Upgrading flax nonwovens: Nanocellulose as binder to produce rigid and robust flax fibre preforms

Marta Fortea-Verdejo [a], Koon-Yang Lee [b], Tanja Zimmermann [c], Alexander Bismarck [a,d,*]

[a] Polymer and Composite Engineering Group (PaCE), Institute for Materials Chemistry & Research, Faculty of Chemistry, Universität Wien, Währinger Straße 42, 1090 Wien, Austria
[b] The Composites Centre, Department of Aeronautics, Imperial College London, SW7 2AZ London, United Kingdom
[c] Applied Wood Materials Laboratory, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, CH-8600 Dübendorf, Switzerland
[d] Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, South Kensington Campus, SW7 2AZ London, United Kingdom

ABSTRACT

Typically in flax fibre nonwovens, the fibrous web is mechanically bonded (via entanglement and interlocking of fibres) or thermally bonded (by melting of polymer fibres). Recently, we showed that bacterial cellulose (BC) can be used as effective binder to produce rigid and robust natural fibre nonwovens without the need for polymer binders. Here, we further expand this work to manufacture flax nonwovens by utilising various types of (nano)cellulose, including nanofibrillated cellulose (NFC), BC and pulp fibres. Two preform manufacturing processes are investigated, namely single-step filtration and layer-by-layer filtration. Both BC and NFC serve as excellent binders for loose flax fibres due to their high surface area whilst pulp fibres are a poor binder for flax fibres. This is attributed to the low surface area of pulp compared to BC and NFC, which leads to a lower contact area between flax fibres and pulp. Furthermore, the larger fibre diameter of pulp results in a poorer packing efficiency and, therefore, a higher porosity of 67% compared to preforms made with BC or NFC as binder, which have a porosity of ~60%. The manufactured preforms possess excellent tensile ($\sigma_T^b = 33$ kN m^{-1}, $\sigma_T^w = 27$ N m g^{-1}) and flexural ($\sigma = 21.1$ MPa, $E = 2.2$ GPa) properties. Layer-by-layer filtration process results in flax nonwovens, which exhibit even better tensile and flexural properties. This is hypothesised to be due to the better distribution of the fibrous nanocellulose network throughout the preform.

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1. Introduction

Natural fibres are excellent reinforcement candidates for polymers to produce bio-based composites with mechanical performance exceeding those of commonly used commodity polymers and engineering materials due to their high specific stiffness and strength, as well as wide availability and renewability [1]. In fact, bio-based composites have already found applications in the automotive [2,3], construction and building industries [4,5], as well as filtration processes [6] and weed suppression [7]. However, natural fibres do suffer from some drawbacks including poor compatibility with hydrophobic polymer matrices and the inherent variability in fibre properties, even for fibres extracted from the same cultivation [1]. There is very little that can be done in terms of the variability

of their properties and dimensions but significant research effort has been poured into modifying the surfaces of natural fibres [8–12] or polymer matrices [13,14] to enhance the fibre–matrix interface.

One method to modify the natural fibre-polymer matrix interface is to deposit bacterial cellulose (BC) onto micrometre-sized natural fibres [15–17], thereby creating "hairy" or "fuzzy" fibres, which can be used as effective reinforcement for polymers [18]. BC is a highly crystalline nano-sized cellulose with a ribbon cross-section of approximately ~50 nm [19] and several micrometres in length synthesised by cellulose-producing bacteria, such as from the *Acetobacter* species [20]. By culturing cellulose-producing bacteria in the presence of natural fibres, BC was found to be preferentially deposited on the surface of natural fibres. Fibre-pull out tests showed that the interfacial shear strength between cellulose acetate butyrate (CAB) or poly-ʟ-lactide acid (PLLA) and sisal fibres improved significantly [15]. Whilst this method successfully improved the fibre–matrix interface, this coating method does suffer from drawbacks including: (i) long culturing times (around 5 days [21]), (ii) the need for expensive

* Corresponding author at: Polymer and Composite Engineering Group (PaCE), Institute for Materials Chemistry & Research, Faculty of Chemistry, Universität Wien, Währinger Straße 42, 1090 Wien, Austria. Tel.: +43 (1) 4277 71301; fax: +43 (1) 4277 871302.
E-mail address: alexander.bismarck@univie.ac.at (A. Bismarck).

bioreactors to culture the cellulose-producing bacteria and (iii) reduction in the tensile properties of some natural fibres.

To resolve these problems, we recently developed a more cost effective method based on slurry dipping to produce "hairy" natural fibres [22], whereby natural fibres are dipped into a suspension containing BC to coat the surface of sisal fibres with BC. This slurry dipping method was further extended to produce nonwoven natural fibre preforms [23] utilising BC as binder for sisal fibres by first creating a suspension containing natural fibres and BC, followed by (vacuum) filtration, consolidation and drying. The resulting sisal fibre preforms containing only 10 wt.% of BC (relative to the amount of fibres) were found to be rigid and robust, possessing a tensile strength[1] of 13.1 ± 2.1 kN m^{-1}.

In addition to BC, nano-sized cellulose fibrils can also be obtained from wood. Nanocellulose was first isolated in 1946 from plant fibres by Wuhrmann et al. [24] using strong ultrasound. More recently, nanofibrillated cellulose (NFC) is typically produced by passing (ligno)cellulosic biomass, such as wood pulp, through high pressure homogenisers [25,26]. In addition to this, nanocellulose from (ligno)cellulose biomass can also be produced using grinders, whereby wood pulp is passed through the slit between rotating and static grinding stones [27]. The high shear generated fibrillates the micrometre-sized wood pulp to nanocellulose with fibril aggregate diameters between 10 and 100 nm and lengths in the micrometer range. Both BC and NFC have been used as reinforcement to produce high performance bio-based nanocomposites. A comprehensive overview of the mechanical performance of BC- and NFC-reinforced polymer composites can be found in literature [28]. Whilst the reinforcing ability of BC and NFC for polymers has been studied [29], the binding efficiency of BC and NFC to produce natural fibre nonwovens was not yet investigated.

Therefore in this work, we follow our previous study [23] of utilising BC as binder to upgrade the properties of nonwoven flax fibre preforms utilising BC and NFC as binders. The mechanical properties of the resulting flax-nanocellulose nonwovens are compared against conventional flax-polymer nonwovens and flax-pulp fibre nonwovens. The manufacturing process of the nonwoven natural fibre preforms from our previous study follows closely conventional papermaking processes [30] based on a single filtration method. In this work, we introduce a layer-by-layer filtration method to produce even better performing nonwoven flax fibre preforms utilising BC and NFC as binders. The morphology, tensile and flexural properties of the nonwoven preforms are discussed.

2. Experimental

2.1. Materials

Short and loose flax fibres of approximately 25 mm in length were kindly supplied by S.A.R.L. Novalin France (Millam, France). Sodium hydroxide was purchased from Sigma–Aldrich. Chlorine free pulp was kindly provided by EMPA (Dübendorf, CH). NFC was produced from chlorine free pulp following the previously published procedure [31,32]. Briefly, 300 g of chlorine free pulp were soaked in 8 L of water at 10 °C for 6 d. The soaked chlorine free pulp was then diluted to 3.5 wt.% consistency and passed 13 times through an ultrafine friction grinder (Masuko Supermasscolloider, MKZA10-20J CE, Masuko Sangyo Co. Ltd., Kawaguchi, Japan). After each pass, additional deionised water was added to avoid the heating of the grinding stones and to dilute the consistency of the suspension. After 13 passes through the Masscolloider, the

cellulose suspension was further diluted to 1.25 wt.% consistency and passed through a high shear microfluidiser (Microfluidics Corporation, USA) consisting of two consecutive chambers, whereby the diameters of the chambers were progressively reduced from 400 to 200, 100 and finally 75 μm, respectively, to further refine the pulp to produce more homogeneous NFC. Neat BC was extracted from commercially available nata de coco (CHAOKOH coconut gel in syrup, Ampol Food Processing Ltd., Nakorn Pathom, Thailand). The extraction and purification of BC from nata de coco can be found in Ref. [22]. Briefly, 5 jars of nata de coco gels were rinsed and soaked in DI water overnight to remove the sugar syrup. The gels were then blended (Braun MultiQuick 5 Jug Blender, Braun GmbH, Germany) for 2 min in 5 L of water, followed by centrifugation at 9000 rpm to remove excess water. In order to purify the BC, the centrifuged BC was re-dispersed in 5 L 0.1 M NaOH solution and heated at 80 °C for 20 min to remove any remaining microorganisms and soluble polysaccharides. The purified BC was then successively centrifuged and homogenised to neutral pH.

2.2. Manufacturing of nonwoven flax fibre preforms

Nonwoven flax fibre preforms were manufactured using a single filtration process following our previously published work [23,30] that resembles a papermaking process. 36 g of short and loose flax fibres were added and dispersed into suspensions containing 10, 20, 30 wt.% BC, NFC or pulp (relative to amount of flax fibres) in 2 L of water and left soaking overnight. The suspensions were then vacuum filtered onto 24 cm diameter filter paper (Qualitative filter paper 413, particle retention: 5–13 μm, VWR Austria) to remove the excess water using a Büchner funnel. The wet filter cakes were then sandwiched between blotting papers (Qualitative filter paper, grade 520A, Whatman, GE Healthcare Europe GmbH, Wien, Austria) and wet pressed 3 times under a weight of 1.5 t (25-12-2HC, Carver Inc., Wabash, IN, USA). Fresh blotting papers were used for each wet pressing step. A final hot pressing step was performed at 120 °C for 2 h to completely dry and consolidate the wet filter cake into robust nonwoven fibre preforms.

In addition to the single filtration process, a layer-by-layer filtration process was also used in this work to prepare nonwoven flax fibre preforms aiming to produce a more homogeneous distribution of nanocellulose within the preform. Suspensions containing flax fibres and nanocellulose were first prepared following the previously described method. The suspensions were then divided into 4 equal volumes of the same consistency. The first suspension was poured into a Büchner funnel and vacuum filtered onto a 24 cm diameter filter paper to remove the excess water. The second suspension was then poured directly onto this wet filter cake and further vacuum filtered to remove the excess water. This method was repeated to build up the wet filter cake layer-by-layer. This method actually mimics the manufacturing of traditional Japanese papers. The wet filter cake was then wet pressed 3 times, followed by a final hot pressing step to dry and further consolidate the fibre preform. The grammage of the manufactured nonwoven fibre preforms containing 10, 20 and 30 wt.% BC, NFC or pulp were 875, 955 and 1035 g m^{-2}, respectively. The grammage increased with increasing nanocellulose loading because the flax fibre content was kept constant.

2.3. Characterisation of BC, NFC, pulp and nonwoven fibre preforms

2.3.1. Morphology of the nonwoven fibre preforms

The morphology of the preforms was studied using scanning electron microscopy (JCM-6000, JEOL GmbH, Eching, Germany) operating at an accelerating voltage of 15 kV. Prior to SEM, the preforms were fixed onto SEM stubs using carbon tabs and gold coated

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[1] It should be noted that the definition of tensile strength in this context is based on paper testing standards (i.e. maximum force required to break the preform per unit width of the specimen, typically 15 mm).