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# Rapid nanopaper production by spray deposition of concentrated microfibrillated cellulose slurries

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ABSTRACT

This study presents a rapid method for nanopaper production by spray deposition of high concentration microfibrillated cellulose (MFC) slurries on a nylon fabric and their subsequent filtration dewatering. The filtration time for the consolidation of a wet MFC mat was of 15 and 90 s for sheets with basis weight of 13.7 and 124 g m$^{-2}$, respectively. MFC films exhibited excellent Young's modulus of ca. 18 GPa and intrinsic air permeability of ca. 0.22 nm$^2$. Nevertheless, the progressive decrease of the basis weight from 124 to 13.7 g m$^{-2}$ induced the decay of the film tensile properties (stress and strain at break dropped from 150 MPa and 4.6% to 50 MPa and 0.4%) and the onset of a brittle behaviour. This trend was ascribed to the presence of residual fibre debris in the MFC slurry which acted as fracture nucleation spots in thin films.



## 1. Introduction

Over the last decade, nanoparticle/nanofibre pressure and vacuum filtration on membranes with sub micrometric retention threshold have been extensively used for the production of a wide variety of new functional materials, i.e. mesoporous polymeric nanotube membranes (Huang et al., 2012), single walled carbon nanotube electrodes for Li-ion batteries (Ng et al., 2005; Chew et al., 2009), strong and highly conducting graphene paper (Chen et al., 2008); multi walled carbon nanotubes paper for shape-memory composites (Lu and Gou, 2011; Lu et al., 2011, 2014); microfibrillated cellulose (MFC) paper and composite films for packaging applications (Henriksson and Berglund, 2007; Henriksson et al., 2008). Despite its outstanding properties and ease of fabrication, nanopaper production by pressure/vacuum filtration is affected by a low dewatering time which represents a major constraint for the mass production of this new class of materials. Currently, this limitation represents a bottleneck for MFC nanopaper production since the high specific energy consumption for microfibrillated cellulose production typical of early disintegration processes (Turbak et al., 1983; Siro and Plackett, 2010; Ankerfors and Lindström, 2007) does no longer represent a limitation for MFC industrial use. Indeed, recently developed disintegration protocols based on chemical or enzymatic pulp pre-treatments allowed decreasing energy consumption from ~30 MW h t$^{-1}$ to 1–10 MW h t$^{-1}$ (Pääkkö et al., 2007; Meyer et al., 2012) thus paving the way to a mass production of MFC and its use in the papermaking industry for MFC based sheets and coatings (Henriksson et al., 2008; Eichhorn et al., 2010; Aulin et al., 2010; Lavoine et al., 2012).

In order to quickly manufacture large area cellulosic sheets approaching the outstanding mechanical and barrier properties of MFC bulky films (Lavoine et al., 2012; Henriksson and Berglund, 2007; Syverud and Stenius, 2009; Henriksson et al., 2008), three main routes have been investigated, i.e.: (i) MFC blend with wood fibres and MFC-wood fibre composite sheets manufacturing by filtration (Missoum et al., 2013; Gonzalez et al., 2012, 2014; Hii et al., 2012; Su et al., 2013); (ii) MFC coating on the surface of pre formed paper (Syverud and Stenius, 2009; Aulin et al., 2010; Aulin and Ström, 2013; Hult et al., 2010; Eriksen et al., 2008; Beneventi et al., 2014a) and (iii) bulky MFC sheet manufacturing by filtration (Zhang et al., 2012; Varanasi and Batchelor, 2013).

The first two approaches led to the increase of the mechanical and barrier properties of the final paper sheet. Nevertheless, for the purpose of manufacturing tough and densely packed cellulose sheets, MFC-wood fibre composite sheets processing by

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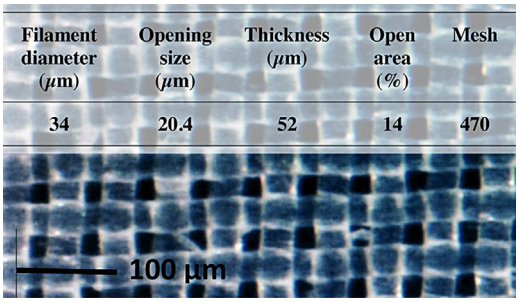


**Fig. 1.** Main characteristics of the nylon fabric used for the MFC sheet formation as determined by optical microscopy.

conventional papermaking and MFC coating of pre-formed papers do not seem optimal routes since the final sheet structure remains strongly affected by the presence of wood fibres. MFC-wood fibre processing by filtration leads to a limited 2–25 fold decrease in the air permeability of the pristine paper sheet with industrially significant drawbacks on retention and dewatering (Missoum et al., 2013; Gonzalez et al., 2012; Taipale et al., 2010), whereas, MFC coating allows reducing air permeability by 2, up to 5, orders of magnitude (Aulin et al., 2010; Hult et al., 2010; Beneventi et al., 2014a) but the MFC coating thickness rarely exceeds 10 μm with a limited contribution on sheet mechanical properties.

Thus, direct manufacturing of MFC sheets by filtration appears as one of the most promising methods for the production of self-standing cellulose nanofibre sheets. Reported methods use 0.2–0.6% consistency MFC slurries, sheet forming fabrics with large openings (viz. 150–110 μm) and dewatering time ranging between 30 s and 9 min.

Owing to the low consistency of the MFC slurry processable by filtration film forming, the slow dewatering stage represents a bottleneck to improve the speed of sheet formation and to implement nanopaper production on conventional paper machines.

According to the excellent processability of both 2% consistency MFC suspensions (Beneventi et al., 2014a) and 20% consistency MFC/graphite (1/9 w/w) slurries (Beneventi et al., 2014b) during paper coating by high pressure spraying, the aim of this study was to produce nanocellulose paper by spray distribution of 2% consistency MFC suspension on a forming fabric and its subsequent dewatering by filtration.

## 2. Experimental section

Microfibrillated cellulose was produced using a commercial bleached hardwood (birch) kraft pulp (BHKP, UPM Betula). MFC was prepared according to a mechano-enzymatic protocol followed by homogenization at high pressure (Meyer et al., 2012). The BHKP was pre-refined, treated with cellulases and refined at a very high drainage index in order to obtain a suspension with a mean fibre length lower than 300 μm. Enzymatic pre-treatment was done with a commercial cellulases solution (FibreCare R, Novozymes). After adjusting the consistency to 2%, the pre-treated pulp was processed in a pilot homogenizer (Ariete, GEA Niro Soavi) using a five passes sequence, i.e. one pass at 1000 bar was followed by four passes at 1500 bar.

The 2% consistency MFC slurry was spray deposited onto an hydrophilic nylon fabric (main characteristics obtained from optical microscopy are summarized in Fig. 1) using an in house assembled spray coater (Beneventi et al., 2014a) composed of a variable speed conveyor and a commercial high pressure spray system (paint crew, Wagner) which were operated at a speed ranging from 0.5 to 3 m min$^{-1}$ and at a constant MFC slurry flow of 0.75 kg min$^{-1}$, respectively.

In order to simulate unit operations present on a conventional paper machine, after MFC spray deposition, the excess water was removed by vacuum suction using the sheet forming section of a rapid köthen hand sheet former. Applied vacuum and dewatering time were recorded for each run. After dewatering, a second nylon fabric and two blotting papers were superposed to the wet MFC mat and the whole stack was compressed using a 3 kg roll (two passes). The wet MFC film sandwiched between the two nylon fabrics was then dried up to full drying (i.e. 90 °C, 10 min films with basis weight up to 55 g m$^{-2}$ and 25 min for higher basis weight) in the vacuum drying section of the rapid köthen hand sheet former. Finally, the two nylon fabrics were peeled off and a 20 cm diameter MFC film was obtained. The main stages of the MFC film fabrication process and the operating conditions of the coating bench are summarized in Fig. 2.

Under the assumption of the complete MFC retention on the nylon fabric and its homogeneous distribution over the main impact zone, the basis weight ($bw_{MFC}$) of the MFC film was estimated using the spray operating conditions (Fig. 2h) and the following equation, which was derived from the geometry of the experimental set up (Beneventi et al., 2014a),

$$bw_{MFC} = \frac{\dot{m} \times c}{2D \tan\theta \times V} \quad (1)$$

where $\dot{m}$ and $c$ are the mass flow and the consistency of the MFC slurry, respectively, $D$ is the nozzle distance from the substrate, $V$ is the conveyor speed and $\theta$ is the spray jet angle calculated using $D$ and the width ($W$) of the main jet impact area, where most of the MFC slurry was projected. Basis weights obtained from Eq. (1) and experimental ones were used to evaluate MFC retention.

In order to evaluate film surface topography, MFC films were imaged by both optical (×430 magnification) and electronic microscopy (SEM, FEI Quanta ESEM) and the overall film thickness was measured using a mechanical caliper (Adamel Lhomargy, MI20).

The film intrinsic air permeability was measured using a Bendtsen tester (Lorentzen & Wettre) operated with a differential pressure of 19.2 kPa and it was expressed using the Darcy's formalism, namely:

$$k = \frac{Q \times \mu \times d}{S \times \Delta P} \quad (2)$$

where $Q$ is the air flow passing through the MFC film, $S$ is the cross sectional area of the test sample (i.e. 10 cm$^2$), $\mu$ is air dynamic viscosity $d$ is the film thickness and $\Delta P$ is the applied pressure.

Tensile properties of the MFC film were evaluated by traction tests (Inströn, 5969) on 5 × 1.5 cm strips with a strain rate of 5 mm min$^{-1}$. Mechanical properties are provided as the average of five replicates.

## 3. Results and discussion

### 3.1. MFC film manufacturing

The spray deposition technique allowed obtaining a stable and homogeneous distribution of the 2% consistency MFC slurry on the nylon fabric. Owing to its high viscosity, the fluid did not flow out of the forming fabric even for the lowest conveyor speed of 0.5 m min$^{-1}$ which corresponded to the deposition of a 5.1 mm thickness gel film (estimated as $d_{wet} = bw_{MFC}\, c^{-1}\, \rho^{-1}$, where $d_{wet}$ is the thickness of the MFC slurry, $bw_{MFC}$ is the dry MFC basis weight given by Eq. (1), $c$ and $\rho$ are the consistency and the density of the MFC slurry).

Water removal by filtration was stopped after the glossy water film disappeared from the surface of the MFC mat and, when the amount of deposited MFC slurry ranged from 500 to