CELLULOSE NANOPAPER COMPOSITES: INFLUENCE OF NANOPAPER CHARACTERISTICS ON COMPOSITE PROPERTIES

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Abstract

Nanocellulose, cellulose in the form of nanofibrils (CNF), has gained considerable attention in recent years as reinforcement agent for the production of composite materials due to its excellent mechanical and chemical properties, with the Young´s modulus even outperforming glass fibres. One promising approach to produce nanocomposites based on nanocellulose is to utilize nanopapers as reinforcement in laminated composites, enabling better exploitation of the outstanding mechanical properties of CNF compared to composites in which CNF are introduced in a different way.

Accordingly, the characteristics of the nanopapers also influence the properties of the composites. One parameter that is anticipated to influence the final properties of composites a lot is the porosity of the nanopaper employed. A low porosity shows high resistance for the resin to enter into the nanopaper structure hence resulting in lower mechanical properties as potentially possible. Our approach was to alter the porosity of the nanopapers by solvent-exchanging the CNF suspension with different types of organic solvents prior to papermaking to allow for a better infiltration of the resin.

1. Introduction

Cellulose – the term was first established in 1839 by Payen [1, 2] – is a natural polymer formed of poly-β(1,4)-D-glucan macromolecules and one of the most abundant organic polymers on earth [3, 4]. Both natural and regenerated cellulose are in use by humans for centuries in the form of wood, cotton, and other plant fibers for their availability and physiological and mechanical performance as an energy source, for building materials, and for clothing [5]. In recent years, nanofibrillated cellullose (CNF), cellulose fibrils with diameters at the nanoscale, has gained significant attention due to its outstanding mechanical and chemical properties [3, 6] especially when utilized for the production of composites [7-17] or membranes [18-20]. Bacterial cellulose (BC) is a special form of CNF, produced by certain types of bacteria. It was first studied by Brown back in 1886 [21]. The pellicles produced by those bacteria consist almost exclusively of cellulose without contaminants such as lignin, hemi-celluloses or pectin as it is usually the case for CNF derived from plant material [22]. Hence, based on the absence of these contaminants, a very high degree of purity and crystallinity can be found for these nanofibrils [23], making this material an ideal compound to study the behavior of cellulose. The high

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purity and crystallinity also results in very high Young's modulus along with high strength [24]. Consequently, BC was applied in many different applications, e.g. in biomedical applications [25-29], but particularly in nanocomposites [8-16].

Cellulose papers are used by humans for thousands of years, for obvious reasons to convey information but also in applications such as filter and membrane material or even construction material [30]. Composites based on paper as reinforcement material have been researched already decades ago and recently, the use of CNF or BC for paper production, so-called nanopapers, have allowed for a wide spectrum of properties of these papers [11, 31] that have already found various applications, e.g. in composite materials [11] but also as membrane material [18, 19].

Nanopapers have been established to be of relatively high density and low porosity [18, 19]. On the one hand this gives rise to excellent mechanical properties, on the other hand, application of those nanopapers, e.g. for composite production via resin infusion or lamination, is impeded. Thus, nanopapers with tailored porosity would be desirable. For the dense packing of cellulose fibrils is based on the extraordinary hydrophilicity of the fibrils, one possible approach to that task might be dispersion of BC nanofibrils in organic solvents rather than in water. It can be assumed that by dispersing BC in organic solvents and subsequent paper making a decrease in density and thus an increase in the porosity of final BC nanopapers can be achieved with the feature of unchanged low pore size. It was proposed already back in the 1950s by Staudinger that organic solvents are capable of modifying cellulose structures by a process called solvent inclusion. However, the underlying mechanism was not satisfyingly explained then [32, 33] and is still not yet.

We here present nanopapers made from bacterial cellulose dispersed in different types of organic solvents (an alcohol (ethanol), a ketone (acetone) and a (cyclic) ether (tetrahydrofuran)) of similar size via solvent exchange. From these suspensions, nanopapers were produced by a simple paper-making process. It is assumed that by filtration of BC from different liquids exhibiting varied hydrophilicity, the formation of the hydrogen bond network is changed resulting in altered fibril network characteristics. Furthermore, it is anticipated that through these alterations an enhancement in overall porosity follows. Prepared nanopapers were characterized regarding their pore size as well as their mechanical properties.

2. Materials & Methods

2.1. Materials

Commercial available bacterial cellulose (BC) was kindly supplied by fzmb GmbH (Bad Langensalza, Germany) in the form of wet pellicles containing 92 wt.-% water. The diameter of BC was found to be approximately 50 nm with fibril lengths of up to several micrometres [10]. Acetone (Ac, >99.5 %) was purchased from VWR (Fontenay-sous-Bois, France), ethanol (Et, >99.8%) from Sigma-Aldrich (Dorset, UK) and tetrahydrofuran (THF, >99.9 %) from Fisher Scientific (Loughborough, UK) and used as received.

2.2. Manufacturing of nanopapers

To produce BC-based nanopapers, the BC pellicles were first cut into small pieces (with a length of approximately 5 to 10 mm) and blended (Breville VBL065-01, Oldham, UK) for 2 min at a consistency of 0.2 wt.-% in deionized water to produce a homogeneous suspension of the BC-in-water. These BC-in-water suspensions were then vacuum-filtered onto a cellulose filter paper (VWR 413, 5-13 µm pore size, Lutterworth, UK). For the production of nanopapers from aqueous suspensions, the filter cake was wet-pressed under a weight of 10 kg between blotting papers (3MM Chr VWR, Lutterworth, UK) for 5 min to further absorb the excess water. These wet filter cakes, which had a

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measured moisture content of approximately 85 %, were then consolidated and dried in a hot-press (25-12-2H, Carver Inc., Wabash, USA) under a compression weight of 1 t for 1 h at 120 °C by sandwiching the wet filter cakes between fresh blotting papers and metal plates [18, 19].

In the case of BC nanopapers from organic solvents (BC-org) the filter cake derived from the filtration of an aqueous suspension of BC was re-dispersed into the respective solvent and shaken with a IKA KS 260 basics (Camlab, Cambridge, UK) overnight to allow for generating a homogeneous suspension of BC fibrils in the solvent. These BC-in-organic solvent suspensions were then vacuum-filtered, the wet filter cake was wet-pressed and finally consolidated and dried in a hot-press following the same protocol as for BC nanopaper production from aqueous suspensions.

2.3. Characterization of nanopapers

2.3.1. Dimensions, density and porosity of nanopapers

The grammage (G) of nanopapers was determined by the ratio between the mass (m) and cross-sectional area (A) of the nanopapers (Eq. 1). The thickness (d) of the nanopapers was measured using a digital micrometre (705-1229, RS components, Corby, UK). From these parameters, the envelope density (ρ_e) was calculated (Eq. 2) and from the absolute density the porosity (P) could be determined (Eq. 3) using a value for the theoretical density of cellulose (ρ_c) of 1500 kg m^{-3} [34].

$$G = m / A. \tag{1}$$

$$\rho_e = G / d = m / (d A). \tag{2}$$

$$P = 1 - (\rho_e / \rho_c). \tag{3}$$

2.3.2. Mechanical properties from tensile tests

To determine mechanical properties of nanocellulose papers, dog bone shape specimens were cut using a Zwick cutter. The specimen possessed an overall length of 35 mm and the parallel section of the specimen was 2 mm. Prior to the test, the specimens were secured onto testing cards using a two-component cold curing epoxy resin (Araldite 2011, Huntsman Advanced Materials, Cambridge, U.K.). This was to prevent the clamp of the tensile testing equipment from damaging the test specimens.

Tensile tests were conducted using a TST350 tensile tester (Linkam Scientific Instruments, Surrey, UK). The load cell and crosshead speed used were 200 N and 1 mm min^{-1}, respectively. The sample thickness was determined using a digital micrometre. A total of 6 specimens were tested for each type of nanocellulose. The machine compliance was determined to be 6.38 x 10^{-3} mm N^{-1}.

3. Results & Discussion

3.1. Nanopaper production

Nanopapers from bacterial cellulose (BC) were produced from various organic solvents and water, in order to facilitate variations of the porosity, by applying a paper-making process [18, 19]. The production of the nanopapers involved cutting of the pellicles, homogenization, filtration, wet-pressing and finally hot-pressing. During the last step, hornification results in permanent hydrogen-bonds that

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further improve the quality of the paper [35]. Nanopapers from aqueous suspensions were produced utilizing this process. For the production of nanopapers from organic dispersion media (BC-org), this method had to be amended. A suspension of BC-in-water was prepared and filtered as for conventional BC nanopapers from aqueous suspensions, but instead of further processing, the filter cake was re-suspended in the chosen organic liquid and shaken overnight to allow for a homogeneous dispersion of the BC fibrils. This suspension was then filtered again to form a filter cake, which was wet-pressed and hot-pressed. Thus, nanopapers from aqueous suspensions or various organic solvents were produced. Nanopapers with grammages between 20 and 70 g m^{-2} (gsm) were prepared.

The envelope density of BC nanopapers from aqueous suspensions or organic solvents, respectively, has been determined by dividing the grammage by the thickness, i.e. the reciprocal slope of a thickness vs. grammage graph (Fig. 1).

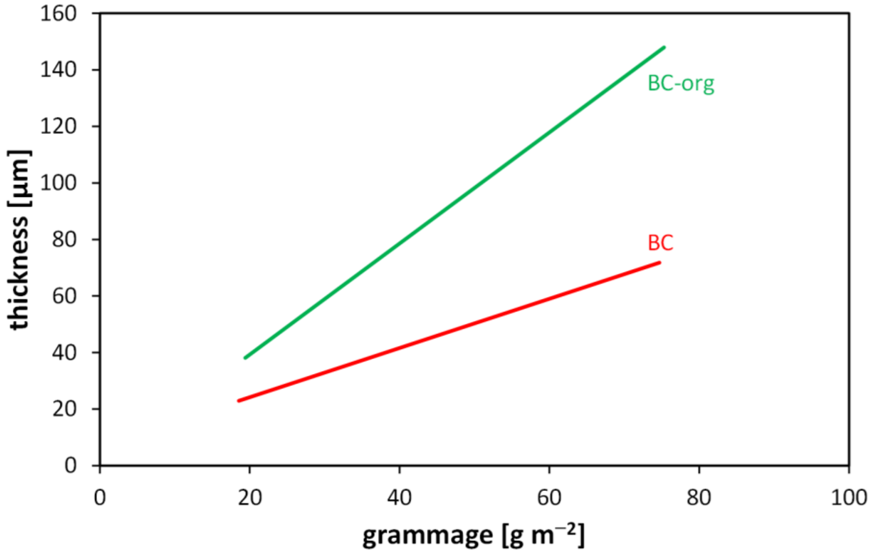

Fig. 1. Correlationship between thickness and grammage of BC nanopapers prepared from aqueous suspensions (BC) or organic solvents (BC-org), respectively.

From the envelope density the porosity was calculated with assuming an absolute density for pure, non-porous cellulose of 1500 kg m^{-3} [34]. BC nanopapers from aqueous suspensions exhibited thicknesses [µm] that approximately value their grammage [gsm]. Thus, a density of 1000 kg m^{-3} could be established from analysis of the slope of the curve. Accordingly, the porosity of BC nanopapers could be calculated to account for 33 %. Opposed to that, for BC-org the thickness [µm] of nanopapers valued for all three organic solvents around 2 times the grammage [gsm], resulting in a density of 500 kg m^{-3} and accordingly a porosity of 66 %. The reason for the higher porosity of nanopapers from organic solvent should be sought in processes taking place during hot-pressing. In BC nanopapers from aqueous suspensions, the hydrogen bonds between the fibrils are fixed during drying and hornification, leading to permanent hydrogen bonds. On the other hand, in BC-org nanopapers this does not happen, or at least to not such an extent. It is anticipated that lack or lower concentration, respectively, of hydroxyl-groups in the organic solvents results in a lower degree of hydrogen bonds being present between the cellulose fibrils. Accordingly, during the drying process, fewer permanent hydrogen bonds could be established. Thus the fibrils were not packed as tightly together leading to a lower density and thus higher porosity.

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3.2. Mechanical properties

Tensile tests were performed for all different types of BC nanopapers to study their mechanical performance. Tensile properties of the different nanopapers are summarized in Table 1. BC nanopapers from aqueous suspensions exhibited a tensile modulus of 8.3 GPa, which is similar to values reported in literature [11]. Thus, the modulus of BC was four times higher than the modulus of BC-Ac, more than 6 times higher as for BC-Et and more than 9 times higher as for BC-THF. If the much higher porosity is taken into account, and thus the modulus of BC nanopapers is corrected for their envelope density, still a lower modulus has to be accepted. Thus, the stiffness was not only reduced due to the enhanced porosity but also proposedly due to a weakened hydrogen bond network.

Table 1. Mechanical properties of nanopapers: Young's modulus (*E*) and tensile strength (σ).

Nanopaper Type	E (GPa)	σ (MPa)
BC	8.3 ± 1.6	144 ± 1
BC-Ac	1.8 ± 0.1	31 ± 3
BC-Et	1.3 ± 0.1	33 ± 2
BC-THF	0.9 ± 0.1	16 ± 2

The tensile strength followed the same trend as the Young's modulus. BC nanopapers from aqueous suspensions exhibited a tensile strength of 144 MPa, similar to results presented in literature [11]. BC-org nanopapers, on the other hands exhibited σ that were lower by a factor between 4 and 9. This was again not only due to increased porosity but also due to weakened inter-fibrillar interactions, larger distances between fibrils and fewer spots at which fibrils are in close contact.

4. Conclusions

Bacterial cellulose nanopapers were manufactured from aqueous suspensions as well as from organic dispersion media (an alcohol – ethanol, a ketone – acetone and a (cyclic) ether – tetrahydrofuran) via a paper-making process. Preparation of BC nanopapers from organic solvents resulted in doubled porosity compared to nanopapers prepared from aqueous suspensions. This is anticipated to allow for better resin-infusion of the nanopaper. These changes shall be explained by a decreased degree of hydrogen bonds between BC nanofibrils. As expected, the mechanical properties of BC nanopapers were significantly influenced by the porosity based on the degree of inter-fibrillar hydrogen bonds. Both modulus and strength were reduced by a factor of 4 to 9.

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