

INCREASE OF COTTON CANVAS STRENGTH BY ADDITION OF NANOCELLULOSE TO THE COATING

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Abstract

Laboratory-prepared particles of nanocellulose were added to acrylic coating material in order to increase the strength of cotton canvas. The size of the cellulose nanoparticles was determined using a Zetasizer device. Changes in tensile strength, in relation to the added amount of nanocellulose, were observed under laboratory conditions. The cotton canvas coated with acrylic coating showed increased strength when the optimum amount of nanocellulose was added. This finding can be utilized eg. to prolong the life of bookbinding canvases (buckrams).

Keywords: Nanocellulose, cotton canvas, coating, strength

1. INTRODUCTION

The term “nanocellulose” is defined as cellulose particles of nanosize. Depending on the method of production they are labelled as cellulose nanocrystals (nanocrystalline cellulose or nanowhiskers), with a length of tens to hundreds of nanometers or they are labelled as cellulose nanofibrils with a high aspect ratio (width of 5 to 20 nm and lengths of up to several micrometers). The cellulose in the plant cell walls forms a nanofibril structure. Van der Waals forces and hydrogen bonds between the neighboring nanofibrils glue them to the cellulose fibre.

Due to its excellent mechanical properties the nanocellulose has become an interesting component in the development and preparation of new composite materials. Nanocellulose has been intensively studied in recent years and besides composite materials there are other new applications eg. in the food industry, in the production of paper and boards, in paper and board coatings, in cosmetics and toiletries, and in filter materials. [1]

Bookbinding canvases (buckrams) are used for cardboard packaging. They form the protective boards for books used in the conservation of library collections, and they are especially utilized with books printed after the year 1800. [2] The base fabric is coated with polymer coating material, which provides further mechanical, visual and useful characteristics for the book canvas. Books in the public domain are mechanically stressed due to their frequent use. They are also intended for long term storage. Therefore a protective book canvas on their surface should have particularly good mechanical properties such as good strength and resistance to light, changes of temperature, humidity and various aging effects.

We prepared in the laboratory crystals of nanocellulose and we tested their ability to increase the strength of cotton canvas after being incorporated, with varying concentrations, into the acrylic coating material. Also, we compared two dimensional types of nanocellulose crystals and their effect on the tensile strength of coated cotton canvas.

1.1. Production of nanocellulose

The chemical structure of nanocellulose is identical to the cellulose: linear chains composed of D-glucoanhydroxyranose units that are associated with ester bonds $\beta 1 \rightarrow 4$. This biopolymer is synthesized by various bacteria (eg. *Acetobacter xylinum* [3]), marine algae (eg. *Oocystis apiculata*, *Pelvetia*, *Vaucheria*,

Erythrocladia, *Valonia* [4]) and fungi (*Saprolegnia* [4], *Achlya* [5]). The principal source of cellulose is plant material (namely the plant cell walls), and as a consequence plants are usually used as the main source of the production of nanocellulose, eg. bleached wood sulfite pulp, crop residue feedstocks (wheat bran, maize bran, empty fruit bunches of oil palm, soybean pods, peels of prickly pears, lemon peels, banana rachis, waste from sugar cane, sugar or potato beet pulp), cellulose fiber materials (cotton, kenaf, sisal) [6], and lignocellulose waste from the furfural industry such as corn cobs residue [7].

Enzymatic, chemical and mechanical treatments are used to isolate nanocellulose from lignocellulosic residues. Nanowhiskers (crystalline cellulose nanomaterial) of 10-20 nm in width and several hundred nanometers in length are produced by strong acid hydrolysis to remove non-cellulosic components and most of the amorphous cellulose from the source materials. Sulfuric acid hydrolysis is a typical method used to isolate crystalline nanocellulose as it has good dispersibility in water. Other acids such as hydrochloric acid, nitric acid, formic acid or other mixtures of acids were also used in crystalline nanocellulose fabrication. [8] Several processes based on chemical treatments with alkaline solutions at different concentrations were used to extract the highly purified nanocellulose. [9] High quality cellulose nanocrystals are also synthesized using a simple one-step procedure with ammonium persulfate [10]. The nanocellulose can be also prepared from microcellulose using NaOH / urea treatment followed by sonication [11]. Cellulose nanofibrils with a fine and individualized structure can be isolated by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation [7] [12]. In this pretreatment, the surface charge of nanofibrils is increased by oxidation, and a minor mechanical treatment is then used to separate them. Chemical treatment is often followed by mechanical treatment such as high-pressure homogenization, microfluidization, ultrasonication, high-speed blending, grinding, and cryocrushing, which breaks the side aggregations. [8] [13]

1.2. Properties of nanocellulose

The nanocellulose has excellent mechanical and thermal properties: crystallinity, tensile strength, elastic modulus (214 MPa and 13.2 GPa for nanocellulose with an average degree of polymerization of 1100) [14], dimensional stability and thermal stability (between 220 °C and 350 °C [16]). Non-solubility in water, high water absorption, rheological characteristics, and optical transparency are its additional features. The excellent oxygen barrier properties of nanocellulose films depend on relative humidity and this is possible due to the combination of high crystallinity of nanocellulose and the network structure of composites. The network structure is held together through strong inter- and intramolecular hydrogen bonds, lamellar nanofiber structure and dense fiber packing. [15] [16] Nanocellulose also has a number of excellent biological properties such as biodegradability, biocompatibility, and low toxicity [17]. Finally, it should be noted that it is a natural polymer produced from natural and renewable resources.

1.3. Use of nanocellulose

Excellent mechanical properties, interesting physical properties and chemical functionality (e.g., for modification) make nanocellulose a versatile multifunctional material with a wide range of applications. Vegetable nanocellulose is used as a food additive and food stabilizer, as a non-soluble dietary fiber and as a new packaging material in the food industry [13]. The addition of nanocellulose to a polymer is one of the methods utilized to reduce oxygen transmission rate in packaging applications [18]. Additionally, the good thermal stability of nanocellulose would provide convenience for the applications and processing with a relatively higher temperature, especially for thermoplastics [19]. Due to its promising properties such as biodegradability and biocompatibility and due to its environment-friendly nature, nano-sized cellulose is becoming an attractive building block for the design of new biomaterials. Nanocellulose has been utilized to fabricate diverse functional materials, including ultrastrong and high gas-barrier films [15], conductive paper [20], aerogels [21], separation membranes [22], reinforcements for polymer composites [23], and many others.

It has been demonstrated that the addition of cellulose whiskers to various synthetic and natural plastics produces improvements of the physical properties of composite materials. [24] For example, the composite films from styrene and butyl acrylate latex with 6 % of nanocellulose whiskers added exhibited a twofold increase in the shear modulus over control films without whiskers. [25] Another study [23] compared the additive effect of acacia pulp fibers, cellulose whiskers and nanocellulose when incorporated into acrylic latex. Composite acrylic film reinforced with cellulosic whiskers exhibited enhanced strength properties of strength when compared with the other forms of cellulosic additives.

2. EXPERIMENTAL PART

2.1. Material and chemicals used

Cotton fabric Sara (Licolor), area weight 135 g·m⁻², fabric thickness 0.37 mm; Acronal S 996 S - aqueous polymer dispersion based on ester of acrylic acid and styrene, viscosity 2 N·s·m⁻² (BASF SE, Germany), sulfuric acid 96% (Lach-Ner, Czech rep.), cellulose precursor

2.2. Preparation of crystalline nanocellulose

The cellulosic precursor was subjected to acid hydrolysis using diluted sulfuric acid, then repeatedly washed with distilled water and finally sonicated, according to the procedure described in [23]. Two mixtures of crystalline cellulose nanoparticles (precisely two aqueous colloids which were thickened in a pasty consistency containing 8 wt.% of nanoparticles) - "Nanocellulose 1" and "Nanocellulose 2" in the next text- were prepared by varying of these conditions.

2.3. Preparation of cotton fabric with coating

Nanocellulose at concentrations of 0.5 - 1.5 - 2.0 - 2.5 and 3.5 weight % (based on the weight of wet acrylic coating material) was added to the acrylic paste. The ratio of water bounded into colloidal paste in acrylic coating with lower concentrations of nanocellulose and in the blank was replaced by direct addition of distilled water with a corresponding weight. The coating mixtures were applied to the cotton fabric on a printing machine by utilizing the pressure of a rolling steel rod with a weight of about 550 g and magnetic pressure stages 2 and feed rate of the rod 2 m·min⁻¹. After condensation at 150 °C (2 min.) and drying at 80 °C (30 min.), the samples of 2x15 cm were cut from the coated canvas for the tests of tensile strength.

2.4. Measuring of the particle size and stability

The particle size was measured using a Zetasizer Nano device (Malvern) based on dynamic light scattering. The instrument measures particles within the range of 0.6 nm to 6 microns. The stability of colloidal particles was measured by the zeta potential by means of laser Doppler electrophoresis. The size of the zeta potential indicates a possible stability of the colloidal systems. The value of zeta potential of ±30 mV is considered to be the boundary between stable and unstable suspension. Values from 0 to ±10 mV indicate the rapid coagulation of particles in the colloidal system.

2.5. Measuring of the tensile strength

The tensile testing machine TIRA test 2300 was used to measure the strength of the coated cotton. Samples of 2 cm in width were clamped in the pneumatic jaws with a clamping length of 10 cm. Strength testing was carried at a cross-head speed of 100 mm·min⁻¹ at a temperature of 23 °C. The ultimate strength characteristics (maximum force and elongation to break) were applied to every type of coating (with varying sizes of nanoparticles and various concentrations of nanocellulose added) and measured by 10 valid measurements.

Measurements were carried out for all samples in only one direction (machine direction). A blank (comparative sample) was applied to the coated cotton fabric without nanocellulose added.

2.6. Results and discussion

Table 1 summarizes the composition and stability of two laboratory prepared samples of nanocellulose which has been used as an additive to the acrylic coating of cotton canvas. **Table 2** contains a strength comparison of two cotton canvases with coatings containing the same concentration of nanocellulose (2 wt%) having different particle sizes.

Table 1 Size and zeta potential of two differently prepared samples of nanocellulose

Sample	Peak 1 (%)	Peak 2 (%)	Peak 3 (%)	Zeta potential
Nanocellulose 1	192.9 nm (93.7 %)	11.3 nm (6.3 %)	-	-41.7 mV
Nanocellulose 2	135.8 nm (78.9 %)	17.5 nm (15.6 %)	3 634 nm (5.5 %)	-37.5 mV

Table 2 The ultimate strength characteristics of canvases with Nanocellulose 1 and 2 added to the coating in the same amount (2 wt.%)

Canvas with addition of	Young's modulus*	Strength to break	Elongation to break
- (blank)	331.633 MPa	242.6 N	16.1 mm
95% confidence interval		<236.6; 248.6>	<15.8; 16.4>
Nanocellulose 1	335.282 MPa	247.5 N	16.9 mm
95% confidence interval		<243.4; 251.6>	<16.8; 17.0>
Nanocellulose 2	344.956 MPa	253.9 N	17.1 mm
95% confidence interval		<250.1; 257.7>	<16.9; 17.3>

* The Young's modulus was calculated from the difference between strength and elongation in the linear part of stress-strain curve in the middle of the load cycle

Table 1 shows that two samples of nanocrystalline cellulose prepared in the laboratory from the same cellulose precursor under different physical conditions had slightly different particle sizes. According to the recorded values of zeta potential both types of nanocellulose were sufficiently stable in an aqueous solution. Almost all of the particles in "Nanocellulose 1" had a size of approximately 193 nm. The sample labelled "Nanocellulose 2" consisted of particles with a size of approximately 136 nm. Even this slight difference in particle size was reflected in the tensile strength of the coated canvases. In **Table 2**, it is evident with the moderate increase of Young's modulus that the strength and elongation of coated canvases is dependent on the amount of nanoparticles added. The addition of 2 % of crystalline nanocellulose with a higher percentage of smaller particles (about 136 nm) incorporated into the coating resulted in its 5 % higher strength compared to the canvas with a higher percentage of smaller particles (about 136 nm), where the strength increased by only 2%.

The graphs in **Figure 1** and **Figure 2** show how the strength and elongation changed depending on the increasing concentration of nanocellulose in the coating. The influence of additive particles in a polymer matrix on the composite strength increase is well documented. Also here the addition of nanocrystalline cellulose into the acrylic matrix manifests itself in an increased tensile strength, as the particles prevent the tearing of the polymer during a linear load. This is partly due to their own cohesion, partly due to cohesion with the polymer (Van der Waals forces and especially a number of inter- and intramolecular hydrogen bonds) and partly also due to changes in the direction of emerging cracks at the (sub) microscopic level. The application of nanoparticles in the form of a thick colloid caused a worse miscibility of the additive in higher concentrations

to the acrylic coating and during sonication a coagulation of the particles occurred. This is probably the reason why the strength of canvas didn't increase continuously with the increasing ratio of nanocellulose (**Figure 1**). Nevertheless, the highest average tensile strength (261 N) was achieved in canvas with the highest concentration of added nanoparticles (3.5 % by weight of the wet coating), which is 10 % more when compared with the placebo (canvas without nanoparticles). The trend of continuous elongation increase in relation to the increasing concentration of nanoparticles, and also depending on the higher surface of smaller nanoparticles added in the same weight ratio, is again a consequence of the particles surface interaction with polymer. Under load, particles and polymeric chains are oriented in line with the force direction. They slide over each other and particles of additive increase the effectiveness of this sliding surface, which leads to greater extension of the whole composite.

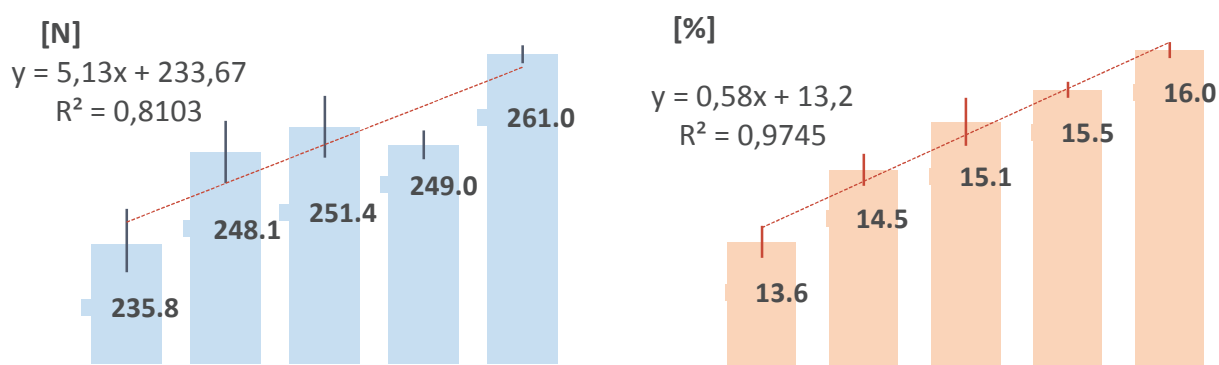


Figure 1 and 2 The values of strength and elongation to break of coatings with varying concentrations of nanocellulose ("Nanocellulose 2")

3. CONCLUSION

Tests confirmed that the addition of crystalline nanocellulose to the acrylic coating of cotton fabric increases the tensile strength of the coated canvas. The tensile strength increased firstly in relation to the increasing concentration of nanocellulose added to the coating up to 10 %, with 3.5 wt. % of nanocellulose. Secondly, the tests indicated the trend of increasing strength and elongation, as well as Young's modulus with the decreasing particle size added to the acrylic coating. The coated cotton fabric with addition of crystalline nanocellulose, which we have developed as buckram with higher strength and mechanical resistance, may also find a wider use in applications where higher demands on the mechanical strength of coated and laminated fabric are placed.

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