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ORIGINAL PAPER

# Flexible spray coating process for smooth nanocellulose film production

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**Abstract** A novel rapid method for high throughput production of smooth nanocellulose (NC) films by spray coating was communicated recently. In this method, we employed spray coating to produce wet films on stainless steel plates moving on a conveyor, forming free-standing films with interesting structural, mechanical and surface properties upon drying. In this research, we investigate the range of mechanical and physical properties of nanocellulose films prepared by spraying. Furthermore, a comparison with NC films prepared via conventional vacuum filtration was conducted to evaluate the suitability of this method as an alternative film preparation process. One set of experiments was completed where the solids concentration of the suspension was fixed at 1.5 wt% and the conveyor velocity was varied, while two series of experiments were completed where the solids concentration of the suspension was varied and the conveyor speed was fixed at either 0.32 or 1.05 cm/s. By varying speed and solids concentration, spray-coating was found to allow efficient production of films with basis weights ranging from 38 to 187 g/m$^2$, with film thicknesses ranging from 58.4 to 243.2 µm, respectively. There was a universal linear relationship between the thickness and basis weight, independent of the process conditions. The optical uniformity of film was also noticeably dependent on the spraying process. The optical uniformity index of films, relative to vacuum filtered films, increased with conveyor speed at 1.5 wt% solids concentration and was independent of solids concentration at low speed. Forming at the higher speed of 1.05 cm/s produced a maximum in optical uniformity in the range 1.5–1.75%, with these films being more uniform than conventional films produced through vacuum filtration. The most uniform films produced by spraying also had a similar tensile index to films made via vacuum filtration. With an understanding of these parameters and effects, we demonstrate this method to be a more time efficient alternative method to produce uniform films where the properties can be tailored to the required application.

**Keywords** Spray coating · Nanocellulose · Nanocellulose film · Optical uniformity · Strength

**Electronic supplementary material** The online version of this article (https://doi.org/10.1007/s10570-018-1677-7) contains supplementary material, which is available to authorized users.

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## Introduction

Throughout the past decade, there has been notable growth in the use of micro fibrillated cellulose/nanocellulose films as sustainable substrates for the development of a variety of functional materials (Abitbol et al. 2016). The literature on this topic has confirmed the applicability of nanocellulose films for nanocomposites, anti-microbial films and barrier materials (Dufresne 2013) among others. Films made from nanocellulose are strong and show good oxygen barrier properties; they also have the capacity for a broad range of chemical modifications which can attain varied and desirable properties. Additionally, this material is biodegradable, renewable, non-toxic and readily available in large quantities (Klemm et al. 2011).

Nanocellulose films are commonly prepared using either vacuum filtration, whereby fibre suspensions are filtered using a mesh filter and fibres gather in the form of a film, or casting, where the suspension is poured onto a surface and left to dry. Casting is a very time-consuming process as it typically requires three days for drying and can cause wrinkling of the film which is difficult to control (Shimizu et al. 2014). It is another laboratory method used for producing nanocellulose film (Rebouillat and Pla 2013). The strength of cast nanocellulose films is lower than that of films prepared using vacuum filtration method, which is a conventional process in paper-making industries (Sehaqui et al. 2010). Vacuum filtration is quicker than casting, however, time consumption is still significant (Siró and Plackett 2010). There are also difficulties in separating the film from the filter mesh and subsequent handling before final drying.

Modifications have improved filtration by increasing the solids content above the gel-point to reduce filtration time, increasing the size of the filter openings to reduce filter resistance and by using polyelectrolytes (Varanasi and Batchelor 2014). Laboratory film preparation time for light weight films less than 60 g/m$^2$ has been reduced from 3 or 4 h (Nogi et al. 2009) to 10 min (Varanasi and Batchelor 2013; Zhang et al. 2012). Despite these modifications, there are still significant issues as larger filter openings can result in a loss of material rendering it difficult to control the basis weight of the product and decreasing yield. Vacuum filtration processes reported in literature require a film preparation time ranging from 45 min to 3–4 h (Nogi et al. 2009) when finer filters are used. In addition, bulky cellulose film preparation via vacuum filtration is challenging; dewatering time increases exponentially with increased basis weight leading to high operation and labour costs. As such, the range of film basis weights that can be manufactured is limited.

Recently spraying nanocellulose (NC) has emerged as a viable alternative method of NC film preparation (Beneventi et al. 2014, 2015), while a rapid laboratory scale method for spray coating of NC suspension on a polished stainless steel (SS) plates to create free-standing recyclable films has been reported. Spray coating results in a very uniform deposition layer of nanocellulose on the base surface; the amount of NC increases with an increase in the suspension concentration or decrease in the velocity of the conveyor. Most significantly, spraying can substantially decrease operating time (Shanmugam et al. 2017).

The present work investigates the effects of process variables on the properties of free-standing NC films prepared by spraying on stainless steel plates. The effects of conveyor velocity, NC suspension concentration and setup configuration are evaluated. The properties of spray coated films are compared with films prepared via vacuum filtration and the effects of process parameters on these properties are quantified. The spraying of nanocellulose on the base surface is hypothesized to produce a stable and uniform distribution of nanocellulose, leading to free-standing films of high optical uniformity. Obtaining quantifiable relationships between process parameters and product properties will allow for tuning product properties such as uniformity and designing processes for desired products.

## Experimental method

### Materials

Micro-fibrillated cellulose, also commonly referred to as Nanocellulose in this paper was used for film preparation. Both spray coating and the conventional vacuum filtration methods were employed. From here on, Nanocellulose will be referred to as NC; nanocellulose films prepared by vacuum filtration, VF-NC; and Spray coated films, SC–NC. NC was supplied from DAICEL Chemical Industries Limited (Celish

KY-100S) with an initial concentration of 25 wt% cellulose fibres. DAICEL NC has fibrils with an average diameter of ~ 70 nm with a wide distribution of fibril diameter, mean length of fibre around 8 μm and an average aspect ratio of 142 ± 28. The crystallinity of the NC sample was measured as 78% (Raj et al. 2016). NC was diluted to the concentration ranges from 1.00 to 2.50 wt% and disintegrated in a Messmer disintegrator Model MK III C for 15,000 revolutions at 3000 RPM. The viscosity of the NC suspension was evaluated by the flow cup method, i.e. measuring coating fluid flow through an orifice as a relative measure of kinematic viscosity expressed in seconds of flow time in DIN-Sec.

### Spray coating

NC suspension was sprayed onto stainless steel plates using Wagner spray system (Model number 117). The experimental set up for spray coating is shown in Fig. 1. It is mainly consisting of variable speed conveyor and pressure driven spray system with a knob for adjusting/controlling pressure. The spraying of nanocellulose is performed on two different geometries like square stainless steel square plate (220 mm × 220 mm) and circular plate (Diameter—159 mm). Experiments were conducted in 3 series.

In experimental series 1, the spray jet angle was 50° and the spray width was 30 cm at a spray distance and pressure of 200 bar, respectively. Suspension concentration was kept constant at 1.5 wt% and conveyor speed was varied from 0.25 to 0.59 cm/s. 30 s time was allowed for pressure driven spray system to reach steady state. (Shanmugam et al. 2017).

In experimental series 2, the spray system setup was similar to series 1; however, the conveyor speed was kept constant at 0.32 cm/s and suspension concentration was varied from 1 to 2 wt%.

In experimental series 3, the conveyor system was changed, as was spray nozzle to attain a jet angle of 30° and beam width of 22.5 cm at a spray distance of 50.0 ± 1.0 cm and 100 bar pressure. The conveyor speed was kept constant at 1.05 cm/s and suspension concentration varied from 1.5 to 2.5 wt%.

After spraying, each film was dried on its plate for 24–48 h at ambient conditions, and subsequently removed from the plate and stored at 23 °C and 50% RH before testing.

### Vacuum filtration

NC films were prepared using vacuum filtration as reported previously (Varanasi and Batchelor 2013). In brief, NC suspension with 0.2 wt% concentration was poured into a cylindrical container with 125 mesh at

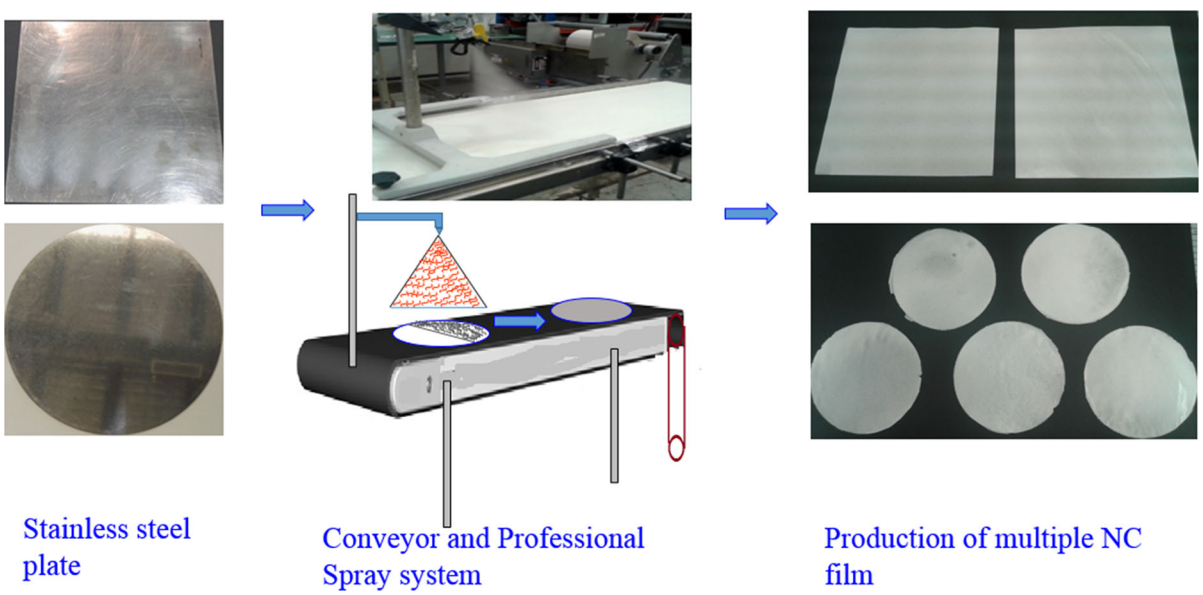


**Fig. 1** An experimental setup for spraying NC suspension on a stainless steel plate to make multiple films

the bottom and filtered, forming a wet film on the mesh. After couching, the wet film was carefully separated using blotting papers, wet pressed at 0.4 MPa by sheet press (Type 5-1, AB Lorentzen & Wettre) for 7 min and drum dried at 105 °C. The drying of the film took up to 10 min. The film prepared by this method is used as a standard reference film to compare the optical uniformity and strength of the spray coated film.

## Characterization of the NC films

### Basis weight of NC films

The basis weight was evaluated by weighing a standard area of the film after 4 h drying in the oven at a temperature of 105 °C.

### Thickness of NC films

The thickness of the spray coated films was determined using a Thickness Tester Type 21 from Lorentzen & Wettre AB, Stockholm, Sweden. The thickness was measured for at least 36 points on each of the spray coated and vacuum filtered NC films and averaged. The thickness of NC film was measured according to Australian/New Zealand standard method 426.

### Apparent density

The apparent density of the NC films was evaluated through dividing basis weight by mean thickness of the film and followed Australian/New Zealand standard method 208.

### Tensile strength

An Instron model 5566 was used to measure the tensile strength of the NC films. The tensile strength test samples were 100 mm in length and 15 mm width. The samples of NC films are equilibrated and conditioned for at least 24 h at 23 °C and 50% RH before dry tensile testing based on the Australian/New Zealand Standard Methods 448 and 437 s. All thickness and tensile tests were done at 23 °C and 50% RH. The samples were tested at a constant rate of elongation of 10 mm/min. The Tensile Index (TI) of the samples was calculated from the tensile strength (expressed in $Nm^{-1}$) divided by basis weight ($gm^{-2}$). The mean value was obtained from six to seven valid tests and the error bars in plots indicate standard deviation. The elastic modulus was calculated from the maximum slope in the stress–strain curve determined by the software.

### Surface investigation

The surface morphology and topography was studied using Scanning Electron Microscopy of iridium coated NC-films. Images were sampled at magnifications of 500× to 50,000× in secondary electron mode-II of FEI Novo SEM 450 for Spray Coated NC film and FEI Magellan 400 FEGSEM for NC film prepared via vacuum filtration. The surface roughness of NC films were evaluated by the Parker print surface roughness tester (M590, Testing machines Inc), Atomic force microscopy (JPK Nanowizard 3) and optical profilometry (Bruker Contour GT-I).

### Formation analysis

The optical uniformity of NC film was measured by the Paper Perfect Formation (PPF) tester (Op Test Equipment Inc, Canada), which measures the optical uniformity of light transmitted through the sample. In brief, the PPF consists of a black and white camera based image analyser and uses a CCD camera interfaced with 256 gray levels and 65 μm/pixel resolution. The analyser uses a diffuse quartz halogen light source with IR filters and automatic intensity control. The PPF classifies formation quality over 10 length scales ranging from 0.5 to 60 mm. The data reported here is the Relative Formation Value (RFV) of each component relative to one of the films made by vacuum filtration, which was used as a reference film. Three to six films were measured for each condition, with the results averaged. RFV value less than 1 means that the optical uniformity of the NC film tested is worse than the reference film at that length scale.

## Results

The operational range of the conveyor's velocity, from 0.25 to 0.59 cm/s, was studied in series 2 of SC–NC experiments where the effects of velocity were studied

and suspension concentration was kept constant at 1.5 wt%. Within these bounds, basis weight ranged from 49.1 ± 5.4 to 102.2 ± 7.5 g/m$^2$ and thickness ranged from 70. 5 ± 2.9 to 130.3 ± 11.3 µm. Figure 2 shows the results for Series 2. At low velocity from 0.37 to 0.25 cm/s, the basis weight of the film is relatively constant at ∼ 100 ± 3 g/m$^2$ for 1.5 wt% consistency, representing a limit to the amount of suspension that remains on the plate after spraying. The plateau in film basis weight with reducing speed indicates that the carrying capacity of the plate has been reached and that excess material is likely to be flowing off the plate. Interestingly no such flow is observable in the films after they have dried, either in the thickness profiles reported in our previous paper (Shanmugam et al. 2017) or, as will be discussed later, in the transmitted light images captured to measure optical uniformity. The most likely explanation is that the fluid on the plate has levelled while the plate is held stationary as the film dried.

Beyond 0.37 cm/s, the basis weight of the film decreases as velocity increases in inverse proportions. In other words, less NC is deposited on the stainless steel when moving at a faster speed, resulting in the formation of a low basis weight NC film due to low suspension consistency of the NC.

The basis weight and thickness of NC films are controlled by the velocity of the conveyor and the consistency of the suspension. Assuming constant flow output of the spray system and positive displacement pump, it may be assumed that deposited mass per unit time would have a positive linear relation with suspension consistency, $C_0$. From the spray system manual, the spray flow is estimated to be 1.00 L/min or $\dot{m} = 17 \times 10^{-3}$ kg/s, assuming a suspension density of 1000 kg/m$^3$. If the film width is $w$, the mass consistency is $C_0$ (kg fibre/kg of suspension) and the conveyor velocity is $\upsilon$ then the film basis weight, $B$, is given by the Eq. (1).

$$B = \eta \frac{C_0}{\upsilon} \frac{\dot{m}}{w} \tag{1}$$

where $\eta$ is an efficiency factor, which includes losses from spraying over the width of the plate, suspension flow and any reduction in flow as suspension viscosity increases.

Figure 3 shows data for three series of experiments of SC–NC demonstrating basis weight as a function of $C_0/v$. It can be seen that in series 3, the optimized configuration shows a higher value for $x$, representing a higher efficiency in the process, which is the result of decreased pressure, change of nozzle and change in setup configuration. The negative values for the y-intercept represent losses of constant value, such as aerosol loss of material. It should be noted that in calculation of trend line for series 2, values below conveyor velocity of 0.38 cm/s were not considered. From Fig. 2, it was inferred that maximum deposition is reached at 0.38 cm/s and lowering velocity further results in any additional material flowing off the steel plates.

When the results for thickness are plotted in Fig. 4, it can be seen that there is a linear relation between thickness and basis weight of films. This relationship

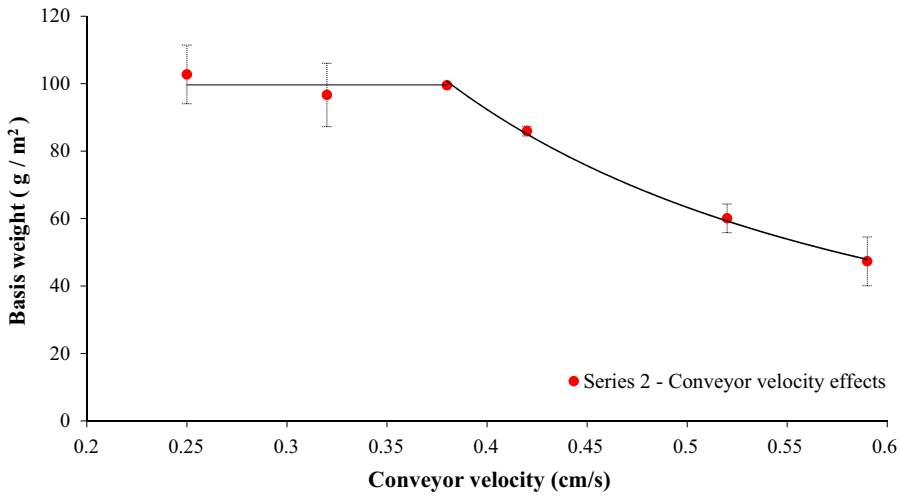


**Fig. 2** Influence of the conveyor velocity on the basis weight of SC–NC

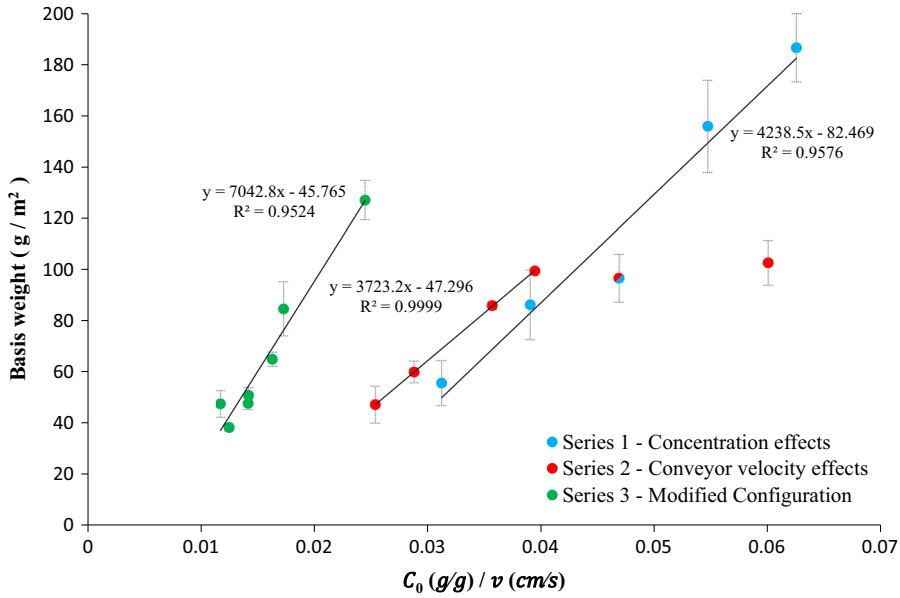


**Fig. 3** Basis weight as proportional to $\frac{c_0(g/g)}{v(cm/s)}$

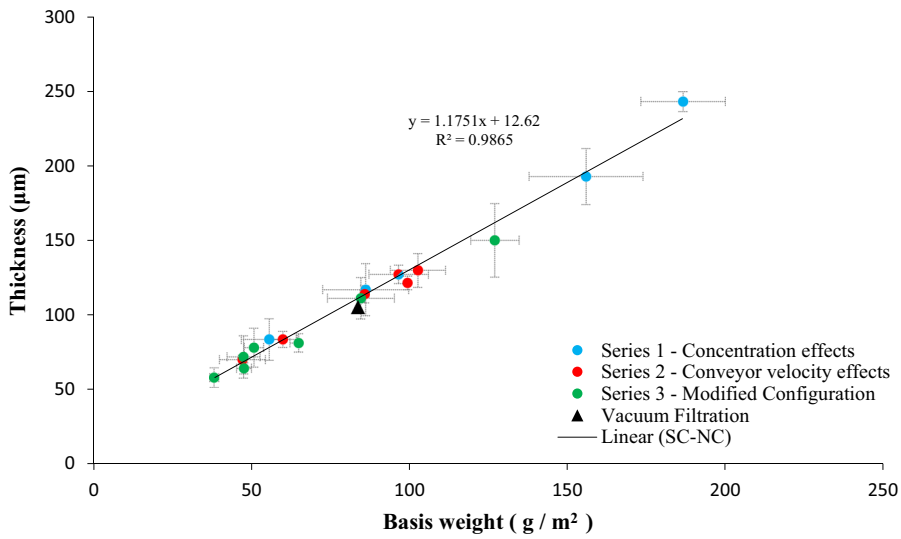


**Fig. 4** Effect of NC suspension concentration and velocity of conveyor on Basis weight and thickness of spray coated NC film

is maintained irrespective of configuration and process parameter changes.

The basis weight and thickness of the NC film can be tailored by two parameters, namely NC concentration and conveyor velocity. Though both can be varied independently, the relationship between thickness and basis weight is a characteristic of these SC–NC films. The figures show that the thickness of VF-NC also lies on the same trend line, irrespective of the fundamentally different production procedure. To calculate the error bars for thickness, all the values measured for a given film were averaged. The average values for the set of films was then used to calculate the overall average shown here, with error bars calculated as the standard deviation of these film averages. The basis weight was only measured once for each film.

The apparent density of films was calculated based on the basis weight and mean thickness of NC films. Figure 5 shows the apparent density as a function of basis weight. It can be seen that for films of basis weight around or higher than 100 g/m$^2$, apparent density is constant. However, for lower basis weights,

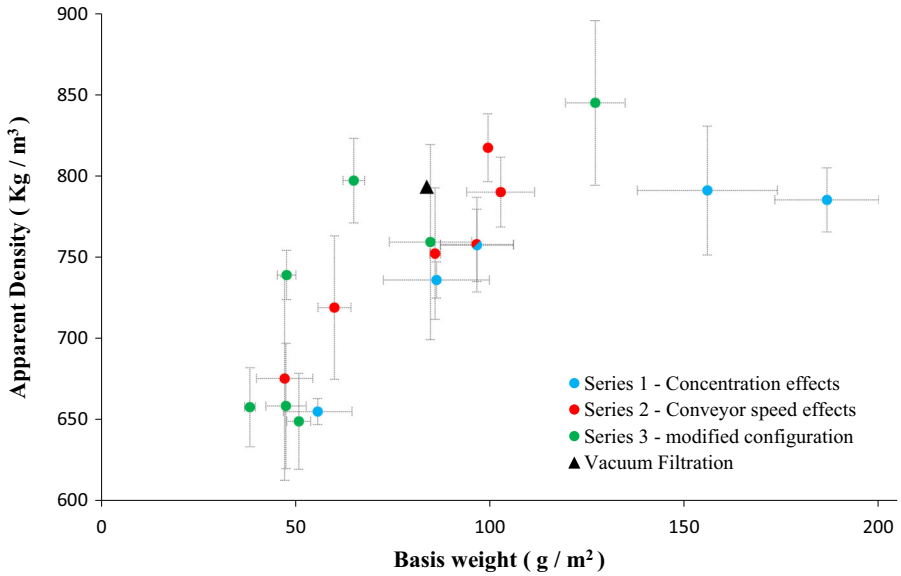


**Fig. 5** Relationship between apparent density and basis weight of the films

apparent density is lower demonstrating the effects of agglomerates and surface non-uniformity fibre clumps which become more significant as basis weight is decreased. This is also reflected by the non-zero y-intercept in Fig. 4.

The apparent densities of SC–NC close to 100 g/m$^2$, (99.5 ± 0.1, 102.7 ± 8.7 g/m$^2$) are 817.2 ± 20.9 and 789.9 ± 21.5 kg/m$^3$ respectively. Measurements for VF-NC films of 100 g/m$^2$ were found to be 822.5 ± 14.6 kg/m$^3$, within the same range and comparable to SC–NC considering the uncertainties.

## Optical uniformity

Within the operational range of the conveyor and spray system, the effects of both velocity and suspension concentration were studied. These parameters were found to distinctly affect the optical uniformity of the films obtained. The optical uniformity of nanocellulose films were quantified at different length scales and analysed with the relative values defined using one of the VF-NC films as a reference. To simplify the presentation, the results are presented as firstly the average of all inspection zone sizes smaller than 1.8 mm and secondly of all inspection zone sizes between 1.8 and 12 mm. It should be noted that some spray coated films contain air bubbles and visible ripples, as can be observed in Figs. 10 and 11. These reduce the measured optical uniformity, although the contribution of bubbles and ripples, in comparison to flocculation driven non-uniformity, is hard to quantify. Our major interest here is to use the measurement to identify the experimental conditions where the optical uniformity is equivalent to or better than the films formed through vacuum filtration. The uniformity of the smaller components of formation of the film tends to strongly influence the print quality while larger components of the film influence its strength.

Figures 6 and 7 show the optical uniformity of SC–NC films, at large and small inspection zones, respectively, as a function of conveyor velocity at 1.5 wt% suspension concentration. Detailed graphs can be found in the supplementary information.

The results show that as conveyor velocity increases, the films obtained are more uniform in both larger and smaller component sizes. The relative optical uniformity of all SC–NC is higher for smaller components than for larger components.

Figures 8 and 9 show the optical uniformity of SC–NC films as a function of suspension concentration at their respective constant velocities (0.32 m/s for series 2 and 1.05 cm/s for series 3), detailed graphs can be found in the supplementary information.

With increasing suspension concentration, an increased amount of agglomerated fibres is expected which would lead to lower optical uniformity. However, a thicker film with higher basis weight is obtained at higher concentrations leading to more overlapped fibres and higher optical uniformity. This compound effect determines the variation in optical

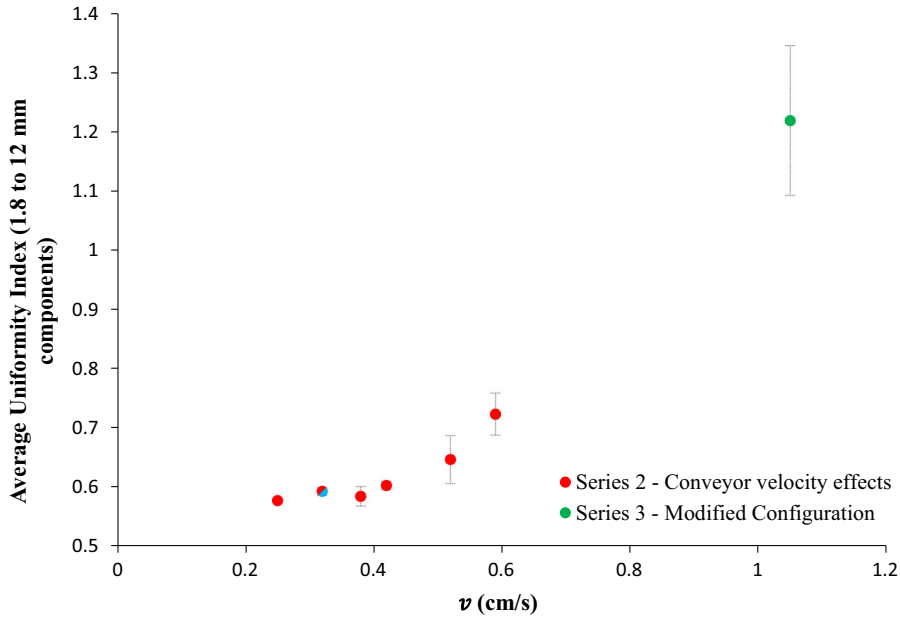


**Fig. 6** Average Optical Uniformity Index of larger components (1.8–12 mm) as a function of conveyor velocity with vacuum filtered film as reference

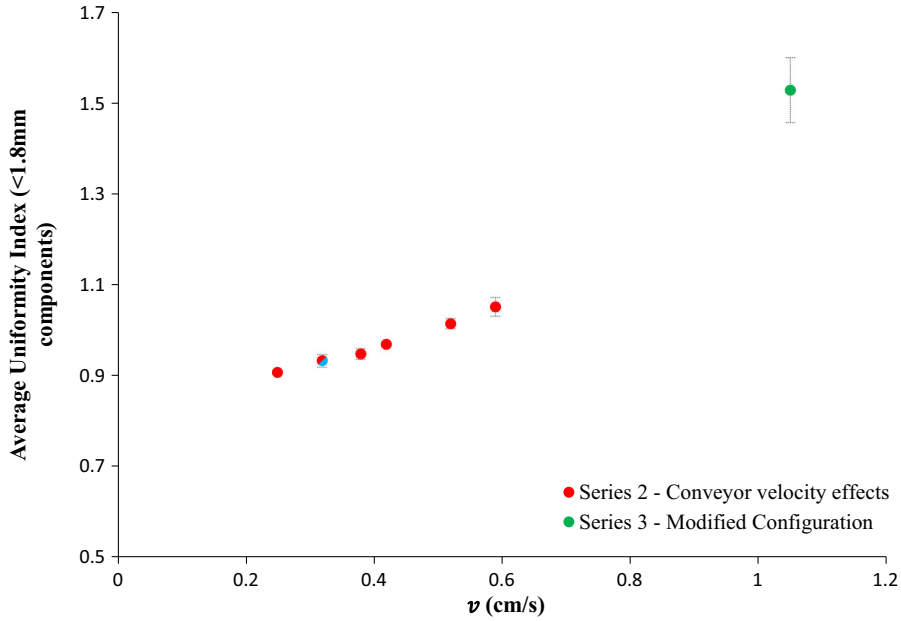


**Fig. 7** Average Optical Uniformity Index of smaller components (< 1.8 mm) as a function of conveyor velocity with vacuum filtered film as reference

uniformity as a function of concentration. Figure 8 shows that at a constant velocity of 0.32 cm/s, higher optical uniformity in larger components is observed with increasing suspension concentration. This trend seems to be less pronounced for smaller components in Fig. 9.

One of the vacuum filtered NC films was used as a reference for all the Paper Perfect Formation comparisons and all data were normalised by the reference film value at each length scale. The values for the vacuum filtered films in Figs. 6, 7, 8, and 9 are all close to but not equal to 1.0 as the complete set of data for all vacuum filtered films was averaged, including the one reference NC film.

Results for series 3 show no universal trend in optical uniformity with the change of concentration,

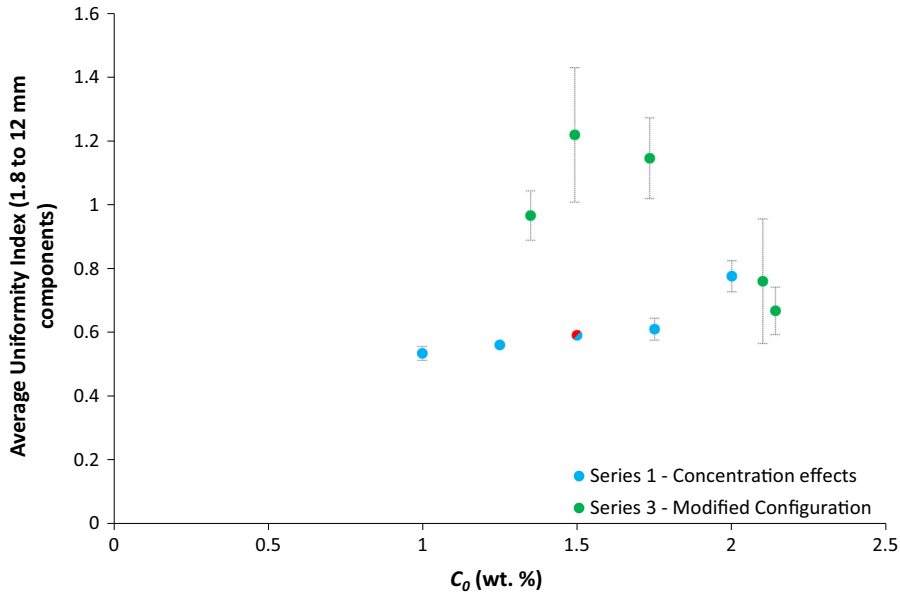


**Fig. 8** Average Optical Uniformity Index of larger components (1.8–12 mm) as a function of suspension concentration with vacuum filtered film as reference

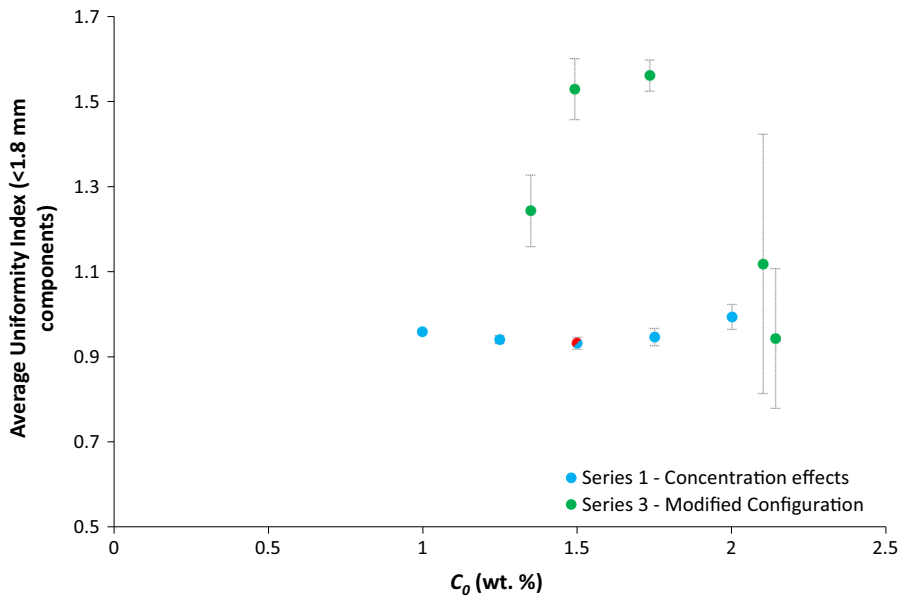


**Fig. 9** Average Optical Uniformity Index of smaller components (< 1.8 mm) as a function of suspension concentration with vacuum filtered film as reference

however, it is noteworthy that these films made at an increased velocity of 1.05 cm/s show higher uniformities in general. This was also demonstrated in Figs. 6 and 7. It is shown that to attain constant basis weight films, operating at higher velocities and higher suspension concentration creates more uniform films across all component sizes.

With the modified configuration operating at a higher conveyor velocity in series 3, the range of uniformities is as high as and above that of the VF-NC film; the spray coated NC film no longer visually shows the presence of non-uniformities and contains pinholes, whereas these could be observed for series 1 and series 2 experiments.

Figures 10 and 11 shows the images captured by the Paper Perfect Tester of NC films prepared via spray coating and vacuum filtration. Each image was recorded of an area of 6.75 cm × 6.75 cm. The optical uniformity of formed NC film worsened upon decreasing suspension concentration and the velocity

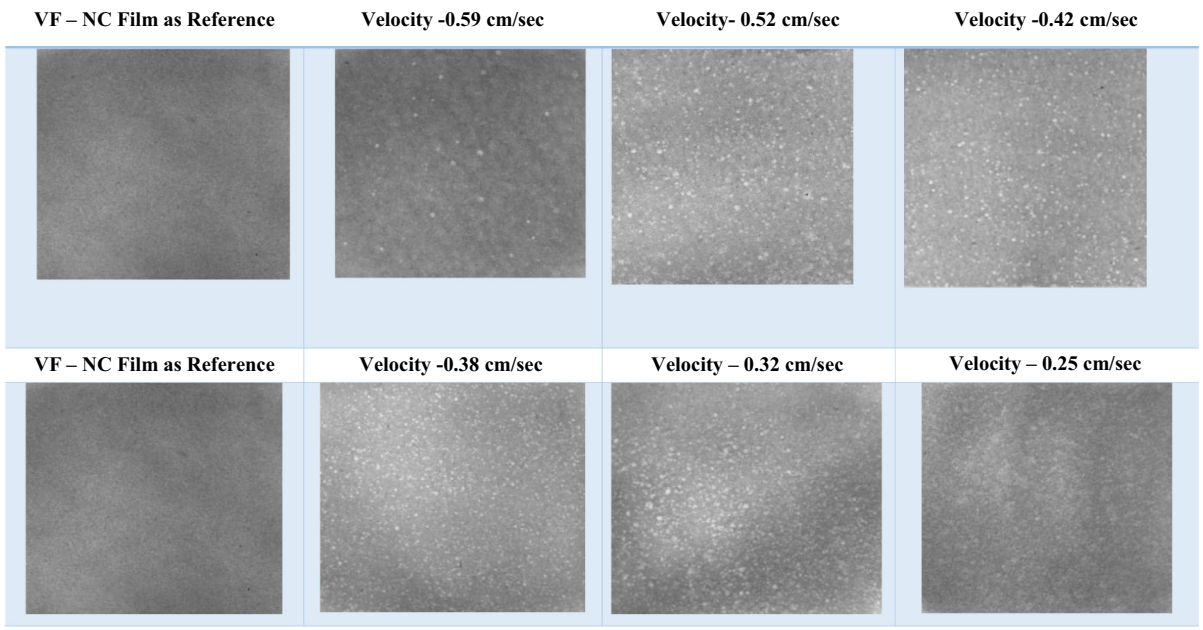


**Fig. 10** Paper formation test for Nanocellulose films prepared spray coating at a different velocity (series 2)

of the conveyor, especially at larger components around 5 mm. Additionally, the 1% wt. NC spray coated film has ripples in the film while the surface of the film remains smooth. The ripples are formed by the transverse flow of the 1% wt suspension NC on the stainless steel plate after the spray impacts the surface. This problem was overcome by increasing the suspension concentration.

It can also be seen that apart from the ripples at low solids concentration, there is no evidence of fluid flow during the forming process, even though the plateau in film basis weight with decreasing velocity, shown in Fig. 2, strongly suggests that such flow must be occurring. As we previously mentioned, the most likely explanation for the apparent discrepancy is that the fluid film on the plate has levelled while the plate is held stationary during drying.

Figure 12 shows the spray coated film prepared via modified configuration and the films are free from glossy points and surface irregularities. Figures 1, 2, and 3 in the supplementary information reveal the relative formation value of each component of spray coated NC films prepared via adjusting NC concentration and velocity of the conveyor and relative to the NC film prepared via vacuum filtration. RFV value of NC film from series 1 is mostly lower than 1 and the NC film made 1.75 wt% is higher than 1 confirming good optical uniformity and formation quality in the film.

## Mechanical properties

The mechanical properties of NC films were investigated by tensile strength testing. Figure 13 shows the tensile index of SC–NC as a function of basis weight and error bars concluding the standard deviation of six films. The actual Load Vs Strain curves of the spray coated films are available in the supplementary information. It can be seen that there is some indication that for series 2, a higher tensile index of a film is associated with a higher basis weight. However, considering standard deviation of measurements, no statistically meaningful difference can be inferred between series 1 and series 2. It can be seen that the SC–NC films from series 3, using the higher spraying efficiency configuration, show somewhat higher tensile strengths, with values equivalent to VF-NC. This is probably due to the higher optical uniformity of these films compared to the series 1 and series 2 films.

Higher basis weight films are significantly more rigid. This was investigated by evaluating the relationships between stress and strain, represented in Figure 14 as Elasticity (E-modulus). The relationship

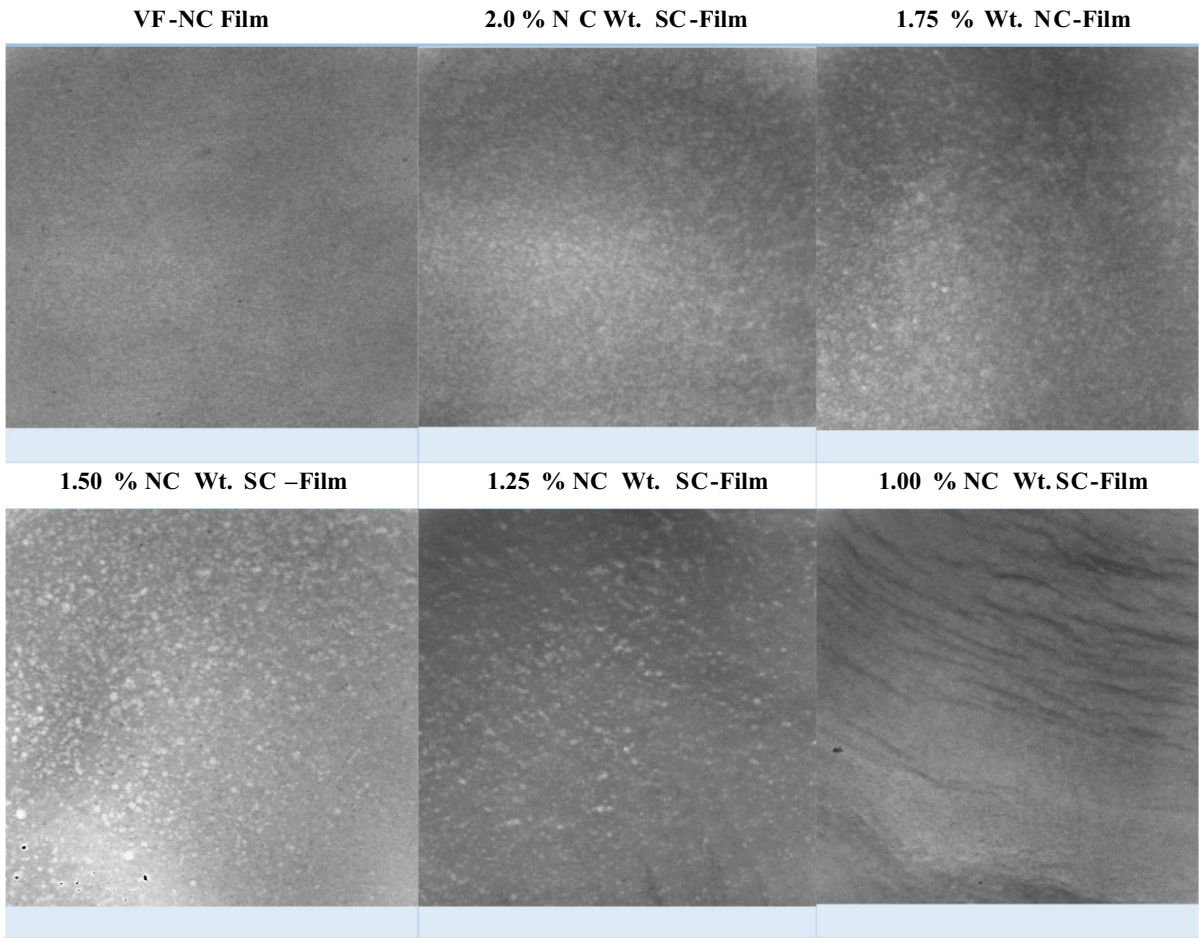


**Fig. 11** Paper formation test for NC-film prepared via spraying different NC concentration (Series 1)

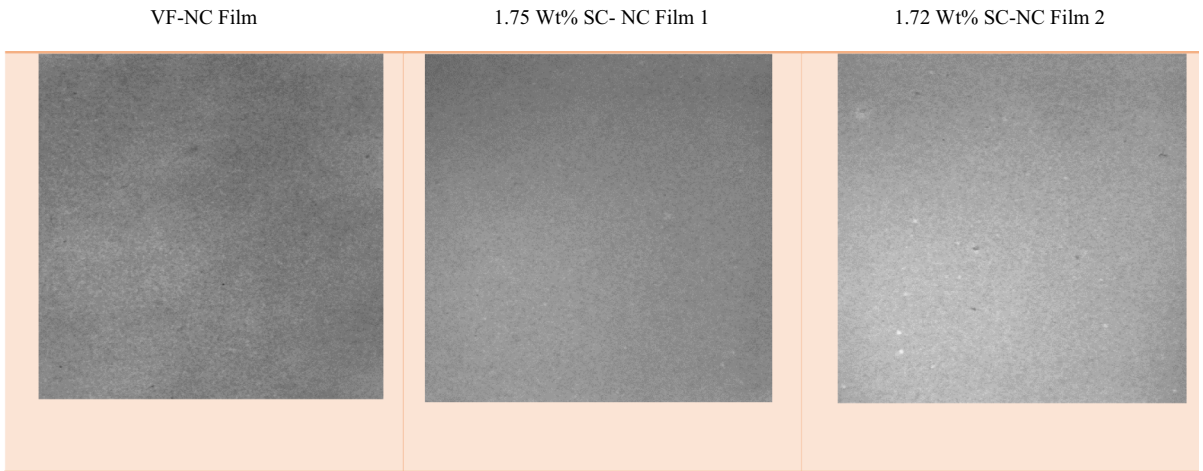


**Fig. 12** Paper formation test for spray coated NC film prepared via modified configuration (Series 3)

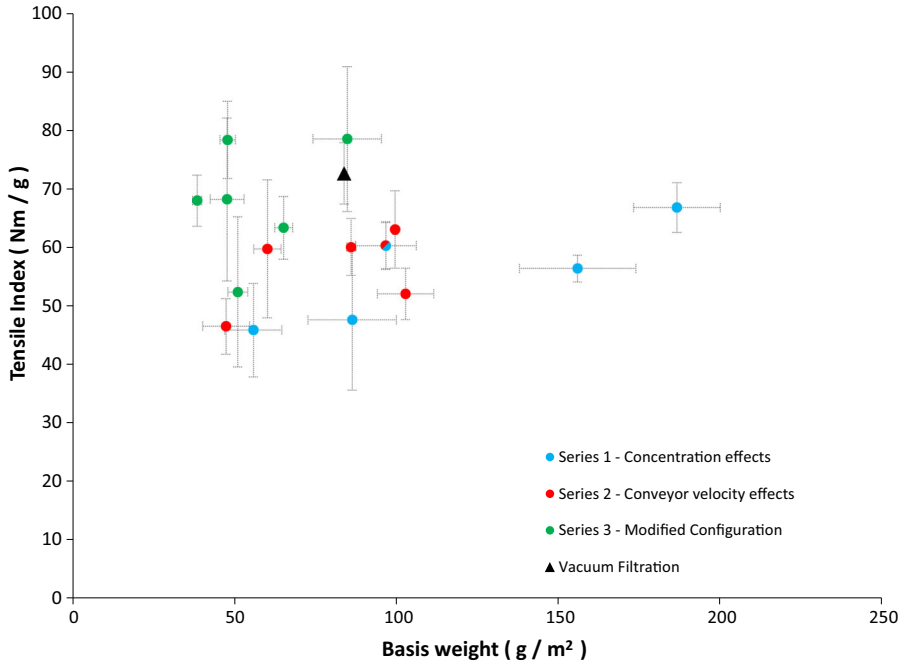


**Fig. 13** Tensile Index of NC films as a function of basis weight

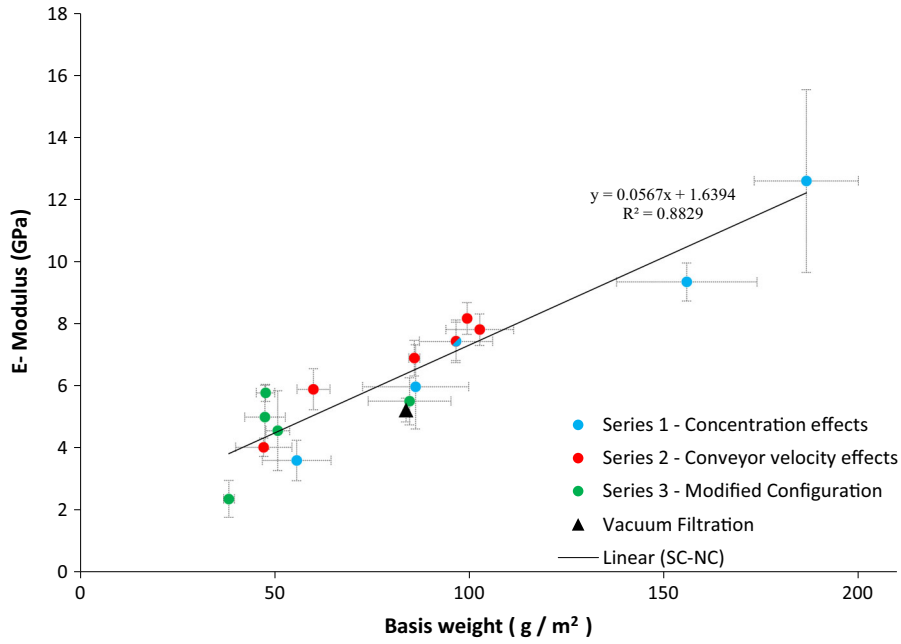


**Fig. 14** Elastic modulus of NC films as a function of basis weight

between the E-modulus and basis weight was found to be linear over the basis weight range investigated.

Figure 14 shows the elastic modulus of NC films against its basis weight, showing a linear increase with increasing basis weight. The E-modulus of the 83.8 g/m$^2$ VF-NC film is 5.22 ± 0.38 GPa, which is slightly lower than that of SC–NC films of similar basis weight. One effect that is certainly contributing to this result is that Fig. 5 shows that film density increases with the basis weight rising from 650 to 850 kg/m$^3$ as basis weight increases. This increase in density will reduce the cross-sectional area for a given basis

weight, thus increasing strength, even if the breaking load has not changed. The second effect that may be important is that a denser fibre network will produce a higher number of fibre–fibre bonds, which for films from conventional cellulose fibres from wood has been theoretically and experimentally established to increase elastic modulus due to an improvement in the stress transfer efficiency in the network (Niskanen 1998). To clarify the effects of density, the data in Fig. 14 has been recalculated as the tensile stiffness index which is independent of thickness and has been plotted against film density and added as Fig. 9 in the supplementary information.

Figure 15 shows the SEM images of the NC films surfaces. It can be seen that the rough side of spray coated NC film is more porous than that of smooth side. Additionally, the spray coated NC film are of similar roughness to vacuum filtered films on the air side, while being much smoother on the spray coated side. The surface roughness of 100.5 ± 3.4 and 95.2 ± 5.2 g/m$^2$ NC film measured via Parker surface instrument reveals 10.7 ± 0.4 µm on the rough side and 6.1 ± 1.8 µm on smooth side (95% confidence interval) for the spray coated (series 1 condition) compared with 10.67 ± 0.3 µm on filter side and 9.88 ± 0.15 µm on the free side of the vacuum filtered NC film.

Figures 16 and 17 shows the optical profilometry images of both surfaces of spray coated (100.5 ± 3.4 g/m$^2$ via series 1) and vacuum filtered (95.2 ± 5.2 g/m$^2$) NC films. The nanoscale RMS surface roughness of the spray coated NC film evaluated via an optical profiler (20× magnification with an inspection area of 235 µm × 310 µm) is

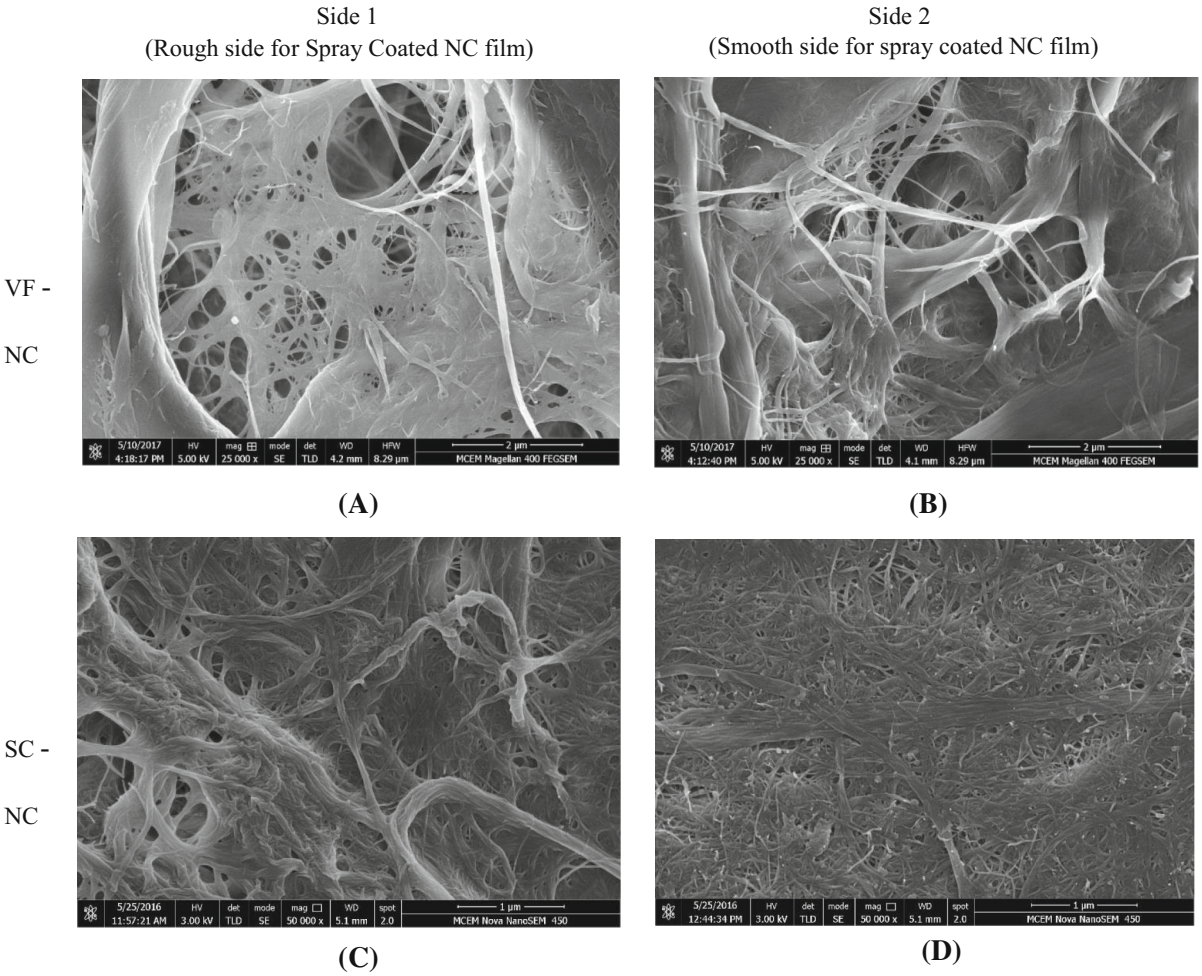


**Fig. 15** SEM micrographs of **a**, **b** two sides of VF-NC films, **c** the rough side of SC–NC film and **d** smooth side of SC–NC film

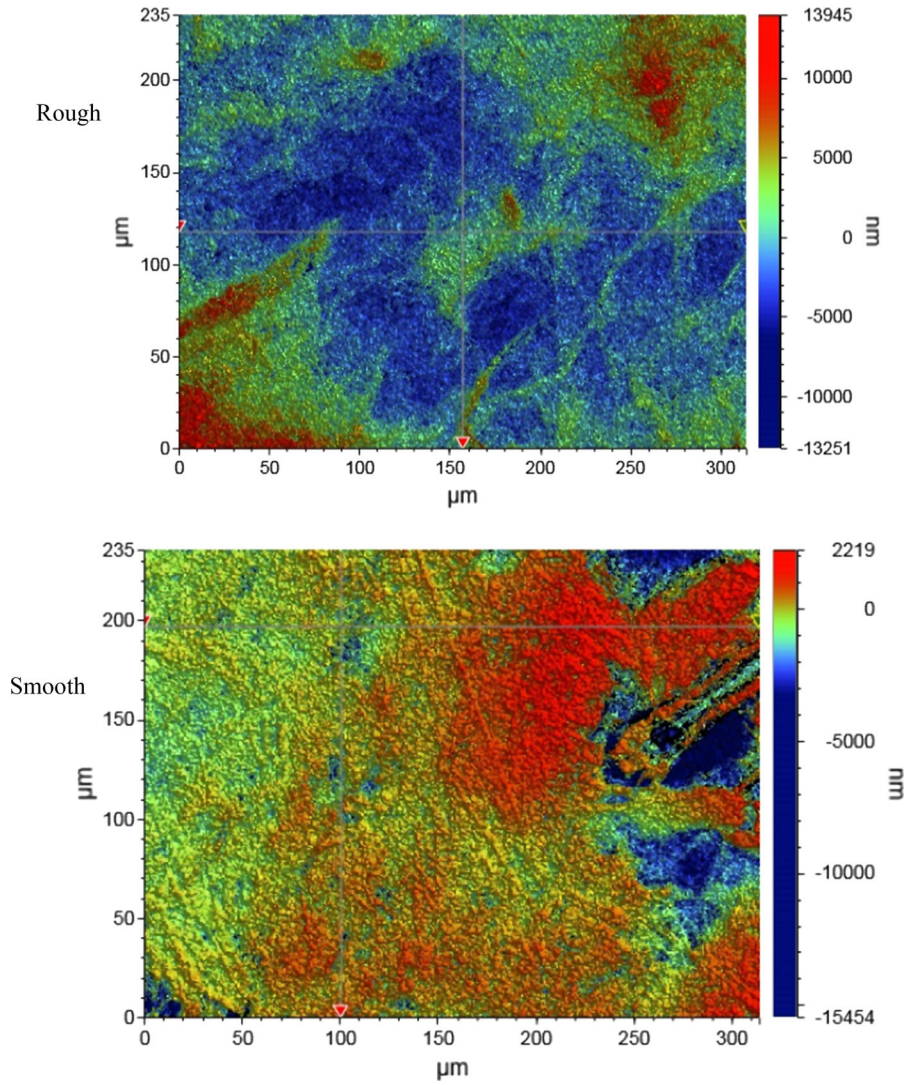


**Fig. 16** Optical Profilometry Images of both surface of spray coated NC Film-×20 magnification

2371 nm on the rough side and 682 nm on a smooth side. The smooth side roughness is much lower compared with the vacuum filtered film, where the roughness at filter side and free sides are 2877 and 4253 nm respectively.

We previously reported AFM measurements of the spray coated (100.5 ± 3.4 g/m$^2$ via series 1) NC film showed a RMS surface roughness of 414.0 nm for 10 µm × 10 µm film area and 51.4 nm for 2 µm × 2 µm film area on the rough side. This compared with a RMS roughness of only 81.1 nm for 10 µm × 10 µm film area and 16.7 nm for 2 µm × 2 µm film area on the spray coated side. When compared with the vacuum filtered 95.2 ± 5.2 g/m$^2$ NC film, the sides had a surface roughness of 417.7 nm (Filter side) and 330.8 nm (air side) at an inspection area of 10 µm × 10 µm, which is approximately the same as the rough side of the film prepared by spray coating (Shanmugam et al. 2017).

## Discussion

Spray coating has been proven to be a rapid and scalable method for the preparation of NC films, rendering it an exciting alternative for vacuum filtration which has many limitations (Shanmugam et al. 2017). To fully understand this process and allow for its implementation, a deeper understanding of the process parameters and properties of spray coated NC

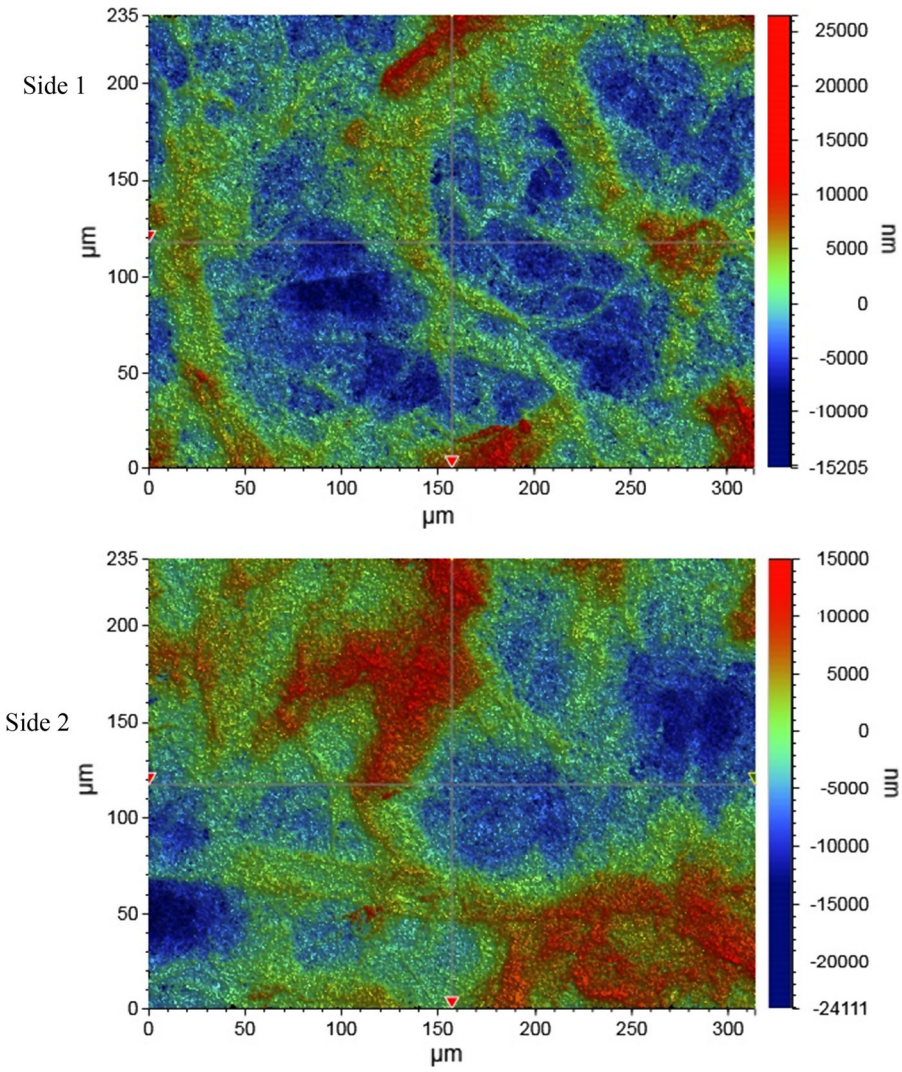


**Fig. 17** Optical Profilometry Images of both surface of vacuum filtered NC Film-×20 magnification

film was required, which this research addresses. Various combinations of conveyor velocity and suspension concentration can be used to produce the film with a given basis weight. Film density and E-Modulus were shown to be linearly related to basis weight of the film, but it was not possible to control film density and E-Modulus independently of each other. It was shown that thickness and basis weight are linearly related, independent of the process (whether vacuum filtration or spray coating) or experimental setup. Spray coating produced NC films with very reproducible thickness and basis weight between films, as shown in Fig. 5. Our previous publication also showed good thickness uniformity within the films, demonstrating the suitability of the spraying process as an alternative to vacuum filtration (Shanmugam et al. 2017).

Certain properties of NC films, including printability and strength, are strongly interlinked to the optical uniformity of the NC film (Varanasi and Batchelor 2014). The optical uniformity of the films was evaluated with a PPF tester, which evaluates the NC film over a range of length scales from 0.5 to 39 mm reporting a formation values as a ratio to the reference film which was film prepared via vacuum filtration. The optical uniformity of spray coated NC films were shown to be adjustable via changing NC concentration and varying velocity of the conveyor. It was found that

increasing suspension concentration and conveyor velocity both increase the optical uniformity within different ranges of component size and that under optimal conditions, the optical uniformity of the spray-coated films was comparable to the reference NC film produced by vacuum filtration. It is noteworthy that with increased conveyor velocity, the operating time is also proportionally decreased.

The most uniform NC films were prepared by spray coating at the highest velocity of 1.05 cm/s using the modified setup. The images are shown in Fig. 12. Figure 16 shows that its optical uniformity evaluated by the PPF is better than the vacuum filtered NC films at both small and large inspection sizes.

In comparison to vacuum filtration, spraying of NC suspension produced films of similar density and mostly lower tensile strength and elasticity. The process setup was shown to have an effect on these properties, correlating lower tensile strength and elasticity with a lower apparent density for series 1 and 2.

A change of nozzle, optimized setup configuration and operation at a decreased pressure in series 3 resulted in a slight increase in the apparent density and an increase in the tensile index of the films to be approximately equal to that produced by vacuum filtration. Notably, the optical uniformity of NC film via modified configuration is actually better than the reference NC film via vacuum filtration. This indicates a change in the formation of a wet film on the stainless steel plate resulting in a more compact structure. It should also be noted that with the optimized configuration, waste was decreased allowing for higher throughput and rapid production of films.

Previous data on spray coating of NC on nylon fabric (Beneventi et al. 2015), showed the tensile index of spray coated NC film ranging from 45 to 104 Nm/g, within the range of the data reported here. However, these literature values are reported for homogenized NC which show better fibrillation potentially leading to an increase in mechanical strength (Syverud and Stenius 2008).

The strength of the spray coated NC film could be tailored by adjusting NC concentration or varying the velocity of the conveyor. In the case of vacuum filtration, the forming of film with high basis weight requires high dewatering time and tailoring film properties is a challenging task.

## Conclusion

Spray coating, a rapid method to produce a strong, dense and robust NC films was examined in depth and process parameters were studied. Basis weight of NC films can be easily tailored with combinations of conveyor velocity and suspension concentration. The strength of the spray coated NC film is up to 45% lower than the strength of NC film via vacuum filtration and the optical uniformity of the spray coated film could be controlled by the adjusting the process setup. Under optimum conditions, both measured optical uniformity and strength were comparable to films prepared by vacuum filtration. The results confirm spraying to be a suitable alternative for fabricating NC films, allowing for high throughput mass production and the tailoring of properties for desired characteristics or applications.

## Supplementary information

The supplementary information includes: 1) the data of film optical uniformity from the Paper Perfect formation tester and 2) SEM micrographs of films at lower magnification, 3) Load-strain curve for NC films and 4) Plot between tensile stiffness index and basis weight and density of NC film.

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