерами в ортофосфорной кислоте. *J. Eng. Phys. Thermophys.* **2011**, *84*, 594. [CrossRef]

31. Boerstoel, H.; Maatman, H.; Westerink, J.B.; Koenders, B.M. Liquid crystalline solutions of cellulose in phosphoric acid. *Polymer* **2001**, *42*, 7371. [CrossRef]

32. Graenacher, C.; Sallmann, R. Cellulose Solutions and Process of Making Same. U.S. Patent 2179181, 7 November 1939.

33. Johnson, D.L. Compounds Dissolved in Cyclic Amine Oxides. U.S. Patent 3447939, 2 September 1966.

34. Golova, L.K.; Romanov, V.V.; Lunina, O.B.; Platonov, V.A.; Papkov, S.P.; Khorozova, O.D.; Yakshin, V.V.; Belasheva, T.P.; Sokira, A.N. Method for Obtaining a Solution for Spinning. Fibers. Patent RF 1645308, 30 April 1991.

35. Golova, L.K. New Cellulose Fiber Lyocell. *Rus. J. Gen. Chem.* **2002**, *XLVI*, 49–57.

36. Rosenau, T.; Potthast, A.; Sixta, H.; Kosma, P. The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process). *Prog. Polym. Sci.* **2001**, *26*, 1763–1837. [CrossRef]

37. Budaeva, V.V.; Gismatulina, Y.A.; Zolotukhin, V.N.; Rogovoi, M.S.; Melnikov, A.V. A Method for Producing Cellulose from Flax-Mezheumka for the Paper. Industry. Patent RF 2566275, 20 October 2015.

38. Kopania, E.; Wietecha, J.; Ciechańska, D. Studies on Isolation of Cellulose Fibres from Waste Plant Biomass. *Fibres Text. East. Eur.* **2012**, *20*, 167–172.

39. Hummel, M.; Ma, Y.; Michud, A.; Asaadi, S.; Roselli, A.; Stepan, A.; Hellstén, S.; Sixta, H. Lignocellulosic Multicomponent Fibers Spun from Superbase-Based Ionic Liquids. *Lenzing. Ber.* **2018**, *94*, 67–76.

40. Zhang, H.; Tong, M.; Shao, H.; Hu, X. Comparison of the structures and properties of Lyocell fibers from high hemicellulose pulp and high α-cellulose pulp. *J. Appl. Polym. Sci.* **2008**, *107*, 636–641. [CrossRef]

41. Golova, L.K. Processing of cellulose via highly concentrated "solid solutions". *Fibre Chem.* **1996**, *28*, 5–16. [CrossRef]

42. Golova, L.K.; Borodina, O.E.; Kuznetsova, L.K.; Lyubova, T.A.; Krylova, T.B. The Solid-Phase MMO Process. *Fibre Chem.* **2000**, *32*, 243–251. [CrossRef]

43. Makarov, I.S.; Golova, L.K.; Kuznetsova, L.K.; Rebrov, A.V.; Berkovich, A.K.; Skvortsov, I.Y.; Kulichikhin, V.G. Composite fibers based on cellulose and polyacrylonitrile copolymers. *Russ. J. Gen. Chem.* **2017**, *87*, 1351–1356. [CrossRef]

44. Segal, L.; Creely, J.J.; Martin, A.E.; Conrad, C.M. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. *Text. Res. J.* **1959**, *29*, 786–794. [CrossRef]

45. Langford, J.I.; Wilson, A.J.C. Scherrer After Sixty Years: A Survey and Some New Result in the Determination of Crystallite Size. *J. Appl. Crystallogr.* **1978**, *11*, 102–113. [CrossRef]

46. Bazarnova, N.G. *Methods for the Study of Wood and Its Derivatives: Textbook*; Alt. State Univ.: Barnaul, Russia, 2002; p. 160.

47. Ivanova, N.V.; Korolenko, E.A.; Korolik, E.V.; Zhbankov, R.G. Mathematical processing of the IR spectrum of cellulose. *Zhurnal Prikl. Spektrosk.* **1989**, *51*, 301–306.

48. Dehant, J.; Danz, R.; Kimmer, W.; Schmolke, R. *Infrared Spectroscopy of Polymers*; Oleinik, E.F., Ed.; Chemistry: Moscow, Russia, 1976; p. 471.

49. O'Connor, R.T.; Du Prè, E.; Mitcham, D. Application of infrared absorption spectroscopy to investigations of cotton and modified cottons. Part I. Physical and crystalline modification and oxidation. *Text. Res. J.* **1958**, *28*, 382–392. [CrossRef]

50. Makarov, I.S.; Golova, L.K.; Bondarenko, G.N.; Anokhina, T.S.; Dmitrieva, E.S.; Levin, I.S.; Makhatova, V.E.; Galimova, N.Z.; Shambilova, G.K. Structure, Morphology, and Permeability of Cellulose Films. *Membranes* **2022**, *12*, 297. [CrossRef]

51. Makarov, I.S.; Golova, L.K.; Kuznetsova, L.K.; Mironova, M.V.; Vinogradov, M.I.; Bermeshev, M.V.; Levin, I.S.; Kulichikhin, V.G. Composite Fibers from Cellulose Solutions with Additives of Bis (Trimethylsilyl) Acetylene and Alkoxysilanes: Rheology, Structure and Properties. *Fibre Chem.* **2019**, *51*, 26–31. [CrossRef]

52. Chowdhury, R.A.; Nuruddin, M.; Clarkson, C.; Montes, F.; Howarter, J.; Youngblood, J.P. Cellulose nanocrystal (CNC) coatings with controlled anisotropy as high-performance gas barrier films. *ACS Appl. Mater. Interfaces* **2018**, *11*, 1376–1383. [CrossRef] [PubMed]

53. Kaplan, D.L. *Biopolymers from Renewable Resources*; Springer: Berlin/Heidelberg, Germany, 2013; p. 420.

54. Kozlowski, R.M.; Mackiewicz-Talarczyk, M. *Handbook of Natural Fibres: Volume 1: Types, Properties and Factors Affecting Breeding and Cultivation*; Woodhead Publishing: Duxford, UK, 2020; p. 838.

55. Charlet, K.; Jernot, J.P.; Gomina, M. Mechanical properties of flax fibers and of the derived unidirectional composites. *J. Compos. Mater.* **2010**, *44*, 2887–2896. [CrossRef]

56. Makarov, I.S.; Golova, L.K.; Bondarenko, G.N.; Skvortsov, I.Y.; Berkovich, A.K.; Bermeshev, M.V.; Mironova, M.V. Carbon—Silicon-Carbide Fibers Prepared from Solid Solutions of Cellulose in N-Methylmorpholine-N-Oxide with Added Tetraethoxysilane. *Fibre Chem.* **2017**, *49*, 231–236. [CrossRef]