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COMPARISON OF PROPERTIES BETWEEN CELLULOSE NANOFIBRILS MADE FROM BANANA, SUGAR BEET, HEMP, SOFTWOOD AND HARDWOOD PULPS

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ABSTRACT

Cellulose nanofibrils were produced from various biobased raw materials by grinding and high pressure homogenization. Films were produced by Erichsen lab-scale coater from banana, sugar beet, hemp, softwood and hardwood pulps, and plasticized with 30 wt% of sorbitol. Water vapor transmission, grease penetration, oxygen transmission, and mechanical properties including tensile strength and strain were measured and compared against each other. All films had high water vapor transmission rates varying between 20-24 g×mm/m^2/day. Due to high number of polar hydrogen bonds in CNF, the films were impermeable to grease. All films had excellent oxygen barrier properties (<0.01 cc×mm/m^2/day) at dry conditions, whereas at 80% relative humidity (RH) the transmission rates increased rapidly. There was not much difference between the oxygen transmission rates (OTR) of different films, thus, all OTRs were ranging between 2.9-5.2 cc×mm/m^2/day at 80% RH. All films were strong, translucent and easy-to-handle. Unbleached softwood CNF films had the best mechanical properties (tensile strength of 150 MPa and strain of 16%).

Keywords: barrier, cellulose nanofibril, film, packaging, strength.

INTRODUCTION

Development of innovative and novel products starts from the raw materials. Packaging industry relies heavily on oil-based materials in most of its applications. Replacing the fossil-based materials with bio-based products might give a competitive advantage due to more sustainable and greener image, not forgetting certain technical improvements. Green economy, also referred to as biobased economy, utilizes biomass-derived raw materials, such as cellulose, for high-volume applications, such as food packaging. Cellulose is the most abundant naturally occurring organic substance [1]. Cellulose nanofibrils (CNF), also referred to as nanocellulose, is one of the most promising innovations for the modern forest sector. Its manufacture and unique properties have been demonstrated already in the early 1980s [2]. In the near future, CNF may have a wide range of potential application areas such as paper, packaging, concrete, oil drilling, cosmetics, feed and composite applications. Several surveys on the toxicity of CNF have been carried out using in well-characterized *in vitro* tests commonly applied in toxicity testing protocols. The results indicated absence of cytotoxic and genotoxic properties, as well as absence of effects on inflammatory system of CNF studied, thus, using CNF in packaging materials does not pose any direct safety risks to human health or the environment [3,4]. According to our very recent studies, CNF films degrade completely in pilot-scale composting test, and added CNF does not decrease the degradation rate of paper. CNF films and coatings have been widely studied in recent years, mostly due to their excellent mechanical strength and oxygen barrier properties [5,6]. Barrier properties of CNF films are highly dependent on the relative humidity, hence, further surface modifications or treatments have been found necessary [7,8]. CNF has extremely high affinity towards water, thus, removal of water and drying is challenging. Typically films have been produced at lab-scale using various filtration methods [9-13]. Filtration, however, has several drawbacks, which limit its industrial exploitability. Pressurized filtration is a slow and energy consuming process, which may take several hours to completely dewater the films. In addition, filter and membrane marking causes increased surface roughness, resulting in lower transparency and poorer printing properties. In this study, we compared the barrier properties of CNF made from banana, sugar beet, hemp, softwood and hardwood pulps.

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METHODS

CNFs were produced from banana, sugar beet, hemp, softwood and hardwood pulps. The materials contained approximately 2 wt% cellulose and 98 wt% water, and were produced as follows: the fibre slurries were first dispersed using a high shear Diaf dissolver 100WH N for 10 minutes at 700 rpm. Suspensions were then fed into Masuko Sangyo´s MKZA10-15J Supermasscolloider, which was used for pre-refining. Grinding stone type was MKE10-46 made of silicon carbide and resins with a diameter of 10". The fibre slurries were forced through a gap between rotary and stator grinding stones at 1500 rpm. The quality of fibril cellulose was controlled by moving the lower stone to set the clearance between the grinding stones. The pre-refined material was further fibrillated by high-pressure homogenization through a microfluidizer (Microfluidics M7115). The machine was equipped with a pair of ceramic 500 µm and diamond 100 µm interaction chambers. The operating pressure of the fluidizer was 1850 bar and fibrillation was done using five passes. Sorbitol was purchased from Sigma and used as a plasticizer. 30% sorbitol was mixed with the cellulose fibrils during fluidization.

Film production

CNF films were produced at lab-scale. Approx. 2 wt% CNF dispersions were first carefully pre-homogenized by mixing with Diaf dissolver for 30 min (200-300 rpm) and then cast with Erichsen Coatmaster 510 onto cPP (cast polypropylene; 30 µm) film using a 1 mm wet film deposit. The dispersion was poured onto the plastic base substrate in front of the moving rod during film making. Spreading and adhesion between the cPP-film and aqueous CNF dispersions were carefully fixed with physical plasma-activation. Vetaphone Corona-Plus (Type TF-415, CP1C MKII 2.0 kW) equipped with argon/nitrogen plasma unit was used for increasing the surface energy of cPP. After drying overnight at ambient conditions, the CNF films were delaminated from the cPP film. Thickness of the films was approx. 20 µm.

Water vapor transmission

Water vapor transmission rates of the films were determined gravimetrically using a modified ASTME-96 procedure. Samples with a test area of 25 cm^2 were mounted on a circular aluminium dish (H.A. Buchel V/H, A.v.d. Korput, Baarn-Holland 45 M-141), which contained water. Dishes were stored in test conditions of 23°C and 50% relative humidity and weighed periodically until a constant rate of weight reduction was attained.

Grease penetration

Grease penetration was determined according to modified Tappi T 507 method. First, standard olive oil was colored with Sudan II dye and applied onto 5 cm×5 cm sized blotting paper. Stain saturated piece of blotting paper was placed against the films and a piece of blank blotting paper (stain absorber) was placed against the other side. The whole stack was pressed between two plates and kept in oven at 60°C for 4 h. At the end of the test period, the assembly was removed and the stain absorbers were examined. For each absorber the area and the number of stained spots, if any, were determined.

Oxygen transmission

Oxygen transmission rates through the films were determined according to standard ASTM D3985 using Ox-Tran 2/21 Oxygen Transmission Rate System (Mocon, Modern Controls Inc., USA). The test area of the sample was 50 cm^2. The tests were carried out at 23°C and 0% and 80% RH using 100% oxygen as a test gas.

Mechanical properties

Lloyd 1000R Materials Testing System (Lloyd Instruments Ltd.) with 100 N load cell was used to determine tensile strength and strain in test conditions of 23°C and 50% relative humidity. The width of the samples was 15 mm. The gauge distance was 20 mm.

RESULTS AND DISCUSSION

The first stage in the production of CNF comprised mechanical pretreatment of the suspension in the grinder. This pretreatment was used to obtain more homogeneous and finer input material for the microfluidizer, as well as lower total energy consumption. By this way, the clogging tendency of the microfluidizer could be significantly decreased, since pretreatment caused disintegration of fibre agglomerates and initiated fibrillation, as well as further swelling of fibres. Fibrillation itself was dominated by the microfluidization process, which caused fibre delamination and separation of macrofibrils into micro or nanofibrils. Also fibre shortening occurred during processing when the amount of fibrillation energy was further increased. As a result, a relatively uniform fibril size distribution was obtained. The CNF films produced by Erichsen Coatmaster 510 were approx. 20 µm thick, strong, translucent and easy-to-handle. Only limited amount of air bubbles or other minor defects were visually observable. The film surface facing towards air during drying had slightly mat-like texture, whereas the surface in contact with cPP substrate had perfectly smooth and shiny surface. The smoothness of cPP surface was clearly replicated to bottom surface of CNF films. Typically water vapor transmission rates through various biopolymer films, including cellulose, are relatively high due to strong hydrophilic nature of these materials. The penetrating water molecules break intramolecular hydrogen bonds, which enables plasticization and swelling of the matrix polymer, finally resulting in increased moisture transmission. Water vapor transmission rates of CNF films were comparable to regenerated cellulose films [14]. All films were also totally impermeable to grease under the conditions tested. High number of polar hydrogen bonds in CNF enabled excellent barrier properties against nonpolar permeants, such as grease (**Table 1**).

CNF films were excellent barriers against oxygen permeation. The oxygen transmission rates were comparable to plasticized regenerated cellulose films at elevated humidities [14-17]. The

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Table 1. Water vapor transmission (WVTR) and grease penetration

Sample	WVTR (g×mm/m²/day)	Grease penetration (yes/no)
CNF sugar beet + 30% sorbitol	22	no
CNF unbleached softwood + 30% sorbitol	21	no
CNF banana + 30% sorbitol	22	no
CNF bleached softwood + 30% sorbitol	20	no
CNF hemp + 30% sorbitol	24	no
CNF bleached hardwood + 30% sorbitol	24	no

Table 2. Oxygen transmission (OTR)

Sample	OTR (cc×mm/m²/day)	
	0% RH	80% RH
CNF sugar beet + 30% sorbitol	<0.01[a]	4.8
CNF unbleached softwood + 30% sorbitol	<0.01[a]	3.9
CNF banana + 30% sorbitol	<0.01[a]	4.0
CNF bleached softwood + 30% sorbitol	<0.01[a]	5.2
CNF hemp + 30% sorbitol	<0.01[a]	4.3
CNF bleached hardwood + 30% sorbitol	<0.01[a]	2.9

[a]Lower detection limit

Table 3. Mechanical properties

Sample	Tensile strength (MPa)	Tensile strain at break (%)
CNF sugar beet + 30% sorbitol	69	8
CNF unbleached softwood + 30% sorbitol	150	16
CNF banana + 30% sorbitol	118	17
CNF bleached softwood + 30% sorbitol	116	14
CNF hemp + 30% sorbitol	119	14
CNF bleached hardwood + 30% sorbitol	109	11

results are also comparable to other studies of CNF at elevated humidity [13,18-20]. Close packing of fibrils reduced the free volume and efficiently prevented the oxygen transmission. High surface area and polarity of nanosized fibrils resulted in enhanced fibril-to-fibril attraction, especially at low humidity. Due to the hydrogen bonds, the movement of fibrils was restricted efficiently preventing the oxygen permeation. Typically, the barrier properties of biopolymers are very sensitive to moisture variations. Water molecules enter the polymer and break the hydrogen bonds that hold the chains together. At high humidity conditions, the CNF films tend to swell, thus allowing permeation to increase. Thus, clearly increased oxygen permeation was measured in films at high humidity conditions (**Table 2**).

Tensile strength of CNF films was varying from 69 MPa to 150 MPa. Sugar beet CNF films were the most brittle and had the lowest strength, whereas unbleached softwood films had the highest strength and also the highest strain of 16% (**Table 3**).

CONCLUSIONS

Cellulose nanofibrils (CNF) films were produced from banana, sugar beet, hemp, softwood and hardwood pulps. Films had some promising technical properties including grease proofness and high barrier against oxygen transmission, especially at dry conditions. However, the moisture resistance and flexibility were still inadequate, which will limit the commercial exploitability in food packaging applications. ■

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