CELLULOSE NANOPAPER COMPOSITES BASED ON NANOCELLULOSE FROM ELEPHANT MANURE

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Abstract
Nanocelluloses (NFC) gained substantial attention in recent years as reinforcement of composite materials due to their excellent properties. One promising approach to yield high fibre volume fraction NFC composites is to laminate nanopapers. Thereby, the characteristics of the nanopapers directly determine the properties of the composites, hence, excellent mechanical properties of the nanopapers are desired. Nonetheless, aiming at ecologically sound solutions, also the raw material of the NFC needs to be considered. In this regard, utilizing agricultural waste rather than high-grade resources (wood) as base material would be vital. We have identified elephant manure to be a suitable precursor for the preparation of NFC, for elephants digest only about 35 % of their diet. Accordingly, their excrements contain large quantities of fibrous cellulosic material, whereby the ingestion and digestion already initiates fibre break-down. Thus, utilizing the elephant as first-stage bioreactor for the defibrillation of cellulose fibres by mechanical and chemical means constitutes an energy-efficient approach for the production of NFC. We demonstrate that by chemical purification of elephant manure, cellulose nanofibrils can be isolated from which papers were produced that had better mechanical properties than most common unmodified NFC nanopapers thus being ideal candidates for the preparation of nanopaper composites.

1. Introduction

Composite materials based on raw materials derived from natural resources have received considerable attention in recent decades due to environmental concerns associated with conventional composite materials produced from synthetic materials [1]. Even though progress was achieved in the process to recycle synthetic composite materials, they still constitute a serious waste problem [2]. To address these issues, composite materials based on renewable resources and prepared utilizing clean and cheap production routes have been proposed; in particular natural fibres from various resources based on cellulose have been employed [3]. Cellulose is the most abundant organic polymer on earth formed of poly-β(1,4)-D-glucan macromolecules [4, 5] as first established in 1839 by Payen [6]. For centuries natural cellulose fibres are utilized in the form of wood, cotton and other plant fibres as an energy source, for construction and clothing but also in composite materials. This is due to their physiological and mechanical performance but also high availability [7].

Cellulose nanofibrils (nanofibrillated cellulose, NFC) have in recent years come into the focal point of research as reinforcing agent for the production of fibre reinforced composite materials due to their excellent mechanical and chemical properties [4]. One promising approach to produce nanocomposites based on NFC is to utilize nanopapers as reinforcement in laminated composites, thus enabling better exploitation of the outstanding mechanical properties of NFC compared to composites in which NFC are introduced in a conventional way [2, 8]. Accordingly, the characteristics of the nanopapers also influence the properties of the composites. It was shown that when applying nanopapers in a lamination process to yield high fibre volume fraction composites, the mechanical properties of the nanopaper directly determine the performance of the composite [9]. Therefore, nanopapers with excellent mechanical performance are the base for the preparation of high-loading composites [10, 11].

However, a parameter that needs to be considered, in particular when aiming at ecologically sound solutions, is the source of the raw material of NFC. Thereby, utilizing agricultural waste as base material instead of a high-grade resource (i.e. wood) would be a vital approach. Globally, the human population and therefore the demand for animal products, such as milk, leather and meat, are on the rise. Consequently, the scale of livestock farming has changed from individual small family farms into large-scale industrial companies whereby the disposal of farming and animal waste, especially manure, has become a huge problem. The uncontrolled dispense of manure onto grasslands and fields results in environmental problems such as the emission of greenhouse gases or over-fertilization of the soil leading to eutrophication of ground water [12, 13]. Innovative ways to address these problems, for example the production of biogas from agricultural waste, were developed in the past decades. Adding to the use of manure as fertilizer or producing biogas the extraction of natural fibres, which can be used for the production of value-added products, would be a very interesting concept [14]. For example, the cellulosic fraction of manure could be used for the extraction of nanocellulose with the energy-intensive process of their preparation potentially being short-cut by utilizing an animal’s digestion system as first stage bioreactor.

We have identified elephant manure to be a suitable model system for using animal manure as precursor for the preparation of NFC for the diet of elephants consists mainly of lignocellulosic fibres contained in grass, weeds and other plants. On an every day base, elephants intake around 1-1.5 % of their body mass in dry matter. This amounts to approximately 60 kg of (wet) fibrous material per day, of which only 30 to 40 % are digested, i.e. their manure contains large quantities of fibrous cellulosic material [15]. This undigested material is majorily composed of cellulose, hemicellulose and lignin: depending on the species of elephant, habitat and season, their dung can contain up to 40 % cellulose and 10 % of hemicelluloses, which is a far higher proportion as e.g. contained in cattle manure (approx. 20 % cellulose) [16, 17]. Furthermore, the mechanical, acidic and enzymatic pre-treatment during ingestion and digestion initiates break-down of the fibres. Thus, utilizing the elephant as the first-stage bioreactor for the defibrillation of cellulose fibres by mechanical and chemical means constitutes an energy-efficient approach for the production of NFC. The pre-treatment inside the animal provides the benefit of reducing time and energy consuming steps during the extraction of cellulose and in particular nanocellulose [18].

In this study we show that by chemical purification of elephant manure through alkaline and bleach treatment, cellulose fibres with controllable properties can be isolated. The cellulose fibrils were further mechanically refined and papers produced from these nanofibrils. The nanopapers prepared had mechanical properties on par with or even better than commonly used unmodified NFC nanopapers, thus demonstrating their suitability for the use in composite applications.

2. Experimental

2.1. Materials

Fresh elephant dung was provided by Tiergarten Schönbrunn (Zoo Vienna). It contained mostly elephant manure but sand, stones and plastic particles were also present. Sodium hypochlorite (NaOCl, 14 % active Cl) was purchased from W. Neuber’s Enkel, Vienna, Austria. Sodium hydroxide (NaOH, 99.6 %) was purchased from Sigma Aldrich. All chemicals were used as received without further purification. Distilled water was used in all experiments unless stated otherwise.

2.2. Manure pre-treatment

The elephant dung was sterilized by heat-treatment at 120 °C in a drying oven. The dried dung was sieved over a 1.7 mm mesh to separate manure from pieces of plastic or stones. The manure was washed and then further treated with various concentrations of NaOH and NaOCl for varying periods of time at various temperatures to establish optimal conditions. The manure extract was analyzed by elemental analysis performed with an EA 1108 CHNS-O (Carlo Erba, Italy) and Fourier transformation infrared spectroscopy (FT-IR) recorded on a Carry 630 spectrometer (Agilent Technology, Austria).

2.3. Paper preparation

To prepare paper, the pre-determined amount of treated manure for 100 g/m^2 papers was blended for 5 min at 3000 rpm with 300 mL distilled water (LB20EG, Waring Commercial, Connecticut, USA) and filtered over a Büchner filter funnel (6", Royal Worcester, UK) lined with a previously wetted filter paper (VWR 413, Lutterworth, UK). The filter cake was placed in an oven (Fistreem, Leicestershire, UK) at 120 °C between two metal plates and two layers of blotting paper (3 MM Chr, VWR, Lutter-worth, UK). Papers were also prepared by using a hot press at 120 °C (Model 412 6CE, Carver, USA).

2.4. NFC and nanopaper preparation

For the preparation of nanopapers, alkaline treated and bleached manure was pulped in a Wahring laboratory blender. Then it was passed through a disk mill (Granomat JP 150, Fuchs, Switzerland). The resulting gel was filtered over a filtration cloth and stored in the fridge. For the preparation of nanopapers, the NFC suspension was diluted, blended and filtered over a filter funnel with a sintered glass disk lined with a filter paper (VWR 413). The paper was consolidated at 120 °C in a hot-press.

2.5. Dimensions, density and porosity of papers

The thickness (d) of the papers was measured with a digital micrometre (705-1229, RS components, Corby, UK). The grammage (G) of the nanopapers was calculated with the mass (m) being dividided by the cross-sectional area (A) of the nanopapers (Eq. 1). Therefrom, the envelope density (ρ_e) was calculated (Eq. 2) and with the skeletal density of cellulose (ρ_c, 1500 kg m^{-3} [19]) the porosity (P) could be determined (Eq. 3).

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

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

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

2.6. Mechanical properties of papers

Tensile properties of the papers were tested on dog bone shaped specimens (shape after Type 1BA, EN ISO 527-2) that were punched from the papers using a specimen press (Zwick ZCP 020 Manual Cutting Press, Zwick, Ulm, Germany) and the thickness and the grammage of every specimen was determined. For each sample, at least five specimens were evaluated. The measurements were performed with an Instron universal testframe (Model 5969 Dual Column Universal Testing System, Instron, Darmstadt, Germany) equipped with a 1 kN load cell and a non-contact video extensometer (Gig ProE, iMETRIUM, Bristol, UK). The specimens were fixed between metal clamps and blotting paper to avoid perforation of the samples. The tests were performed at 25 °C and a relative humidity of 50 % with a test velocity of 1 mm min^{-1}. The gauge length was set to 25 mm. Tensile tests resulted in values for the ultimate tensile strength (σ) and the Young's modulus (E). E was analyzed in the linear elastic region of the stress-strain curve as secant between strength values separated by 0.2 % strain.

3. Results and Discussion

3.1. Cellulose from elephant manure

Cellulose fibres were extracted from sterilized elephant manure by an alkaline and bleaching treatment. It was found that with a relatively mild alkaline treatment and additional bleaching white fibres could be extracted. The fibre's chemical composition as determined by elemental analysis was found having a high degree of similarity with pure cellulose (Table 1).

Table 1. Elemental composition of extracted cellulose fibres and pure cellulose.

Sample	C (mol.-%)	H (mol.-%)	O (mol.-%)	N (mol.-%)
Untreated elephant manure	46.9	6.2	45.9	1.0
Treated elephant manure	44.1	6.6	49.3	0.0
Pure Cellulose	44.3	6.7	49.0	0.0

This result was confirmed by FT-IR spectroscopy. Bands signalling cellulose but also by-compounds such as lignin, amino-acids or proteins were present in the IR-spectrum of the untreated sample. A peak at 3320 cm^{-1} was assigned to –OH stretching and two peaks at 2920 cm^{-1} and 2850 cm^{-1}, respectively, indicated the alkyl –CH symmetrical and asymmetrical stretching present in cellulose, hemicelluloses and lignin. The typical band for cellulose and hemicelluloses between 1000 and 1100 cm^{-1} identified as C–O–C stretching [20, 21] was present, too, with an intense peak at 1030 cm^{-1} of the C–O stretching in cellulose [22]. The peak at 1735 cm^{-1} was attributed to the C=O stretching in pectin, waxes and hemicellulose [23], whereas the aromatic C=C signal at 1500 cm^{-1} and 1600 cm^{-1} was referred to lignin. These peaks vanished after the pre-treatment procedure, indicating the removal of by-compounds. The peak at 1225 cm^{-1} was the C–O stretching of primary alcohols present in lignin but also in cellulose and hemicelluloses. Due to the presence of this functional group in all three components, the intensity of this peak was higher in the raw material compared to the treated material [24, 25]. Ultimately, the spectrum of treated manure was basically identical to the spectrum of pure cellulose.

3.2. Paper from cellulose fibres extracted from elephant manure

Papers were prepared, following an easy and scalable papermaking protocol, from treated elephant manure by consolidation in an oven or a hot-press, respectively. Papers were also prepared from nanocellulose by hot-pressing. It was found that the ρ_e and P of the papers were significantly influenced by the processing method (Table 2). Whereas papers produced by consolidation in an oven had rather low ρ_e and thus high P, hot-pressing resulted in densified papers of lower P, as expected. Nanopapers from nanocellulose had an even higher ρ_e and lower P. These physical properties had consequently a strong impact onto the mechanical properties of the papers. While papers prepared in an oven only had a σ of around 20 MPa and a E of 2 GPa, by hot-pressing the mechanical properties could be more than tripled. Thereby, not only enhanced ρ_e and reduced P were responsible for higher strength but also higher connectivity of the fibres contributed. The connectivity allowed for the formation of a denser hydrogen bond network resulting in very good mechanical properties that were better than those of copy paper. Furthermore, the preparation of nanocellulose via defibrillation in a disc mill resulted in a material with very high mechanical properties. Papers from this nanocellulose reached σ of more than 130 MPa and a E of 12 GPa, respectively. This is on par with conventional nanopapers prepared from wood pulp [3]. However, in this case, an animal waste material derived from low grade biomass was utilized rather than using a valuable high-grade biomass.

Table 2. Physical and mechanical properties of papers and nanopapers derived from elephant manure.

Sample	ρ_e (kg m^{-3})	P (%)	σ (MPa)	E (GPa)
Extracted cellulose (oven)	480 ± 20	69	18.5 ± 0.8	2.3 ± 0.1
Extracted cellulose (hot-pressed)	810 ± 50	46	64.1 ± 7.2	7.1 ± 0.4
Nanocellulose	1100 ± 10	27	134 ± 5	12.0 ± 0.8

3. Conclusions

Cellulose fibrils were extracted from elephant manure provided by Zoo Vienna. By chemical pre-treatment with an alkaline solution and by bleaching pure cellulose fibrils could be extracted. Papers from these fibrils had tensile properties that were better than those of conventional copy paper. Moroever, nanocellulose fibrils were prepared from these cellulose fibrils by defibrillation in a disc mill. Papers prepared from this nanocellulose had tensile properties on par with those of common nanopapers prepared from wood pulp. Thus it was demonstrated that animal waste can serve as a potential raw material for nanopaper laminate composites in which the mechanical properties of the nanopapers determine the mechanical performance of the composite.

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