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The effect of low frequency ultrasound on the production and properties of nanocrystalline cellulose suspensions and films

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ABSTRACT

Suspension of nanocrystalline cellulose (NCC) produced from bleached cotton by controlled sulphuric acid hydrolysis was treated with low frequency ultrasound at 20 kHz and 60% amplitude for 0, 1, 2, 5 and 10 min and the effects of sonication on the properties of both the cellulose nanocrystals and their aqueous suspensions were investigated. Furthermore, a series of nanocellulose films were manufactured from the suspensions that were sonicated for different periods of time and tested. Laser diffraction analysis and transmission electron microscopy proved that sonication not only disintegrated the large NCC aggregates (D_{v50} 14.7 μm) to individual nanowhiskers with an average length and width of 171 ± 57 and 17 ± 4 nm, respectively, but also degraded the nanocrystals and yielded shorter and thinner particles (118 ± 45 and 13 ± 3 nm, respectively) at 10-min sonication. The ultrasound-assisted disintegration to nano-sized cellulose whiskers decreased the optical haze of suspensions from 98.4% to 52.8% with increasing time from 0 to 10 min, respectively. Sonication of the suspensions significantly contributed to the preparation of films with low haze (high transparency) and excellent tensile properties. With the increasing duration of sonication, the haze decreased and the tensile strength rose gradually. Irrespectively of sonication, however, all films had an outstanding oxygen transmission rate in a range of 5.5–6.9 cm^3/m^2 day, and a poor thermal stability.

1. Introduction

Over the past twenty years, there has been intense and continuing interest in the development of new and high value-added cellulose based materials to increase the use of cellulose in consumer and industrial products. Currently, the fastest growing research activity is concentrating on nanocelluloses, the novel forms of cellulose, because they are renewable, environmentally sound and biodegradable [1]. Of the three main types of nanocelluloses (i.e. microfibrillated [2], nanocrystalline and bacterial nanocellulose [3]), nanocrystalline cellulose (NCC) is prepared from different cellulose containing sources, such as lignocellulose based biomass, wood, cellulosic fibres, etc. by removal of the amorphous phase with acid hydrolysis usually followed by an ultrasonic treatment in order to disintegrate the aggregates of liberated crystalline cellulose particles [4–6]. NCC is a promising new material with unique properties, including nanoscale dimension, high specific strength and modulus, high surface area, high crystallinity and unique optical properties, etc. [7].

Acidic hydrolysis is most often done with sulphuric acid, usually in the range of 60–70% (w/w), at temperatures approaching 45 °C or greater and for various durations differing from some minutes to some hours [8]. After acidic hydrolysis, the NCC is produced as defect-free, rod-like crystalline residue, with a diameter of 10–20 nm and lengths of a few hundred nanometers [9]. During sulphuric acid hydrolysis, negatively charged sulphate ester groups are generated on the surface hydroxyl groups of cellulose nanocrystals, providing highly stable aqueous suspensions owing to the limitation of agglomeration and flocculation of the nanoparticles. Except for the origin of cellulose and the conditions of acidic hydrolysis, subsequently applied sonication to the acidic treatment in order to disintegrate the nanocrystal clusters has also a crucial effect on the properties of the NCC [7]. Although extensive research was carried out in the area of NCC production focusing on the use of different acids with various hydrolysis time, temperature, acid concentration and acid/fibre ratio [10], only a very few previous research studies had shown that sonication of the nanocellulose suspension, when applied subsequent to the acid hydrolysis, could have significant effects not only on the properties of the suspension, but also on the products created from the sonicated suspension.

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Different sonication techniques were applied in the field of nanocellulose production. A sonifier cell disrupter was used for further treatment of the Whatman No 1 filter paper suspension after sulphuric acid hydrolysis and the time effect of ultrasonication on the properties of the cellulose microcrystallites was examined [7]. The particle size decreased with increased treatment time for the first 5 min, but remained practically unchanged upon further treatment. The applied ultrasonication did change the surface charges on the cellulose crystallites.

An ultrasonic horn type reactor was used for sonication of the suspension of Avicel in deionised water, subsequent to the maleic acid hydrolysis, centrifugation and washing processes [11]. Only the longest sonication treatment (9 min, at 15 °C and 90% power output) resulted in cellulose nanocrystals which were cylindrical in shape and were of dimensions, length 65 ± 19 nm and width 15 nm. In another study, response surface methodology was applied to investigate the effect of selected factors on the separation of cellulose nanocrystals from microcrystalline cellulose and sonication as a single factor turned out to be unimportant in the process [12]. Low-intensity ultrasound-assisted hydrolysis in a sonication bath resulted in higher yield and lower viscosity [13].

Ultrasonication of the NCC suspension prior to film casting increased the pitch of the chiral nematic phase in suspension and moved the reflection band of the final iridescent film to longer wavelengths [14]. The effect of sonication on the rheology of the NCC suspensions prepared from freeze-dried NCC powder was also investigated [15]. It was proved that ultrasound treatment severely affects the viscosity and influences the microstructure of NCC aqueous suspensions.

The listed results above proved that ultrasonication can have an effect on certain properties of the final product prepared from sonicated NCC suspensions, but since the available literature in the field is limited, further studies would be needed for a better understanding of the effects of sonication on the NCC production. In this research, NCC was prepared from bleached cotton with sulphuric acid hydrolysis. Bleached cotton is an attractive source of nanowhiskers, since it can be considered as pure cellulose with almost 100% cellulose content. After hydrolysis, low frequency ultrasound (20 kHz, horn type reactor) at 60% amplitude was applied varying the duration of sonication in the range of 0–10 min to study how the length of sonication influences the properties of suspensions and those of the films prepared subsequently from the suspensions. Changes in size of particles i.e. NCC agglomerates and individual cellulose nanocrystals present in the suspensions were followed by laser diffraction analysis and transmission electron microscopy, respectively. For characterising the surface charge of NCC particles zeta potential was measured. Haze as well as stability of the suspensions were characterised by the optical haze which measures the percent of transmitted light that diffusely scatters. The films prepared from the suspensions were tested by measuring the haze, oxygen transfer, thermal and tensile properties. The results presented in this paper prove that sonication not only affects the disintegration of the assembly of cellulose particles, but also affects the individual nanocrystals. Furthermore, sonication influences the properties of the NCC suspensions and has significant effect on the characteristics of films cast subsequently from the sonicated suspensions.

2. Materials and methods

2.1. Production and sonication of NCC suspension

NCC was prepared from a bleached cotton fabric (135 g/m^2, plain-weave) kindly provided by Pannon-Flax Linen Weaving Co. (Hungary) and used without any further wet treatment. The fabric was ground in a Mixer Mill MM400 (Retsch GmBH, Germany) at a frequency of 30 1/s for 2.5 min. The fraction studied in this work was composed of particles with length between 200 and 315 μm, collected by sieving. The ground cotton (10.0 g) was hydrolysed in an Erlenmeyer flask with 64% w/w sulphuric acid (8.75 mL of a sulphuric acid solution/g cotton) at 45 °C for 25 min under constant stirring with a Teflon-coated magnetic bar rotating at 250 rpm [16]. Thereafter the cellulose suspension was diluted with cold, deionised distilled water and allowed to settle overnight in a refrigerator. The clear upper layer was decanted and the remaining white milky suspension was washed with cold deionised water and centrifuged at 5 °C with a refrigerated high speed Hermle Z326 K centrifuge (Labnet, USA) at 13,000 rpm for 10 min. The process from washing to centrifugation was repeated three times. Thenceforth the white suspension was dialyzed against water for about 5 days until it was neutralized, using a dialysis tube (MWCO 12–14 kD, Spectra/Por®, Spectrum Laboratories, Inc, USA). A schematic representation of the multi-step process of the NCC production is shown in Fig. 1.

The total volume of the stock suspension from the dialysis tube was measured and divided into 5 equal volumes in order to subject each to ultrasonication for 0, 1, 2, 5 and 10 min, respectively. The ultrasonic treatment of the NCC suspensions was carried out in an ice/water bath to avoid overheating the suspensions by using an ultrasonic horn type reactor (Sonics & Materials, Model: Vibra-Cell VC505) at 60% amplitude with a driving frequency of 20 kHz, a power of 500 W supplied by a piezoelectric transducer and with a 13 mm diameter replaceable tip [17]. NCC concentration in each of the suspensions was determined by drying and weighing 2 ml of the suspension. From these data the NCC yield was calculated as percentage of initial weight of the starting bleached cotton (i.e. 10/5 g). The final aqueous suspensions contained 3.2–3.6% of cellulose nanocrystals by weight.

2.2. Characterisation of NCC particles and suspensions

The size of the cellulose particles and their aggregates present in the original and sonicated NCC suspensions was measured by a Horiba Partica LA-950V2 laser diffraction particle size analyser (PSA). In spite of the method being able to measure the dimension of spherical particles, the analysis can provide useful information for comparison of the size of non-spherical rod-like cellulose whiskers and their aggregates before and after sonication. The median particle size ($D_{v50,}$ for volume distribution) in microns was given for characterisation of the suspensions. The median can be defined as the diameter value where half of the particles lie below the value. Other values, such as D_{v90} and D_{v10} can also be defined, where 90% and 10% of the population, respectively, lie below the values. The width of distribution was described by the Span, which was calculated by the equation: Span = $(D_{v90} - D_{v10})/D_{v50}$.

More accurate description of the size of NCC particles was obtained by transmission electron microscopy (TEM). TEM data were acquired with a Morgagni 268D TEM (100 kV; W filament, top-entry; point-resolution = 0.5 nm, line-resolution = 0.3 nm). Images were recorded with a Megaview III CCD camera (1376 × 1032 pixels). A drop of each of the diluted NCC suspensions (0.05 w/v%) was deposited onto a copper grid covered by a thin carbon film and stained with 2% uranyl acetate. Then the specimens were allowed to dry at room temperature for 1 h. The width and length of at least 100 cellulose whiskers from each of the suspensions were precisely measured on the TEM images (20,000×) by using the Leica IM 50 software.

For determining the zeta potential and the haze, the NCC suspensions were diluted to a concentration of 0.5 w/v%. A Zetapals Zeta Potential Analyser (Brookhaven Instruments Corporation, USA) was used for measuring the electrophoretic mobility of the