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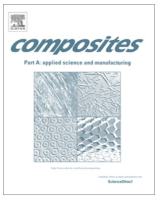

Binderless all-cellulose fibreboard from microfibrillated lignocellulosic natural fibres

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ABSTRACT

Fully biobased all-cellulose fibreboards are produced without the use of additional bonding agents such as polymer resins or binders as in the case of e.g. medium density fibreboard (MDF) or natural fibre reinforced plastic (NFRP). These materials make use of the self-binding capability of cellulose, exploiting the enhanced hydrogen bonded network present in micro- and nanofibrillated cellulose, resulting in good mechanical performance. After the optimisation of refinement, drying and hot-pressing conditions, binder-free panels from microfibrillated flax fibres with excellent mechanical properties of around 17 GPa and 120 MPa for flexural modulus and strength, and relatively low water sorption are achieved, making these materials competitive with conventional cellulose based composite materials. The work shows the potential of creating all-cellulose engineering materials using only the intrinsic bonding capacity of microfibrillated lignocellulose, potentially leading to environmentally friendly panel board materials, which are entirely based on renewable resources, recyclable and biodegradable.

1. Introduction

Cellulosic materials are the most abundant renewable biomaterial of photosynthetic origin on earth. In terms of mass units, their net annual production far exceeds that of synthetic polymers. Cellulose is present in plants cells as aligned and chain extended poly-β-(1,4)-glucan molecules assembled into nanofibrils. Natural fibres composed of assemblies of such nanofibrils have had great success as reinforcing fibres in polymer composites [1–3], mainly because of their combination of good mechanical properties with low weight. Moreover these lignocellulose fibres have benefitted from eco-performance advantages since they come from a renewable resource, are biodegradable and can be incinerated with good energy recovery without producing much residue. In more recent years, the use of cellulose nanofibres (CNFs) extracted from biomass as reinforcing elements in polymer nanocomposites has attracted great attention [3–5], mainly because of their high mechanical properties [6–8], in combination with high aspect ratios (>100) [9].

Despite these advantages there are certain drawbacks which have resisted the large scale use of cellulose fibres in engineering applications. The poor compatibility of the hydrophilic cellulose with the often hydrophobic polymeric resin typically leads to a weak interface, and for this reason numerous strategies have been employed to improve their compatibility [10,11]. However, usually such treatments will add costs and affect the "green" character associated with cellulose fibres. An alternative solution to enhance fibre–matrix adhesion in cellulose fibre based composites, while at the same time creating a fully biobased material, is through the development of all-cellulose composites [4,12]. Following earlier developments in the area of all-polymer composites [13,14], the concept of all-cellulose based composites generally involves the selective dissolution of cellulose fibre skins to form a matrix phase that bonds the cellulose fibre cores together, forming a high-performance all-cellulose composite or nanocomposite [15,16]. However, despite the impressive mechanical properties of these all-cellulose composites, with moduli approaching 20 GPa and tensile strengths in excess of 200 MPa, their processing method often still involves the use of environmentally hazardous chemical substances and solvents, increasing their carbon footprint.

Since plant fibres have a lower carbon footprint than polymers or synthetic resins [17], the ideal eco-composite material would be solely based on cellulose fibres, use no solvents, and has no polymer, resin or binder. This way a fully biobased material is obtained while at the same time creating a material that is potentially recyclable. The elimination of polymer matrices would also eliminate

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the need for coupling agents or fibre treatments, which all lower the environmental impact of cellulose fibres. Hence, there is a clear incentive to create high-performance cellulose based engineering materials without the use of synthetic resins or binders.

An interesting approach towards high-performance binder-free cellulose materials is through the exploitation of the self-binding capacity of cellulose networks. Bacterial cellulose (BC), can be considered as the primus inter pares of such cellulose network materials. Here, cellulose nanofibres are directly obtained from bacteria, which under special static culturing conditions produce a fine fibrous network of cellulose nano-ribbons. Drying of these cultured network gels results in BC film based on high-modulus nanocellulose, bonded together through an extensive hydrogen bonded network [4,18–20]. This extensive self-binding network, which is responsible for its high mechanical performance, with typical values for Young's modulus and tensile strength of 20 GPa and 250 MPa, respectively, is achieved due to the extremely high specific surface area of BC nano-ribbons.

After refinement, similar nanofibrous networks can be obtained from biomass as well. Cellulose nanofibres (CNFs) extracted from wood can be suspended in water, which after casting or vacuum-filtration followed by drying can lead to cellulose nanopaper with strong interfibrillar interactions [3,4,21,22]. Interestingly, polymer binders are not needed as the process relies on self-binding, with hydrogen bonding and nanofibre entanglements being mainly responsible for network formation. Such nanopapers exhibit a fibrous network analogous to conventional paper, albeit at the nanoscale rather than at the microscale of conventional paper. As a result of the much higher specific-surface area of CNFs, greatly increased interfibrillar hydrogen bonding is achieved, leading to increased mechanical properties of these nanopapers. Following these concepts, Henriksson et al. [21] created cellulose nanopaper with a tensile strength of 250 MPa and high work-to-fracture, while in a later study, Saito et al. [22] reported even higher strengths (310 MPa) for their nanopaper system.

Clearly an increase in surface area of cellulose fibres is key to producing high-performance binder-free cellulosic materials. Turbak et al. [23] were the first to report the microfibrillation of cellulose from wood pulp using a mechanical homogenisation process in which the fibre cell wall was disintegrated into CNFs. In recent years, several methods including TEMPO-catalysed oxidation [22] and/or enzymatic [24] pre-treatments have been developed in order to decrease the energy demands and facilitate the fibrillation process [5,9,25]. These pre-treatments usually consist of multi-step processes where fibres are not only subjected to several aggressive non-environmentally friendly chemical substances, but also to mechanical refining. Even though chemical and enzymatic pre-treatments can successfully promote fibre disintegration, the required mechanical treatments for CNF production remain fairly energy intensive and costly [26].

So far, most of the research into CNF networks has been in the area of films and paper, with only few studies being aiming at construction materials for industrial applications. This is rather surprising as these types of materials could be interesting alternatives to panel board products such as medium-density fibre board (MDF), or oriented strand board (OSB).

Over the last decade some studies have been devoted to the development of self-binding fiberboard materials but the general trend here has been to use lignocellulosic materials like softwood with a high lignin content (>20%) and high hot-pressing temperatures of around 200 °C to ensure *in-situ* plasticization and flow of the lignin to effectively bind the cellulose fibres together [27–29]. Typical moduli of such self-binding cellulose panels are 2–4 GPa, while strength values reported are around 20–30 MPa. Nilsson et al. [30] created thick fibreboard panels from cellulose nanofibres of high cellulose content (~97%) using wood fibre pulp as a raw material, exploiting the intrinsic hydrogen bonding capacity of cellulose nanofibres rather than using lignin as the bonding agent. Young's modulus of these panels varied from 4 to 13 GPa, and tensile strength from 30 to 75 MPa depending on cellulose pretreatment and hot-pressing conditions, out-performing most lignin based self-binding fiberboard materials.

A commercial product based on self-binding nanofibrillated cellulose aiming at the construction market is Zelfo® [31]. In the Zelfo® process, the first production step is again mechanical refining, where the raw material is simultaneously hackled and ground and mixed with water. The result of this process is a microfibrillated pulp, which is subsequently pre-dried, cast or moulded into a final shape and then finally dried. Depending on raw material and process conditions, reported properties of Zelfo® varied from 1.5 to 6.5 GPa for Young's modulus and 7 to 55 MPa for strength [31].

In the current work, self-binding fibreboard materials are produced using Zelfo-like technology based on a mechanical refining process using water as the only processing aid. Flax fibres are used as a source for microfibrillated lignocellulose pulp which after dewatering and pre-drying, is compression moulded into flat binderless all-cellulose panels. The current technology is based on the microfibrillation of lignocellulosics rather than the use of highly purified enzymatic or TEMPO pretreated cellulose nanofibres as generally used in nanopaper studies. Flax fibres are used because of their low lignin content (~2%), which reduces thermal degradation effects, odour and discoloration. At the same time it ensures a self-binding mechanism based predominantly on hydrogen bonding, rather than using lignin as an in-situ bonding agent as in previous binderless fibreboard studies, making the current binderfree cellulose panels in principle recyclable using a simple re-pulping process.

2. Experimental

2.1. Sample preparation

Different natural fibre sources including plants and wastes with high cellulose content can be used for the production of self-binding all-cellulose materials. Here, flax fibres kindly supplied by EKOTEX Co. Ltd. (Japan) have been used, containing 70% cellulose, 16% hemicellulose and 2% lignin [1]. Fig. 1 shows the outline of the experimental procedure for the manufacture the self-binding all-cellulose materials. First, the raw material in the form of cut flax fibres of 20 mm length were subjected to a mechanical refining treatment using a standard Valley (or Hollander) beater where the fibres were further cut and fibrillated in the presence of a large amount of water (98%). For this 100 g of flax fibres were weighed and mixed with 15 l of water. The second step involved filtering of the refined pulp and partial dewatering in order to get the desired consistency of the fibrillated pulp for subsequent pressing. Optimal consistency for room temperature pressing was measured by checking the water content, and corresponds to 90% water content. The initial step in the formation of interfibre interactions occurred when the samples were subjected to a room temperature pressing (10 bar) where further removal of water took place. This partially dewatered precursor cake (50% water content) was then finally dried using a hot press where the application of pressure combined with moderate temperatures (140 °C) allowed the complete removal of all retained water, giving flat panels of 30 cm × 30 cm, with a nominal thickness of 2 mm. Although the lignin content in the final pulp is very low, a moderate hot-pressing temperature of 140 °C was selected to limit any possible effects of lignin plasticization to the self-binding mechanism, while

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