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COMMUNICATION

Rapid preparation of smooth nanocellulose films using spray coating

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Abstract Spraying of nanocellulose (NC) on a solid surface to prepare films is an alternative technique to vacuum filtration, which requires a long drainage time and produces films which can sometimes be difficult to separate from the filter. This letter reports a rapid preparation technique for nano-cellulose films using a bench scale system spray coating nanocellulose suspension onto stainless steel plates. After spraying NC suspension onto a smooth steel plate travelling on a constant velocity conveyor, the films can be dried directly on the plates using standard laboratory procedures, saving processing time and effort. By adjusting the suspension consistency, we were able to reproducibly make films with a basis weight ranging from 52.8 $\pm$ 7.4 to 193.1 $\pm$ 3.4 g/m^2 when spraying on to a plate moving at a velocity of 0.32 cm/s. The operator preparation time for the nanocellulose film was 1 min, independent of the sample basis weight, which compares to production times reported in the literature of 10 min using filtration techniques. The films made by spray coating showed higher thickness, but comparable uniformity, to those made by vacuum filtration. Optical profilometry measurements showed that over a 1 cm $\times$ 1 cm inspection area that the surface roughness (RMS) of the NC film is only 389 nm on the spray coated side in contact with the steel plates, compared to 2087 nm on the outside surface. Thus, the reduction in preparation time for producing the nanocellulose film recommends this spray coating technique as a rapid and flexible method to produce NC films at the laboratory scale.

Keywords Nanocellulose (NC) · Spray coating · Nanocellulose film · Uniformity · Roughness

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Introduction

Nanocellulose is a promising renewable, biodegradable nanomaterial available in large quantities in nature. The interest in nanocellulose material is growing due to outstanding properties such as high specific strength, thermal stability, hydrophilicity, and easy chemical functionalization. Nanocellulose materials can provide an excellent alternative material for most plastic films which have limitations in recycling and biodegradability. Films prepared from nanocellulose have outstanding mechanical, optical and structural properties enabling the fabrication of many functional materials and devices such as organic transistors and conducting materials (Chinga-Carrasco et al. 2012), or immunoassays and diagnostics tests

(Orelma et al. 2012). The surface chemistry of nanocellulose can be easily tailored for applications such as photonics, biomedical scaffolds, optoelectronics and developing barrier materials (Abitbol et al. 2016). Recently, nano cellulose film has been investigated for use as filters (Metreveli et al. 2014; Varanasi et al. 2015), adsorbents, catalyst (Koga et al. 2010), cell culture substrates, thermal insulators and drug carriers (Huang et al. 2013).

Even though the nanocellulose films have potential uses in many areas, progress and applications are significantly hindered by the difficulty of simply and reproducibly preparing nanocellulose films both at the laboratory and industrial scales. Stand-alone nanocellulose films have been prepared using either vacuum filtration or casting. Casting is a time-consuming process which typically requires three days for the film to dry and wrinkling is difficult to control (Shimizu et al. 2014). Vacuum filtration is a considerably quicker process when compared to the casting method. Laboratory film preparation time for light weight films less than 60 g/m^2 has been reduced from 3 to 4 h (Nogi et al. 2009) to 10 min (Varanasi and Batchelor 2013; Zhang et al. 2012) by increasing the solids content above the gel point and using polyelectrolytes to increase the size and strength of the flocs to reduce filter resistance. However, there can be significant issues in separating the film from the filter and subsequent handling before it is finally dried. Vacuum filtration is also a manufacturing method with a limited range of film basis weight as the filtration time increases exponentially with film thickness (basis weight).

Spraying of nanocellulose on permeable substrates is an alternative technique for making nanocellulose films that has been used to produce continuous nanocellulose films by spraying onto a fabric or to produce composite laminates by spraying onto a base sheet (Beneventi et al. 2014). Spraying has significant advantages such as contour coating and contactless coating with the base substrate. The topography of the surface of the base substrate does not influence the coating process. The range of basis weight achievable with spraying is much higher than has been obtainable with filtration. A maximum mass of the film of 124 g/m^2 was obtained by spraying nanocellulose onto a nylon fabric running at a speed of 0.5 m/min (Beneventi et al. 2015). So far, spraying of nanocellulose on fabric or paper has been used to prepare sheets and barrier layers, respectively. Spraying has also been used to prepare multilayer nanocomposites for electrodes (Krol et al. 2015; Zolin 2017).

Spraying of cellulose microfibres onto impermeable substrates has also been investigated. In a recent study, spraying was used to produce free-standing micro-fibrillated cellulose film with 3D structures on preheated metal surfaces (Magnusson 2016). The spray coated MFC film had a basis weight from 59 to 118 g/m^2 and thickness of the sheet varied from 46 to 68 μm. The major reported disadvantage of the approach was the formation of cracks in the film. In an earlier study, ethyl cellulose dispersed in water with plasticizer was sprayed on Teflon plates and produced a uniform film with better tensile strength and elastic modulus than a cast film (Obara and McGinity 1994). However, this method required extensive pre-treatment of the cellulose prior to spraying in comparison to our method, where the cellulose nano fibrils are directly used for spraying without additional preparation.

Spraying can also be performed at a higher solids content compared to filtration, reducing the amount of water to be removed by drying. Spraying has not so far been used to make discrete films for laboratory investigations, or for small scale products. It is still an open question about the sheet quality produced by spraying compared to handsheets made by laboratory vacuum filtration. It is the purpose of this paper to describe a new and efficient method for the laboratory production of nanocellulose films by spraying nanocellulose directly onto smooth steel plates. The nanocellulose films thus formed can subsequently be dried in many ways: in air under restraint, heat contact, etc. The uniformity of spray coated nanocellulose films is evaluated by thickness mapping and then compared with the thickness mapping of a nanocellulose film prepared via vacuum filtration.

Experimental method

Materials

The nomenclature for nanocellulose has not been reported in a consistent manner in the previous scientific investigations. As well as nanocellulose (NC), it is also called micro fibrillated cellulose (MFC), cellulose nano-fibrils, cellulose micro-fibrils and nano-fibrillated cellulose (NFC). In this paper, we use NC as the generic term for all the cellulose nanomaterials used.

NC supplied from DAICEL Chemical Industries Limited (Celish KY-100S) was used to prepare films. NC samples were used at consistencies ranging from 1.0 to 2.0 wt%, prepared by diluting the original concentration of 25 wt% with distilled water and mixing for 15,000 revolutions in a disintegrator. The viscosity of the NC suspension was evaluated by the flow cup method, which evaluates coating fluid flow through an orifice, to be used as a relative measurement of kinematic viscosity, with the results expressed in seconds of flow time in DIN-sec.

Preparation of nanocellulose films through spray coating and vacuum filtration methods

The experimental system for a lab scale spray coating system is shown in Fig. 1. The NC suspension was sprayed on a circular stainless steel plate moving on a variable speed conveyor using a Professional Wagner spray system (Model number 117) at a pressure of 200 bar. The type 517 spray tip gave an elliptical spray jet. The spray jet angle and beam width are 50° and 22.5 cm, respectively. The spray distance is 30.0 ± 1.0 cm from the spray nozzle to the circular steel plate. The conveyor was operated at a constant speed of 0.32 cm/s for the spraying of NC on the plate surface. During the spraying, the pressure driven spray system was run for 30 s before forming the first film, so as to allow the system to reach equilibrium.

After spraying, the film on the plate was air dried under restraint at the edges for at least 24 h. The NC film can then be readily peeled from the stainless steel plate and stored at 23 °C and 50% RH for further testing. For comparison, NC films were also prepared using vacuum filtration method as reported in (Varanasi and Batchelor 2013). In brief, 1000 g of NC suspension with 0.2 wt% concentration was poured into a cylindrical container having a 150 mesh filter at the bottom and then filtered until it formed a wet film on the mesh. The wet film was carefully separated using blotting papers and then dried at 105 °C in a drum drier for around 10 min. The film prepared by this method is used as a reference film to compare the uniformity and thickness of the spray coated film. The basis weight (g/m^2) of each NC film was calculated by dividing the weight of the film, after 4 h drying in the oven at a temperature of 105 °C, by the film area.

Evaluation of thickness distribution and thickness mapping

The NC film thickness was measured utilizing L&W thickness analyzer (model no 222). The circular NC film was divided into six regions and thickness was measured in six evenly spaced locations in each region. The thickness mapping of a centre square region of the circular film is done by plotting a contour plot using Origin Pro 9.1. The visual explanation is given in Fig. 2. The mean thickness of all the films is plotted against the suspension concentration of nanocellulose. The mass of the film per unit area is evaluated for various concentration of nanocellulose sprayed on the stainless steel plate.

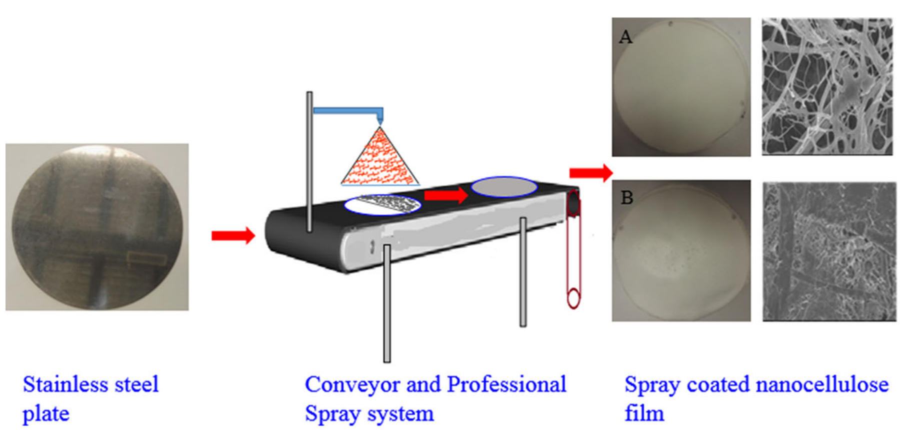


Fig. 1 Experimental set up for laboratory scale spray coating system for preparation of nanocellulose film. **a** The rough surface of the NC film, **b** the smooth surface of the NC film

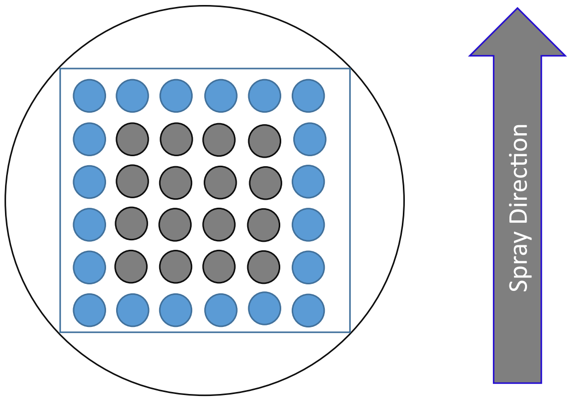


Fig. 2 Mapping of thickness of the NC film. The thickness is measured in the centre region of the film. The *square section* of centre part of the film is used for *contour plotting*. The *grey points* are used for mapping to confirm the uniformity of the film

Evaluation of tensile strength and air permeance

The strength of the nanocellulose films were evaluated by an Instron model 5566. The test specimen were 100 mm in length and 15 mm width and were conditioned for 24 h at 23 °C and 50% RH. The barrier properties of the 100.5 g/m^2 spray coated film and film prepared via vacuum filtration were evaluated by air permeance through an L&W Air permeance tester.

Surface topography of nanocellulose film

The surface morphology and topography of the iridium coated NC film were measured with a FEI Novo SEM450. The images of both surfaces of the nanocellulose films are captured at magnifications from 500 to 50,000 in secondary electron mode-II. Furthermore, the surface roughness of both sides of the film at nanoscale was evaluated by atomic force microscopy (JPK Nanowizard 3) and optical profilometry (Bruker Contour GT-I).

Results and discussion

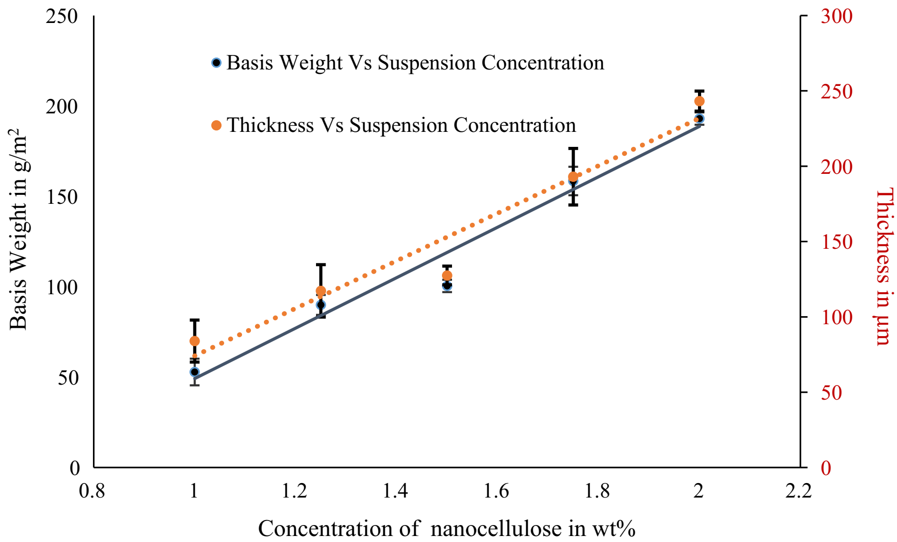
The operational range for spraying NC suspension was between 1.0 and 2.0 wt%. Below 1 wt%, the suspension was too dilute and flowed over the metal surface producing an uneven film, which was difficult to peel from the plate after drying. Above 2 wt%, the suspension becomes too viscous to spray. The lower and upper limits, corresponded to suspension viscosities of 17.0 ± 0.6 and 32.2 ± 0.9 DIN sec, respectively.

Figure 3 shows the effect of NC suspension concentration on the basis weight of the film and mean thickness of the film. Each point is the average of 4 replicates of NC film with the error bars providing the standard deviation. Both film basis weight and thickness increased approximately linearly with increasing NC concentration. Basis weight ranged from 52.8 ± 7.4 to 193.1 ± 3.4 g/m^2 by spraying suspension with a concentration of 1.0 and 2.0 wt%, respectively. The significant reduction in variability is most likely due to the more rigid suspension at 2.0 wt% consistency, which produces a more stable suspension sprayed onto the surface of the plate. The film thicknesses were 83.9 ± 13.9 and 243.2 ± 6.6 µm for the lowest and highest consistencies.

Figure 4 presents the contour plot of the thickness distribution of the 1.5 wt% spray coated film compared with a film made by the established method of vacuum filtration. The basis weight of the film prepared by spray coating and vacuum filtration are almost identical at 100.5 ± 3.4 and 95.2 ± 5.2 g/m^2, respectively. The direction of conveyor movement was from bottom to top. Compared to spray coating, vacuum filtration required a much higher dewatering time of 15 min to produce the film. When compared to the film made from vacuum filtration, the spray coated nanocellulose film is slightly thicker, even when correcting for the slight difference in basis weight. The apparent density of the spray coated film and film prepared via vacuum filtration were 793 and 834 kg/m^3, respectively. In addition, there is a somewhat wider distribution of thickness for the spray-coated film. The thickness of the NC film prepared via vacuum filtration process and spray drying were 113.4 ± 5.4 and 127.1 ± 12.1 µm, respectively. The uncertainties give the standard deviation of the distribution of measured thickness.

Figure 5 shows the surface morphology and topography of both surfaces of the spray coated NC film investigated by scanning electron microscopy and optical prolifometry. The AFM images are given in the supplementary material. At all the length scales investigated, the surface in contact with the stainless steel plate is notably smoother and less porous than the reverse side, where some fibre clumps from the suspension were retained on the film surface as it dried.

Fig. 3 Effect of suspension concentration on the basis weight and thickness of the nanocellulose film prepared using spray coating



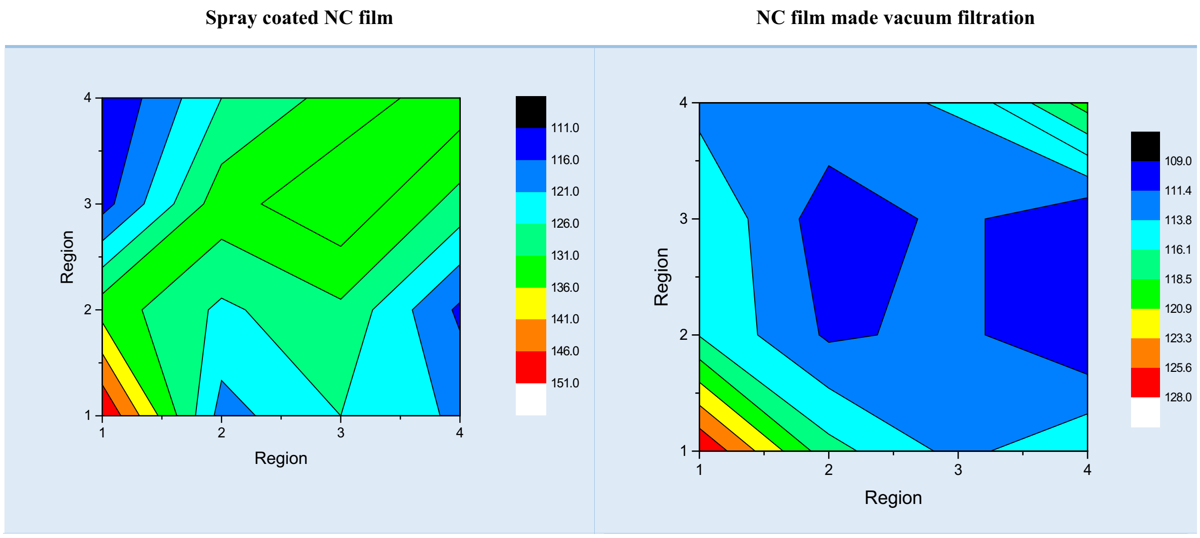


Fig. 4 Thickness distribution of the NC films—spray coated at conveyor velocity of 0.32 cm/s and vacuum filtration

Visually the smooth surface of the sprayed film has a glossy, shiny appearance. The RMS roughness from the AFM images of the rough side is 414.0 nm for 10 µm × 10 µm film area and 51.4 nm for 2 µm × 2 µm film area whereas the RMS surface roughness of the smooth side is only 81.1 nm for 10 µm × 10 µm film area and 16.7 nm for 2 µm × 2 µm film area. AFM measurements of the film prepared by filtration are also given in the Supplementary information and show the sides had a surface roughness of 417.7 nm (Side 1) and 330.8 nm (Side 2) at an inspection are of 10 µm × 10 µm, which is approximately the same as the rough side of the film prepared by spray coating. Similarly, the RMS roughness of the spray-coated NC film measured using the optical profilometry at an inspection area of 1 cm × 1 cm is 2087 nm on the rough side and 389 nm on the spray coated side when comparing with NC Film prepared via vacuum filtration which had a RMS roughness of 2673 nm on side 1 and of 3751 nm on side 2.

The results reported in this investigation confirm that laboratory scale spraying NC on a stainless steel plate is viable for the rapid preparation of NC film with

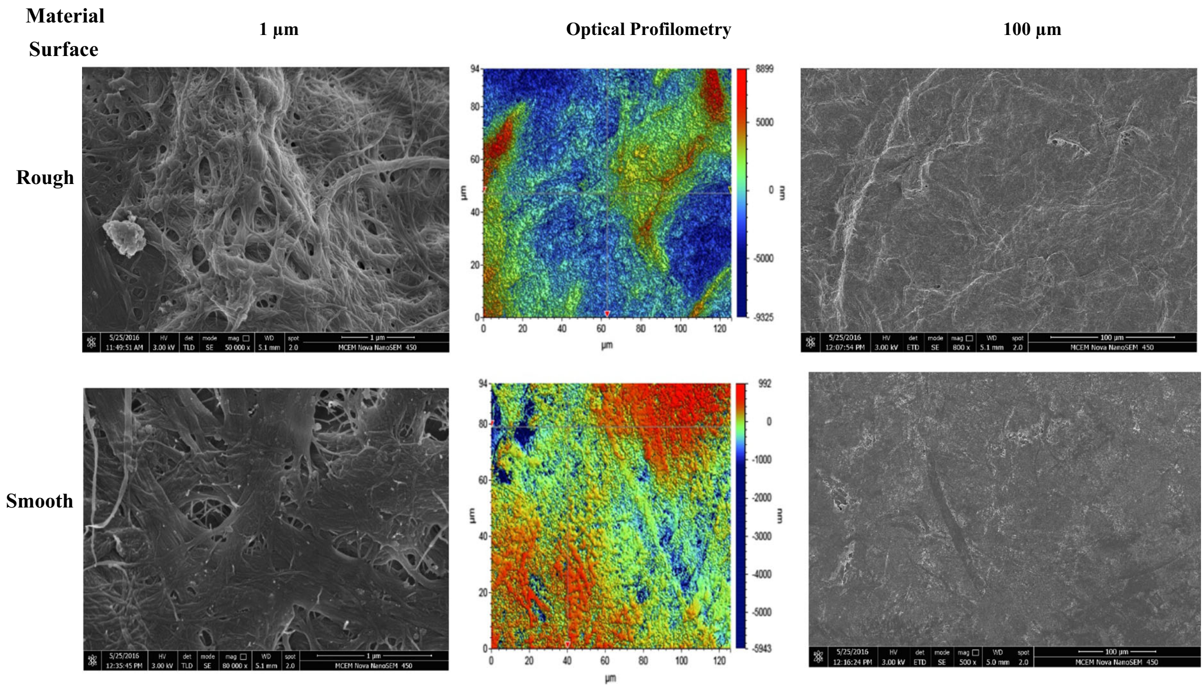


Fig. 5 SEM image of the sprayed NC film—rough and smooth surface and optical profilometry image of both sides of the NC film

a basis weight ranging from 53 to 193 g/m^2. The basis weight of the NC film was readily controlled by the concentration of nanocellulose suspension sprayed.

In our investigation of spraying, the processing time was 50.2 s to spray 15.9 cm diameter films, independent of the basis weight from 53 to 193 g/m^2. The quickest time reported in the literature for sheet/film formation with filtration was from work in our group (Varanasi and Batchelor 2013), where 2.8 min was required for filtering a low basis weight of 56.4 g/m^2, formed from 0.6 wt% suspension. In contrast, the 95.1 g/m^2 film formed at 0.2 wt%, made for the work in this paper, took 15 min to filter.

When the mechanical properties of the spray-coated and vacuum filtered films were compared, it was found that they were the same within the uncertainties. The tensile index of a 104.03 g/m^2 of film prepared via vacuum filtration was 62.3 $\pm$ 3.4 Nm/g while the tensile strength of the 100.5 g/m^2 of spray coated nanocellulose film was 60.2 $\pm$ 1.5 Nm/g. The tensile stiffness values were also the same within uncertainties at 946 $\pm$ 86 and 941 $\pm$ 78 kN/m, for the spray coated film and film prepared via vacuum filtration, respectively. The uncertainties give the 95% confidence interval. It is interesting to note that the tensile index of the 100 g/m^2 sheet prepared vacuum filtration is somewhat lower than 60 g/m^2 sheet made via vacuum filtration or spray coating/filtration of 72 Nm/g (Varanasi and Batchelor 2014) and 79 Nm/g (Beneventi et al. 2015), respectively. The air permeance of both the spray coated and vacuum filtered films were less than the measurement limit of the instrument of 0.003 μm/Pa s. This value confirms that the spray coated sheet is highly impermeable.

The current spray coating method is innovative because it allows the production of flat films with uniform thickness. These films require less operator time to produce than films prepared either by filtration or spraying onto porous media (Beneventi et al. 2014) and can be prepared without cracking unlike the moulded structures produced by Magnusson (2016). In addition, in contrast to Obara and McGinity (1994) we have created a cellulose film with one very smooth surface without regenerating or in any way chemically treating or modifying the cellulose.

After filtering, the nanocellulose films can often be difficult to separate from the filter, taking additional time to complete the transfer to the blotting paper without destroying the film. Drying the filtered film then requires repeatedly manually feeding the film into a rotating drum dryer until dry, with the overall process taking at least 10 min from the start of filtration. In the spray coating method, the drying time for nano cellulose films in ambient conditions is from 24 to 48 h, which is reduced to 30–60 min when drying in an oven at 105 °C. While the total time to prepare and dry a film is longer with spray coating onto a stainless steel plate, the key strength of the method is the reduction in operator time. Leaving aside, the preparation of the nanocellulose suspension, which is common for the two methods, preparing ten 100 g/m^2 sheets requires less than 9 min of operator time with spraying compared to 220 total minutes with filtration.

Conclusion

We have developed a method of spraying a nanocellulose suspension onto a polished stainless steel plate to rapidly make smooth films with a basis weight ranging from 50 to 200 g/m^2, simply by adjusting the suspension consistency. This method greatly reduces the operator time to produce nanocellulose films. Further, spray-coating on to stainless steel creates a two-sided film structure with a very smooth surface in contact with the stainless steel plate.

Supporting information

SEM image of spray coated NC film; AFM image of Spray coated NC film and film prepared via vacuum filtration; Data set for thickness mapping; Optical prolifometry image of NC film prepared via vacuum filtration.

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References

Abitbol T, Rivkin A, Cao Y, Nevo Y, Abraham E, Ben-Shalom T et al (2016) Nanocellulose, a tiny fiber with huge applications. Curr Opin Biotechnol 39:76–88. doi:10.1016/j.copbio.2016.01.002

Beneventi D, Chaussy D, Curtil D, Zolin L, Gerbaldi C, Penazzi N (2014) Highly porous paper loading with microfibrillated cellulose by spray coating on wet substrates. Ind Eng Chem Res 53(27):10982–10989. doi:10.1021/ie500955x

Beneventi D, Zeno E, Chaussy D (2015) Rapid nanopaper production by spray deposition of concentrated microfibrillated cellulose slurries. Ind Crops Prod 72:200–205. doi:10.1016/j.indcrop.2014.11.023

Chinga-Carrasco G, Tobjörk D, Österbacka R (2012) Inkjet-printed silver nanoparticles on nano-engineered cellulose films for electrically conducting structures and organic transistors: concept and challenges. J Nanopart Res 14(11):1–10. doi:10.1007/s11051-012-1213-x

Huang L, Chen X, Nguyen TX, Tang H, Zhang L, Yang G (2013) Nano-cellulose 3D-networks as controlled-release drug carriers. J Mater Chem B 1(23):2976–2984. doi:10.1039/C3TB20149J

Koga H, Tokunaga E, Hidaka M, Umemura Y, Saito T, Isogai A, Kitaoka T (2010) Topochemical synthesis and catalysis of metal nanoparticles exposed on crystalline cellulose nanofibers. Chem Commun 46(45):8567–8569. doi:10.1039/C0CC02754E

Krol LF, Beneventi D, Alloin F, Chaussy D (2015) Microfibrillated cellulose-SiO_2 composite nanopapers produced by spray deposition. J Mater Sci 50(11):4095–4103. doi:10.1007/s10853-015-8965-5

Magnusson J (2016) Method for spraying of free standing 3D structures with MFC. Master Thesis, Karlstad University

Metreveli G, Wågberg L, Emmoth E, Belák S, Strømme M, Mihranyan A (2014) A size-exclusion nanocellulose filter paper for virus removal. Adv Healthc Mater 3(10):1546–1550. doi:10.1002/adhm.201300641

Nogi M, Iwamoto S, Nakagaito AN, Yano H (2009) Optically transparent nanofiber paper. Adv Mater 21(16):1595–1598. doi:10.1002/adma.200803174

Obara S, McGinity JW (1994) Properties of free films prepared from aqueous polymers by a spraying technique. Pharm Res 11(11):1562–1567. doi:10.1023/a:1018949502392

Orelma H, Filpponen I, Johansson L-S, Österberg M, Rojas OJ, Laine J (2012) Surface functionalized nanofibrillar cellulose (NFC) film as a platform for immunoassays and diagnostics. Biointerphases 7(1):61. doi:10.1007/s13758-012-0061-7

Shimizu M, Saito T, Fukuzumi H, Isogai A (2014) Hydrophobic, ductile, and transparent nanocellulose films with quaternary alkylammonium carboxylates on nanofibril surfaces. Biomacromol 15(11):4320–4325. doi:10.1021/bm501329v

Varanasi S, Batchelor WJ (2013) Rapid preparation of cellulose nanofibre sheet. Cellulose 20(1):211–215. doi:10.1007/s10570-012-9794-1

Varanasi S, Batchelor W (2014) Superior non-woven sheet forming characteristics of low-density cationic polymercellulose nanofibre colloids. Cellulose 21(5):3541–3550. doi:10.1007/s10570-014-0370-8

Varanasi S, Low Z-X, Batchelor W (2015) Cellulose nanofibre composite membranes—biodegradable and recyclable UF membranes. Chem Eng J 265:138–146. doi:10.1016/j.cej.2014.11.085

Zhang L, Batchelor W, Varanasi S, Tsuzuki T, Wang X (2012) Effect of cellulose nanofiber dimensions on sheet forming through filtration. Cellulose 19(2):561–574. doi:10.1007/s10570-011-9641-9

Zolin L (ed) (2017) Electrode preparation exploiting the spray coating technique. In: Large-scale production of paper-based Li-ion cells. Springer International Publishing, Cham, pp 77–94. doi:10.1007/978-3-319-39016-1_6