Peculiarities of cellulose nanoparticles

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ABSTRACT: The effects of sulfuric acid concentration and temperature have been studied to optimize the preparation of crystalline nanoparticles (CNP) and amorphous nanoparticles (ANP) of cellulose. To isolate CNP with increased yield (67%-70%) requires hydrolysis with warm 58-60 wt% sulfuric acid. CNP having average sizes of 150 × 15 nm and heightened yield can be obtained by using optimal hydrolysis conditions together with vigorous disintegration. Because of its highly crystalline structure, CNP have increased specific gravity and low hydrophility and accessibility. CNP potentially can be used as a nano-filler to improve properties of pastes, glues, paints, and coating compositions. To isolate ANP having an average diameter of 100 nm with the optimal yield (65-67%), cold 65-66 wt% sulfuric acid should be used in combination with vigorous disintegration. Because of their amorphous structure, ANP acquire such specific features as increased content of functional groups, high accessibility, enhanced sorption ability and hydrophility, and high viscosity and thickening ability. Given the specific features of ANP, their main application area might be for immobilization of biological active substances and drugs, filling and thickening of cosmetic and medicine remedies (e.g., pastes, creams, sprays, etc.).

Application: The results of this study may help in achieving optimal conditions for production of CNP and ANP.

Among various organic materials, cellulose is the most appropriate for preparation of various types of nanomaterials. Cellulose is an abundant natural polymer. It has a nanostructured organization and unique properties such as low density, hardness, and abrasivity; the ability to be structurally and chemically modified; biocompatibility; biodegradability, etc. Currently, several kinds of nano-scale celluloses are manufactured: nanowhiskers or crystalline nanoparticles (CNP), microfibrillated or nanofibrillated cellulose (NFC), and bacterial nanocellulose (BNC). These nano-scale celluloses are characterized by developed specific surface, improved biodegradability, and stability under increased temperatures, aggressive media, and proteolytic enzymes [1-3]. Such nanomaterials are the subject of continuing research and have a commercial interest in terms of manufacturing of improved and new products.

BNC is a nanomaterial with unique properties produced by several species of ubiquitous fermentation bacteria, most importantly *Gluconacetobacter xylinus* [4-6]. During formation, long and thin elementary nanofibrils having a lateral size of 7-10 nm are aggregated to flat microfibrils with a width of 60–150 nm. The neighboring microfibrils interlace and form bands having spongy structure filled with water. Therefore, never-dried BNC contains extremely high amounts of embedded water, up to 99%. The formation of BNC by fermentation opens new vistas for the in situ shaping of cellulose. This bioshaping allows the production of flat pellicles, fibers, spheres, and hollow bodies with high effectiveness by changing the conditions of the bacteria cultivation. BNC is characterized by its high purity. The degree of polymerization of BNC is 2000–8000. This nanocellulose contains about 80% of CI(alpha) crystalline allomorph; the crystallinity of BNC is 70%–80% and the lateral size of crystallites is 7-10 nm [5-7]. Because of high water content, BNC is applicable in cosmetics as a moistening mask, as well as an ingredient of moistening cream. BNC also has medical and veterinary applications in biocompatible nano implants.

Microfibrillated cellulose was first developed by Herrick, Turbak, et al. via grinding of diluted pulp suspensions in a high pressure mill [8,9]. Today, because of better equipment, it is possible to produce the NFC, which typically consists of disintegrated microfibrillar bundles with lateral sizes of 10-30 nm and lengths of several microns [10]. A major obstacle to be overcome for successful commercialization of NFC is the high energy consumption connected to mechanical disintegration of fibers into nanofibers, often involving several passes through the disintegration device. However, preliminary chemical modification and hydrolysis of cellulose with acids or enzymes significantly decreases the energy consumption during subsequent mechanical disintegration [10,11]. The main application areas of NFC are as reinforcing additives to paper, polymers, and other composite materials [10-13].

CNP can be made by hydrolysis of cellulose samples with concentrated solutions of sulfuric acid or hydrochloric acid at moderate temperatures and following mechanical or ultrasound disintegration of the acid-treated cellulose in water [2,3,7]. The history of CNP began more than 60 years ago, when Rånby reported for the first time that colloidal suspensions of cellulose can be obtained by controlled sulfuric acid-catalyzed degradation of cellulose fibers [14]. Currently, CNP are obtained from celluloses of various origins: tunicate, cotton, wood pulp, ramie, hemp, flax, sisal, microcrystalline cellulose, and other materials. The concentration of sulfuric acid can vary from 45 wt% to 70 wt%, the temperature can range

from 25°C to 70°C, and the hydrolysis time can be from 30 min to overnight, depending on the temperature [2,7,12,16-21]. Typical hydrolysis conditions of the initial cellulose are as follows: sulfuric acid concentration = 55-65 wt%, temperature = 40°C-50°C, and time = 1-2 h. CNP prepared from various celluloses have widths of 4-50 nm and lengths of 50-500 nm.

Bondenson et al. [22] investigated the hydrolysis of microcrystalline cellulose as a starting cellulose material at various conditions. The main factors that were varied during the process were the concentration of sulfuric acid and time and temperature of the hydrolysis. The result was that after hydrolysis with 63.5 wt% sulfuric acid at 45°C for 2 h, the yield of CNP was only 30%, and even less if a more concentrated acid was used. Therefore, the hydrolysis conditions need further optimization to achieve the higher yield.

Uncommon nanocelluloses, such as amorphous nanoparticles (ANP), have been investigated much less than other nanocelluloses. In the process described in the patent for ANP [23], the acid hydrolysis of the amorphous cellulose regenerated from solutions in 65 wt% sulfuric acid was carried out; then the dispersion of hydrolyzed cellulose was disintegrated to obtain the ANP. Engelhardt and coauthors [24] performed acid hydrolysis of the amorphous cellulose regenerated from solutions in N-methylmorpholineoxide. On the second stage, a high-shear mechanical grinding of the water dispersion of hydrolyzed cellulose was carried out, and spherical nanoparticles of amorphous cellulose with average diameter of 300 nm were isolated. To reduce crystallinity, cellulose samples also underwent mercerization. The amorphized samples were then hydrolyzed with a sulfuric acid and hydrochloric acid mixture and finally sonicated [25,26]. The final spherical particles had average diameters of 200-500 nm, but the prolonged sonication resulted in a decrease of the particle diameters to 50-80 nm. The main drawback of the methods is a broad size distribution of the ANP and the prolonged duration of the processes. Thus, these methods need improvement and optimization.

Despite an abundance of published studies, methods for isolation of cellulose nanoparticles are far from the optimal. Moreover, most studies have focused on the dimensions and mechanical properties of nanoparticles, while other characteristics were studied to a much lesser extent. Therefore, the main objective of this study was to develop optimal methods for the isolation of CNP and ANP, as well as study their distinctive features.

EXPERIMENTAL

Materials

The starting material was cotton cellulose (98% α-cellulose; DP = 2700). The cellulose was ground in an aqueous medium in a Waring mill, and the resulting slurry was squeezed to a final solids content of about 20-25 wt%. Chemically pure 95 wt% sulfuric acid was diluted at cooling in an ice bath up to 80 wt% and density 1.727 g/cm^3.

Preparation of CNP

Wet pulp was mixed with an additional amount of water in a laboratory glass, and then 80 wt% sulfuric acid was slowly added with cooling to obtain the required final concentration of sulfuric acid (50-70 wt%) and an acid:cellulose ratio of 8-10 [27]. The glass was placed into a 45°C water bath, heated, and stirred for 40-60 min. After acidic treatment, contents of the glass were poured into a tenfold volume of cold water while stirring. Cellulose sediment was separated from the liquid phase by centrifugation at an acceleration of 5000 g for 10-15 min; washed with water, 5 wt% sodium bicarbonate, and finally with distilled water to a pH of about 5, separating it from the water by centrifugation. Then, the washed cellulose sediment was diluted with distilled water to a solids concentration of 1 wt% and disintegrated in a Branson S-450 Digital Ultrasonic Sonifier (Emerson Industrial Automation; Danbury, CT, USA) at 20 kHz for 10-15 min. The 1 wt% water dispersion was evaporated under vacuum at 80°C to increase its consistency to 5-15 wt%.

To obtain a dry nanopowder, the concentrated water dispersion of the CNP was washed with absolute ethanol, acetone, and hexane, and finally dried at 50°C up to a constant weight.

Preparation of ANP

Wet pulp was mixed with an additional amount of water in a laboratory glass, then 80 wt% sulfuric acid was slowly added while cooling to obtain the required final concentration of the sulfuric acid (55-70 wt%) and an acid:cellulose ratio of 8-10 [28]. The glass was placed into a cold water bath having a temperature of 10°C-15°C (±5°C) and stirred for 40-60 min. After acidic treatment, the contents of the glass were poured into a tenfold volume of cold water while stirring to regenerate flocs of the dissolved amorphous cellulose. The flocs were separated from the liquid by centrifugation at 5000 g for 10-15 min, washed with distilled water to a pH of about 5, then separated from water by centrifugation. The separated flocs of amorphous cellulose were diluted with distilled water to a solids concentration of 1% and disintegrated in an ultrasound disperser at 20 kHz for 10-15 min. The 1 wt% water dispersion was evaporated under vacuum at 80°C to increase its consistency to 5-15 wt%.

To obtain a dry nanopowder, the concentrated water dispersion of the ANP was washed with absolute ethanol, acetone, and hexane, and finally dried at 50°C to a constant weight.

Methods of investigations

The degree of crystallinity of the cellulose samples was determined by method of wide-angle X-ray scattering (WAXS) [29]. The size and shape of the nanoparticles were investigated by electron microscopy [30]. The concentration of sulfonic groups in the nanoparticles was calculated from a sulfur assay [28]. The average degree of polymerization (DP) was measured by the viscosity method using diluted solutions of cel-

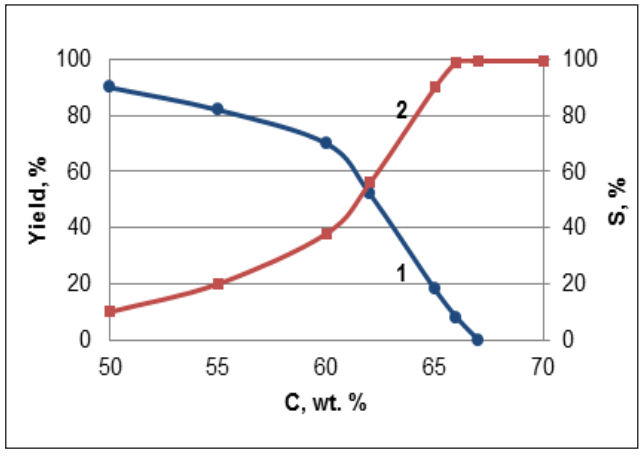
lulose in a solution of cadmium oxide in aqueous ethylenediamine (cadoxen) [3]. Sorption experiments were carried out at 25°C on a vacuum apparatus having helical spring quartz scales [31]. The viscosity of water dispersions of nanoparticles was studied using a Brookfield viscometer [32]. Enzymatic hydrolysis of the nanoparticles was carried out with a mixture of commercial cellulolytic enzyme and β-glucosidase at 50°C, pH = 4.8 for 24 h [33].

RESULTS AND DISCUSSION

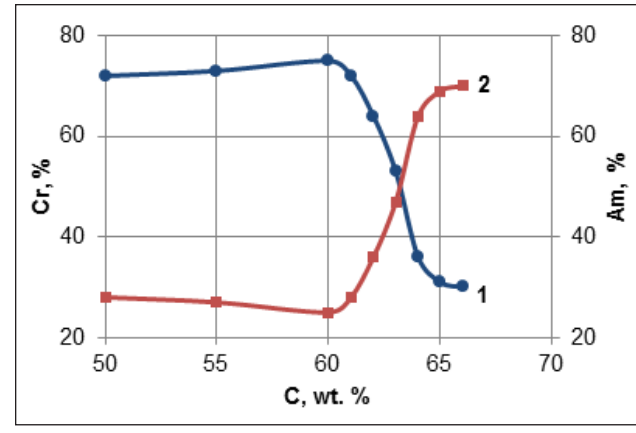
Study of CNP manufacturing process

The starting cellulose sample was hydrolyzed at 45°C using 50-70 wt% sulfuric acid. The investigations showed that increasing the acid concentration from 50 wt% to 60 wt% caused a reduction in the yield of the cellulose particles from 90 wt% to 70 wt% (**Fig. 1**). When the concentration of sulfuric acid reached 65 wt%, the cellulose sample dissolved completely. The yield of the particles made of cellulose regenerated from solution in 65 wt% sulfuric acid was low (20 wt%); furthermore, these particles had a decreased degree of crystallinity (30%) and DP (60). Increasing the sulfuric acid concentration to more than 65 wt% led to further diminution in yield, crystallinity, and DP of the regenerated particles. After hydrolysis of the initial sample with 67 wt% sulfuric acid, the yield of the particles was zero because the hydrolyzed and dissolved cellulose cannot be regenerated from the acidic solution by dilution with water. This was caused by the fast acidic depolymerization of cellulose with 67 wt% sulfuric acid and formation of the water-soluble oligomers [34].

According to WAXS results, in the range of sulfuric acid concentration of 50-60 wt%, the degree of crystallinity of obtained particles increased slightly (**Fig. 2**). On the other hand, when the sulfuric acid concentration was more than 60 wt%, the decrystallization of the particles occurred as a result of increased solubility of the cellulose in a sufficiently concentrated sulfuric acid; as a result, low-crystalline particles were formed.



1. Dependence of yield (1) and solubility (2) of cellulose particles on concentration of warm sulfuric acid.

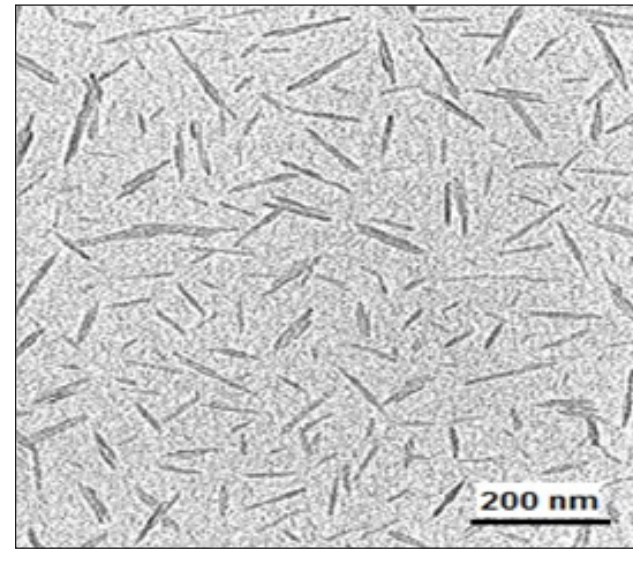


2. Dependence of crystallinity (1) and amorphicity (2) degrees of cellulose particles on concentration of warm sulfuric acid.

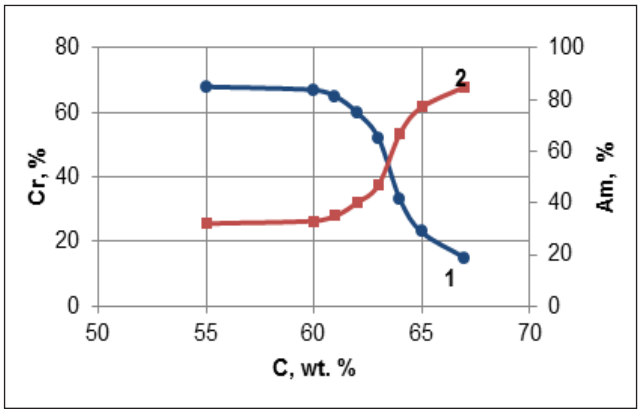
As follows from transmission electron microscopy investigations, after cellulose hydrolysis with 50-55 wt% sulfuric acid, the aggregates of CNP that are formed have an increased length (300-500 nm) and lateral size (40-60 nm). Raising the acid concentration to 58-60 wt% contributes to formation of smaller CNP, with sizes of 100-200 × 10-20 nm (**Fig. 3**).

Thus, the reduced acid concentrations, 50-55 wt%, led to aggregates that are too coarse, while high concentrations, >60 wt%, lead to low yield of the nanoparticles and their decrystallized structure. To obtain the highly crystalline nanoparticles of small-sizes with the increased yield of about 70%, the concentration of sulfuric acid used for hydrolysis of the starting cellulose sample should be in the range of 58-60 wt%.

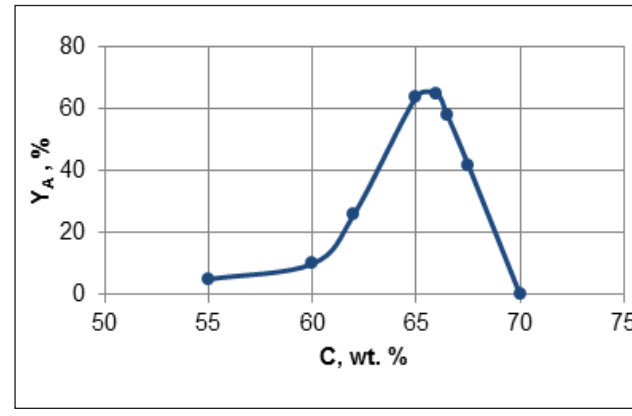
The mechanism of crystalline nanoparticle generation is unclear, and it is a subject of discussion. The phenomenon is explained usually by selective acid hydrolysis of disordered noncrystalline domains of cellulose nanofibrils, whereas the more resistant nanocrystallites remained intact and can be isolated in



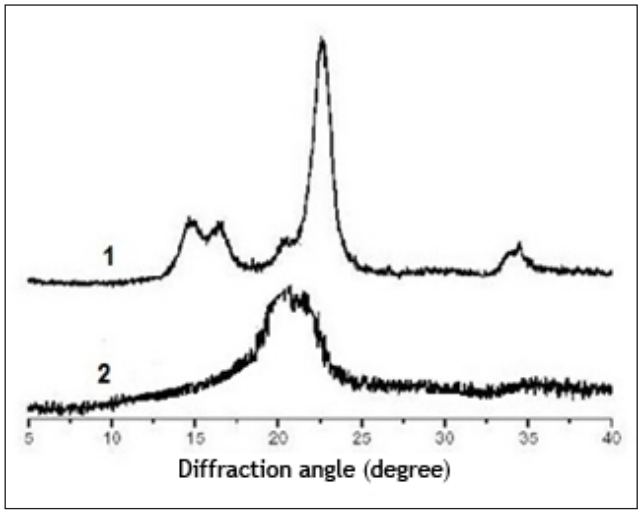
3. Transmission electron microscopy image of rod-like crystalline nanoparticles of cellulose.



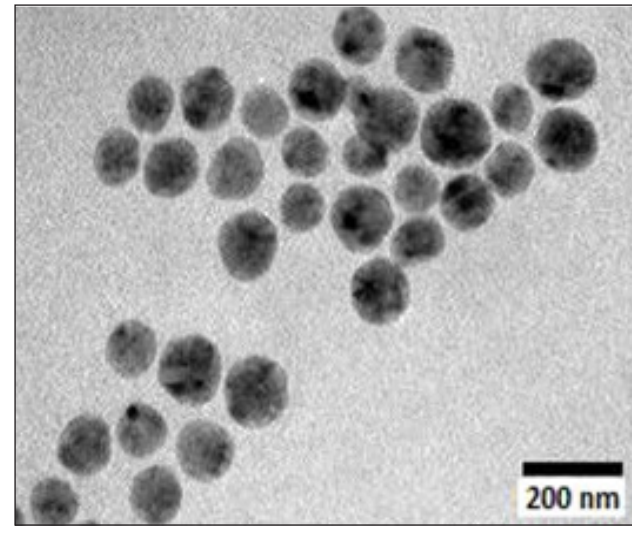
4. Dependence of crystallinity (1) and amorphicity (2) degrees of cellulose particles on concentration of cold sulfuric acid.



6. Dependence of yield of amorphous nanoparticles on concentration of cold sulfuric acid.



5. X-ray diffractograms of crystalline (1) and amorphous (2) cellulose nanoparticles.



7. Transmission electron microscopy image of amorphous nanoparticles of cellulose.

a form of rod-like particles [2,35]. However, this mechanism does not explain why the free nano-size particles cannot be isolated when the hydrolysis is performed by diluted acids, 8-10 wt% hydrochloric or 10-40 wt% sulfuric, despite achieving the level-off DP of cellulose [30,35]. For example, after cellulose hydrolysis with 20 wt% sulfuric acid together with vigorous stirring, only long microfibrillar bundles are formed [35]. To obtain the individual nanowhiskers, the cellulose should be hydrolyzed with at least 60 wt% sulfuric acid.

During cellulose hydrolysis with diluted acids, not only depolymerization but also lateral co-crystallization of released nanocrystallites takes place [36]. The aggregates of the crystallites that form are joined in lateral directions by means of strong crystalline contacts [7,30]. To break these strong contacts and release free nanocrystallites, a sufficiently high acid concentration is required.

When the cellulose is hydrolyzed with diluted acid, the strong inter-crystallite contacts remain intact, and instead of nanoparticles, micron-size crystalline aggregates are formed. On the other hand, treatment of cellulose with a sufficiently high acid concentration (58–60 wt% sulfuric acid) causes etching of the lateral contacts and sulfonation of the surface of individual nanocrystallites. As a result, the crystalline contacts are replaced by weaker amorphous contacts. After breakdown of these contacts on disintegration water, the CNP can be released.

Study of ANP manufacturing process

To obtain ANP, the starting cellulose sample was first dissolved in sufficiently concentrated solutions of sulfuric acid at decreased temperatures, then the cellulose flocs were regenerated from the solutions and disintegrated in an ultrasound disperser. WAXS investigations of the cellulose particles showed that the highly amorphous structure of the particles can be achieved when the concentration of sulfuric acid was ≥65 wt% (**Fig. 4**).

In contrast to CNP, the cellulose particles prepared after regeneration from 65-66 wt% sulfuric acid have a diffuse X-ray diffractogram typical of the amorphous phase state (**Fig. 5**). A maximum yield of amorphous cellulose of about 65%-70% was achieved after regeneration from the solutions in 65-66 wt% sulfuric acid (**Fig. 6**). Increasing the sulfuric acid con-

Characteristics	Crystalline Nanoparticles	Amorphous Nanoparticles
Average particle sizes, nm	150 × 15	100
Aspect ratio	10	1
Degree of polymerization	120-140	70-80
Degree of crystallinity, %	75-77	20-25
Allomorph type of crystallites	CI	CII
Specific gravity, g/cm^2	1.57-1.58	1.50-1.51
Specific volume, cm^3/g	0.63-0.64	0.66-0.67
Content of sulfonic acid (SO_3H)-groups, meg/kg	40-50	200-220

I. Characteristics of the cellulose nanoparticles.

centration more than 66 wt% led to a decrease in the yield, but after treatment with 70-72 wt% sulfuric acid, the dissolved cellulose cannot be regenerated from the acidic solution by diluting with water because of the fast acidic depolymerization of cellulose and formation of water-soluble oligomers.

As seen in the transmission electron microscopy image, the ANP of cellulose have spherical shapes with diameters of 80-150 nm (**Fig. 7**).

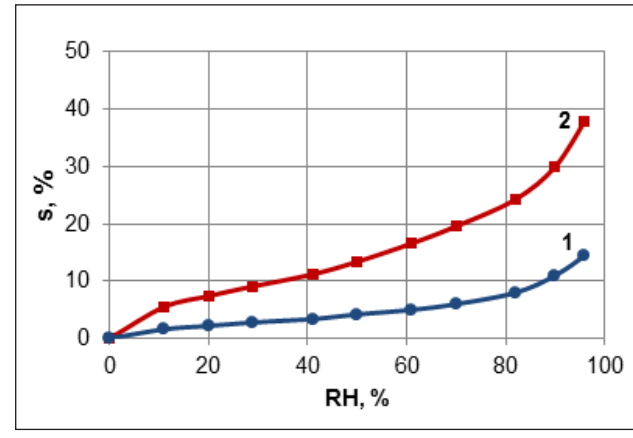
To obtain ANP with an increased yield of about 65%, the concentration of sulfuric acid used for treatment of the starting cellulose sample should be in the range of 65-66 wt%.

The probable mechanism of the generation of ANP consists of depolymerization, sulfonation, and dissolving of cellulose in a sufficiently high sulfuric acid concentration (65-66 wt%), followed by regeneration of the amorphous flocs and their comminution in water.

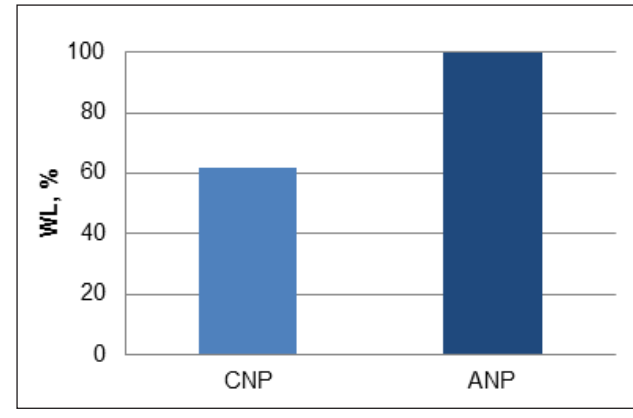
Comparative study of properties of CNP and ANP

Table I shows the main characteristics of the CNP and ANP. Because of their highly crystalline structure, the CNP had an increased specific gravity, low hydrophility, and accessibility (**Fig. 8** and **9**).

CNP of cellulose have high mechanical properties [1,37-39]: axial modulus of 130-150 GPa, transverse modulus of 10-30 GPa, axial tensile strength (TS) of 8-10 GPa, and transverse TS of 500-700 MPa. Because of these properties, CNP can be used as nanofillers for polymer composites [12,15,17,21]. However, the aspect ratio of NFC is high (50-100) [10,11], which gives an advantage for NFC as reinforcing nanofillers in comparison with CNP, which have a lower aspect ratio. Therefore, it is better to use CNP in other areas (e.g., as an improving additive for glues, paints, paper coating compositions, etc.) [3,13,35,40-42]. As seen from **Fig. 10**, covering



8. Sorption isotherms of water vapor by crystalline nanoparticles (1) and amorphous nanoparticles (2).



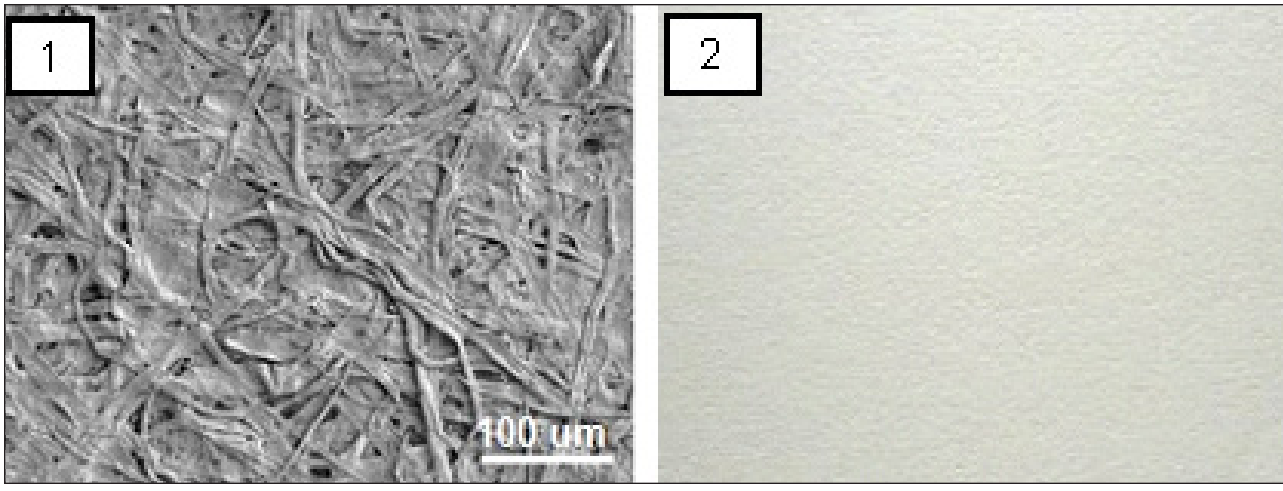
9. Weight loss (WL) of crystalline and amorphous nanoparticles after enzymatic hydrolysis for 24 h at enzyme loading 15 FPU/g.

paper with a latex composition containing 10% CNP provides a smoother surface.

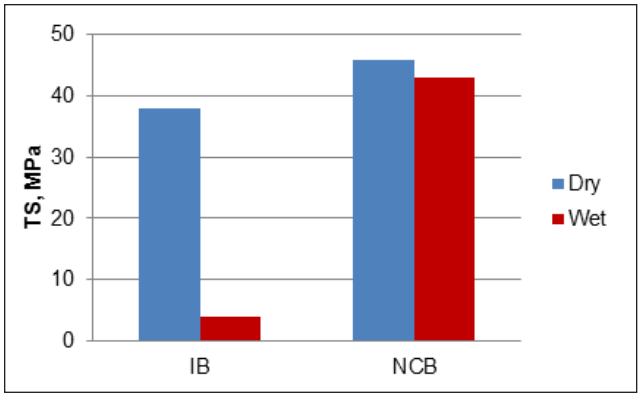
Another example is a CNP composition for hydrophobic protective coating of hydrophilic paperboards [42]. On its own, the paperboard substrate loses about 90% of its strength after wetting. In contrast, the coated substrate in a wet state maintains up to 90% of its strength. Introduction of CNP into coating compositions helps achieve higher mechanical properties of the coated board (**Fig. 11**).

In contrast to CNP, the mechanical properties of ANP are poor (modulus <1 GPa, TS <50 MPa) [27, 39]; therefore, these particles are not suitable for use as a reinforcing nanofiller. On the other hand, because of their amorphous structure, ANP acquire such specific features as increased content of functional groups, high accessibility for reagents and enzymes, enhanced sorption ability and hydrophility (Fig. 8), high viscosity and thickening ability, etc. Because of their high accessibility, ANP are completely hydrolyzed by cellulolytic enzymes (Fig. 9).

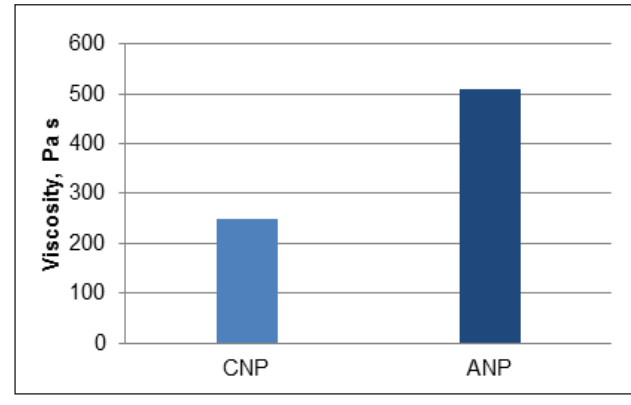
Analysis of rheological properties of water dispersions of ANP showed that with increasing concentration, viscosity rises, and the ANP dispersion turns to a thick gel (**Fig. 12**). Because of expressed thickening properties, a low additive of



10. Surface of initial (1) and nano-coated (2) paper.



11. Tensile strength (TS) of initial board (IB) and board coated with protective hydrophobic composition containing 10% crystalline nanoparticles (NCB) in dry and wet states.



12. Viscosity of 5% dispersions of crystalline nanoparticles and amorphous nanoparticles at shear rate 1 s^{-1}.

ANP (1-2 wt%) prevents the phase separation of some drug dispersions (e.g., "Maalox") [28].

Increased content of acidic (sulfonic) functional groups in ANP (Table I) contributes to immobilization of various therapeutically active substances (TAS) containing basic functional groups. The ANP-TAS complex can be applied in remedies designed for effective skin care and cure. In particular, the ANP-trypsin complex is capable of removing dead skin cells and cleaning wounds without damage to healthy tissues [28]. Low-acidic and soft ANP also can be used for gentle skin peeling. Given the specific features of the ANP, the main application area can be immobilization of biological active substances and drugs, and filling and thickening of cosmetic and medicine remedies (e.g., pastes, creams, sprays, etc.).

CONCLUSIONS

The effect of concentration of sulfuric acid and temperature was studied to optimize the preparation of CNP and ANP of cellulose. To isolate CNP with increased yield (67%-70%), hydrolysis with warm 58-60 wt% sulfuric acid is required. Treatment of cellulose with that concentration of sulfuric acid causes etching of the lateral crystalline aggregates and sulfonation of the surface of crystallites that contribute to breakdown of the aggregates and isolation of the free nanocrystalline particles after vigorous disintegration in water. Use of optimal hydrolysis conditions (58-60 wt% sulfuric acid, acid:cellulose ratio = 8-10; T = 45°C; t = 40-60 min) together with vigorous disintegration makes it possible to obtain CNP having sizes of 150-200 × 10-20 nm with heightened yield (67%-70%). Because of their highly crystalline structure, CNP had an increased specific gravity and low hydrophility and accessibility. CNP of cellulose have high mechanical properties; however, the aspect ratio of these particles is lower than of NFC. Potential application areas of CNP include filling of glues, paints, and coating compositions.

To isolate ANP with an optimal yield (65%-67%), cold 65-66 wt% sulfuric acid should be used in combination with vigorous disintegration. The probable mechanism of the generation of ANP consists of depolymerization, sulfonation, and dissolving of cellulose in the concentrated sulfuric acid, followed by regeneration of the amorphous flocs and their comminution in water. ANP have a spherical shape with an average diameter of 100 nm. The nanoparticles are characterized by a high degree of amorphicity and increased content of sulfonic

groups. Because of their amorphous structure, ANP acquire such specific features as increased content of functional groups, high accessibility, enhanced sorption ability and hydrophility, and high viscosity and thickening ability. ANP are completely hydrolyzed by cellulolytic enzymes with forming of glucose that can be used further for biological, cosmetic, or medical application. A concentrated paste of ANP has expressed thickening properties; therefore, its addition can prevent the phase separation of various water dispersions. Increased content of acidic functional groups in ANP contributes to immobilization of various therapeutically active substances containing basic functional groups. The main application area of ANP can be immobilization of biological active substances and drugs, filling and thickening of cosmetic and medicine remedies (e.g., pastes, creams, sprays, etc.). **TJ**

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I chose this topic to research because it shows peculiarities of various types of nanocelluloses. This research supplements previous studies and shows differences in various types of nanocelluloses.

The most difficult aspect of this research was achieving a high yield of nanoparticles. The research revealed that very small changes in the preparation conditions cause a drastic change in phase state and shape of nanoparticles.

Mills and other cellulose factories can use the proposed information to produce crystalline and amorphous nanoparticles. The next step is to research reactive nanoparticles.

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