

Project Report

Development of Cellulose Nanofibre (CNF) Coating on (1) Metal Surface for Free Standing CNF Film and (2) Paper Substrates for CNF Barrier Laminates

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Abstract: Paper is widely used in packaging applications and is biodegradable and therefore perfectly safe as green packaging wrap for the environment. The hydrophilic nature of cellulose fibrils limits the water vapour and oxygen barrier properties of paper. To mitigate these limitations, paper is often associated with other materials, such as plastics, wax and aluminum, for achieving their good barrier properties. However, these materials suffer from serious environmental issues, as difficult and inefficient to recycle. Recently, cellulose nanofibre (CNF) based materials has been considered as an alternative to produce eco-friendly barrier materials. Existing techniques to prepare cellulose nanofibre films/sheets/composites/ laminates on the paper substrates are commercially not feasible and expensive. Therefore, other cost effective and readily implementable methodologies are required to achieve cellulose nanofibre barrier layers. In the present report, a novel approach is developed using spray coating technique to produce CNF materials with excellent barrier properties. Among many coating techniques, the spray coating has many advantages such as the production of even coating surface on the base sheet and contactless coating with the substrate. A laboratory scale spray coating of cellulose nanofibre suspension on a paper substrate was developed. When the cellulose nanofibre suspension concentration was varied from 0.5 to 1.5 wt. %, coat weight is increased from 2.9 ± 0.7 to 29.3 ± 6.9 g/m². As a result, the air permeability of composite was decreased 0.78 ± 0.17 to < 0.0030 $\mu\text{m}^3/\text{Pa}\cdot\text{s}$. Scanning electron microscopy studies of spray coated CNF laminates on the paper confirms that the surface pores in the paper substrates are filled with sprayed cellulose nanofibre and forms a continuous film on the surface of the substrate. These are the probable reasons for the reduction of air permeability of composites. A rapid preparation technique to prepare free standing cellulose nanofibre films/sheets was also developed using a bench scale spray coating system. Cellulose nanofibre suspension with concentration ranging from 1 to 2 wt% was sprayed onto a stainless steel plate, which is moving on a conveyor at a velocity of 0.32 cm/sec and then air dried. The basis weight of produced cellulose nanofibre films is varied from 52.8 ± 7.4 to 193.1 ± 3.4 g/m². Processing time taken to prepare films was approximately 1.0 min, which is much less than processing times reported in the previous literature. Thus, the significant reduction in preparation time for producing the cellulose nanofibre sheet recommends that this spray coating technique can be utilized for the development of a scalable process for the fabrication of various cellulose based nanocomposite. Therefore, the laboratory scale spray coating confirms that the spraying could provide a platform for development of films/sheets/nanocomposite and also a CNF barrier layer on the base sheet. The future work is the development of a continuous spray coating of cellulose nanofibre on the base sheet and evaluation of mechanical and barrier properties spray coated barrier layers on the base sheet.

Keywords: Cellulose nanofibre (CNF), CNF Coating, Spraying, Free Standing Film, Air Permeability, Tensile Strength, Uniformity

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1. Introduction

Polymer based packaging materials are extensively used because of low oxygen and water permeability. However, they have poor recyclability and biodegradability and the waste is harmful to the environment. In conventional process, aluminum foil is used as layer for enhancing barrier properties of the paper board and paper surface. Neither the plastic materials nor the aluminum are renewable and these composites are difficult to recycle. To resolve this problem for the food packaging materials after use, major efforts are being taken the way to identify alternative materials from natural source to improve the barrier performance as well as minimize disposal or recycle problems [1].

Cellulose nanofibre, also known as cellulose nano-fibres or nano-fibrillated cellulose, is made by breaking down cellulose fibres into fibres with diameters ranging from 4-100nm and is considered to be as building block for development of new cellulose based functional materials. Recently, cellulose fibrils are used in the development of high strength and barrier materials and nanocomposites [4]. The preparation of these materials generally based on filtration and dewatering of dilute cellulose nanofibre suspensions was investigated for the preparation of cellulose nanofibre sheet which has an excellent mechanical and barrier properties. Vacuum filtration has processing time constraints for preparation of nanocomposite sheets as it required 1 to 24 hours of filtration time [5-7]. Recently, the technique in vacuum filtration to reduce the preparation time to 10 mins was developed. [43]. However, this is still high enough to make scale up difficult [8]. Therefore, the rapid and flexible method for developing the cellulose nanofibre sheet is required. Cellulose nanofibre has a potential of renewable, recyclable, compostable and biodegradable alternatives to the synthetic polymer based products [2]. Cellulose nanofibre is used as coating materials for enhancing the barrier properties of a base sheet and fabrication of cellulose nanofibre sheet and films [3].

Spraying cellulose nanofibre is an alternative technique for making nanofiber sheets that has been used to produce either continuous self-standing films by spraying on to a fabric or composite laminates by spraying onto a base sheet [6,7]. Spraying has some significant advantages such as formation of homogeneous layer and contour coating on the substrates [7]. The range of basis weight achievable with spraying is much higher than has been obtainable with filtration. Spraying can also be performed at higher initial solids content compared to filtration, reducing the amount of water that has to be removed in subsequent drying. Spraying has not so far been used to make discrete sheets for laboratory investigations, or for small scale products. It is still an open question about the sheet quality produced by spraying compared to hand sheets made by laboratory vacuum filtration.

The spray coating of cellulose nanofibre on the base surface could produce sheet with enhanced barrier and mechanical properties. Based on the laboratory performance of spray coating, the cellulose nanofibre sheet could be prepared rapidly and coating cellulose nanofibre on the base sheet quickly to create barrier layers.

The aim of this research is to develop spraying as a rapid and flexible method to prepare both free-standing cellulose sheet and to coat cellulose nanofibre on the base sheet. This report consists of the review of the literature of cellulose nanofibre, barrier layers and the spraying process, a review of the work done so far and a detailed research plan.

This research has broadly three main objectives.

1. To make free standing cellulose nanofibre film/sheet by spraying, determining the range or properties achievable

2. To develop spray coating of cellulose nanofibre on the base sheet to create barrier layers on a base sheet in a continuous mode and to determine the performance

2. Background

2.1. Cellulose nanofibre

Cellulose is the most important bio-renewable, biodegradable and biopolymer available in nature and is an excellent feedstock for the development of various sustainable functional materials such as coatings, films and membranes on an industrial scale for production [9]. These bio-based products could provide an outstanding solution to various international problems such as recycling, disposal and incineration of waste. It is produced by disintegration and delamination of cellulose fibrils from pulp produced from a variety of green sources such as wood, potato tuber, hemp and flax. It has dimension diameter ranging from 5 to 100 nm and is typically several micrometres in length [10]. Moreover, having a smaller dimension and a larger surface, nano cellulose is a great opportunity to be developed more functional materials for various applications [11, 12]. These Cellulose fibrils at micro/nano scale are used to functionalize base sheets by coating or to make freestanding sheets/films and nanocomposites. [13]

The nomenclature for cellulose nanofibre has not been reported in a consistent manner in the previous scientific investigations. It is also called as micro fibrillated cellulose (CNF), nano-fibrils, micro-fibrils and nano-fibrillated cellulose (NFC). Nano-cellulose fibres are isolated and processed from wood via various chemical, enzymatic, and/or mechanical treatment. Due to nano size of fibres, it possess various outstanding properties, such as high aspect ratio, high specific strength, flexibility, large specific surface area, and thermal stability, combined with biodegradability and biocompatibility. These properties could make cellulose nanofibre suitable for a wide range of applications, such as cellulose nanofibre film [14], reinforcing phase in composite materials [15], barriers in packaging [16], rheology modifiers for suspensions [17], filters for virus removal and water treatment technologies [18,19], flexible platforms for biomedical applications [20] and printed electronic applications [21].

2.2. Cellulose nanofibre and Barrier Properties

It has been proved that the films/sheets and its nano composites made from cellulose nanofibre and coated with fibre substrates increased the barrier and mechanical properties. [22]. Due to outstanding multifunctional barrier properties such as oxygen and water transfer rate, it has the potential for application of packaging materials for foods. [23]

2.3. Conventional methods for producing barrier surface on the base sheet

Barrier materials required low gas and water permeability to protect the contents from the external influences and to preserve the flavour and nature of the packaged product. The barrier properties of paper-based packaging can be tailored by applying layer of either synthetic or natural polymer using coating process. The previous studies confirmed that cellulose based coating on the paper based substrates substantially improved their barrier and surface properties [24, 25]. The various coating process using cellulose nanofibre from the literature were reported in the Table 1.

The cellulose nanofibre could be applied either on the paper or paperboard by several techniques such as solvent casting, dispersion coating, foam coating, bar and blade coating, and vacuum filtration. The different coating processes are mentioned in Figure 1 and Table1.

Table 1. Coating Process of CNF

Type of Cellulose	Substrate	Methods	Function	Coat Weight	WVTR (g/m ² day)	OTR or Air Permeability	Reference
Cellulose Nano fibrils (CNF)	Packaging Paper board (178±4 gsm) and 190±5 µm.	Roll to Roll coating with slot	Packaging	10 g/m ² (0 -16 gsm)	500 -100	NA	[38]
Carboxy-methylated micro-fibrillated cellulose film	Kraft paper Grease proof paper Free standing film	Dispersion Casting	Packaging material	1.3 1.0 g/m ² 5 and 8gsm	NA	0.3 nm/Pa s. 0.2 nm/Pa s 0.009 and 0.0006 cm ³ µm/ (m ² day kPa)	[22]
Micro-fibrillated cellulose	calendared paper (41 gsm)	Bar Coating Size Pressing	-	7 gsm 4 gsm	NA	786 ± 166 nm/Pa.s 4856 ± 1717 nm/Pa s.	[31]
Micro-fibrillated cellulose	Card board (300)	Bar coating	-	17±1 gsm	NA	0.18±0.01 cm ³ /m ² pa.s	[30]
Cellulose nanofibre	Fibre based substrates	Foam Coating	Tailoring the surface properties of the sheet and Functionalization	0.3 -2 gsm	NA	NA	[29]
Micro-fibrillated cellulose	Composite paper	Forming and Dewatering-Filtration	CNF composite Paper	NA	NA	NA	[37]
Nano-emulsified Cellulose nanofibre	Addition of the Nano emulsified Cellulose nanofibre	Vacuum Filtration	Cellulose nanofibre sheet	NA	NA	2.75*10 ⁻⁰⁸ ± 0.9*10 ⁻⁸ K(m ²)	[39]
Micro-fibrillated cellulose	Porous Paper substrate	Spray Coating	Barrier and Mechanical Properties Enhancement	6 gsm	NA	Drastically Reduced	[6]
Graphite Carbon Black Micro – Fibrillated cellulose	Wet Paper Substrate	Spray Coating	Electrode	NA	NA	NA	[7]

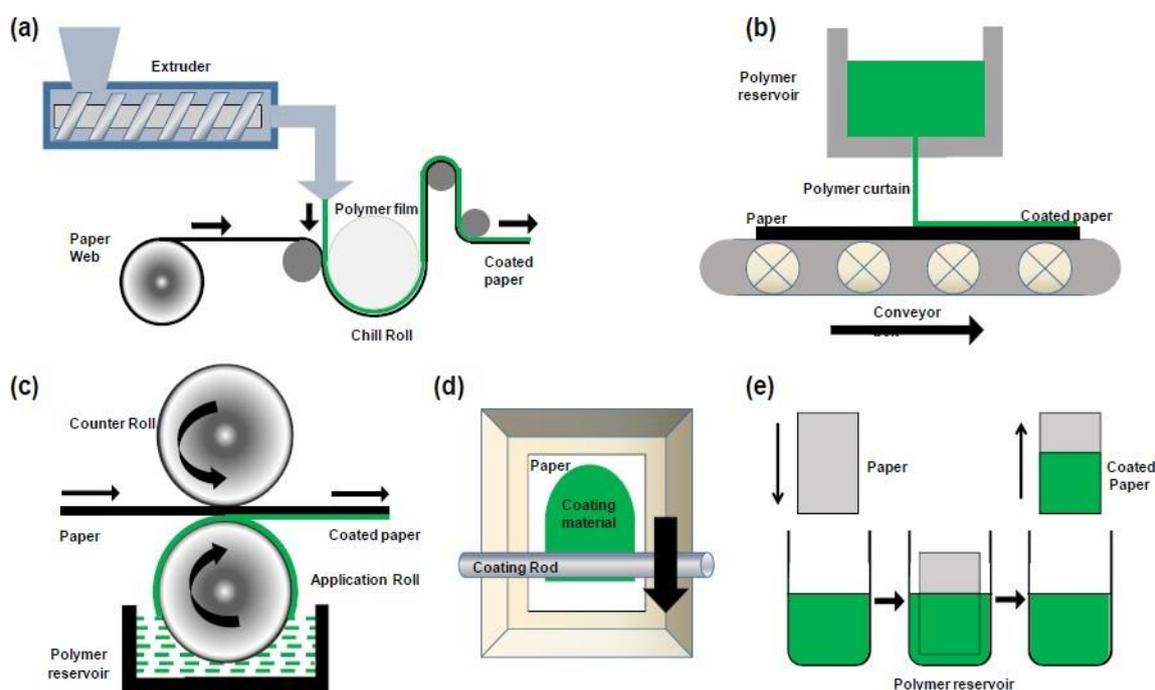


Figure 1. Different coating processes for paper applications, (a) extrusion coating; (b) curtain coating; (c) Size press coating; (d) bar coating; and (e) dip coating. (Vibhore Kumar Rastogi *et al*, Coatings, 2015, 5, 887-930)

Extrusion coating method is a common technique for coating synthetic polymers, such as poly-ethylene. It provides a continuous processing, uniform coating, minimal pinholes and cracks in the surface of base sheet, and solvent-free application. However, it has shortcomings in the coating performance such as being unable to produce a high coat weight to achieve the necessary barrier properties, instability of the polymer during melting stage and coating speed and efficiency. It is only suitable for coating of thermoplastic polymers. Given that cellulose nanofibre is not thermoplastic, it can only be suitable as a coating formulation by either dissolving cellulose nanofibre in a suitable solvent (*i.e.*, solvent coating/casting), or dispersing the polymer in solvent (*i.e.*, dispersion coating) [26, 27].

In dispersion and solvent coating methods, low coat weights around 10g/m² can be used to achieve the barrier layers of the base sheet, but sometimes two layers are mandatory to coat to eliminate the surface pinholes and achieve a sufficient water vapour performance. In this case, post coating process is expensive process including evaporation and drying of the coated surface [1]. Aulin *et. al.* reported that the preparation of carboxymethylated micro-fibrillated cellulose (CNF) films by dispersion-casting from aqueous dispersions and by surface coating on base papers and confirming that the oxygen permeability of the sheet prepared via dispersion coating and air permeability were reduced. [22]

Curtain coating is a coating process where a uniform coating is applied and found sufficient to cover the entire surface with better gas and water vapour barrier properties. In size pressing, the coating is not covered the paper surface completely and does not provide expected barrier properties. Bar Coating and rod coating techniques provides a better control over the thickness of the coating layer, but can only be used at the laboratory or pilot scale [28]. Dip Coating is the quick testing performance of coating at laboratory scale. However, the coating thickness of the base sheet is difficult to control and hence always find practical application at the laboratory scale [1]. Vacuum Filtration is the most common method for making the sheet. Time required to prepare sheets is varied to 10 min to 4 hours. This method achieves excellent barrier and mechanical properties, but

preparation time is a bottle neck for scaling up the process. Due to its film forming capacity, cellulose nanofibre could be used as coating layer on the base sheet which enhances strength and barrier functions of the base sheet. It proved that cellulose nanofibre would be a potential coating material [1]. Size press is not able to significantly alter papers properties as the CNF coat weight barely reached 4 g/m² resulting from ten successive CNF layers on the base sheet. The bar coating of CNF on the paper board was found not to substantially enhance its barrier properties, however did increase stiffness while reducing compressing strength [30, 31]. The cellulose nanofibre with multilayered resin coated on the paper board is proved to decrease the water vapour permeability of paper board. The coating is performed by the dispersion coating process or lithographic printing. [35]

Micro-fibrillated cellulose (CNF) and shellac were coated on the paper and paper board using a bar coater or a spray coating technique to enhance its barrier properties of the substrates. The coating performance is evaluated by the decreasing barrier properties of the sheet through decrease of the air permeance of the paperboard and papers with a multilayer coating of CNF and shellac. Furthermore, the oxygen transmission rate decreased several logarithmic units and the water vapour transmission rate reached values considered as high barrier in food packaging (6.5 g/m²/day)[36].

Although above mentioned conventional processes offers some advantages, they poses serious limitations such these methods should as they are done in batches and/or not capable of producing high coat weight on the base sheet to achieve barrier properties of the sheet. Therefore, spraying is a potentially promising approach for the preparation of cellulose nanofibre sheet and coating of cellulose nanofibre on the base sheet [29, 38].

2.4. Spray coating of Nano cellulose

Spraying cellulose nanofibre is an alternative technique for making nano-fibre sheets that has been used to produce either continuous self-standing films by spraying on to a fabric or to produce composite laminates by spraying onto a base sheet [6, 7]. Spraying has some significant advantages such as contour coating and contactless coating with the base substrate. The comparison of spray coating with other coating techniques is shown in Figure 2. The topography of the surface of the base substrate does not influence on the coating process.

- Contactless
- Contour coating
- Coating of tear sensitive material
- Controlling the coating material

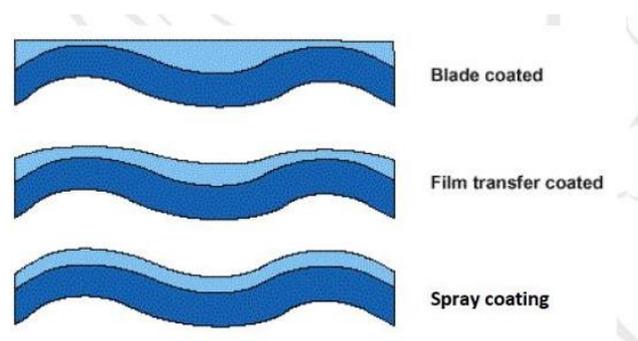


Figure 2. Concept of Spray coating and surface finishing. (Vilho Nisssonen, 2002) [48].

It is a novel technique for creating barrier film on the base surface rapid manner. Beneventi *et. al.* reported that the laboratory scale spray coating of micro fibrillated cellulose on different kinds of paper substrate enhances the barrier and mechanical properties of the spray coated sheet [6]. However, after spraying, they used vacuum filtration which is similar to the conventional paper making process to remove the excess water. As a consequence, it leads to time consuming process.

2.4.1. Spray coating of Cellulose nanofibre to make self stand cellulose nanofibre sheet

Stand-alone Micro-fibrillated sheet have been prepared using either vacuum filtration or casting. Casting is a time consuming process as it typically requires three days for the film to dry and it is difficult to control the wrinkling of the film as it dries [40]. Vacuum filtration can be considerably quicker. It recently reported that the laboratory sheet preparation time for light weight sheets less than 60 g/m² has been reduced from three or four hours [41] to 10 minutes [42,43] by increasing the solids content above the gel-point, increasing the size of the filter openings to reduce filter resistance and using polyelectrolytes to control. However, there can be significant issues in separating the sheet from the filter and subsequent handling before it finally dried. In addition, in vacuum filtration method, the range of sheet basis weight that can be manufactured is limited, as the filtration time increases exponentially with sheet basis weight. In the case of spray coating, the range of basis weight achievable in CNF film/barrier coating is much higher than that of vacuum filtration. A maximum mass of the film of 124 g/m² was obtained by spraying micro-fibrillated cellulose onto a nylon fabric running at a speed of 0.5 m/min [5]. Spraying can also be performed at a higher initial solid content compared to filtration, reducing the amount of water that has to be removed in subsequent drying. Spraying has not so far been used to make discrete sheets for laboratory investigations, or for small scale products. It is still an open question about the sheet quality produced by spraying compared to hand sheets made by laboratory vacuum filtration. In this method, they failed to explain about the quality of cellulose nanofibre sheet through the uniformity of the sheet, surface roughness and smoothness, thickness and coat weight when high suspension concentration used and tailoring the barrier and mechanical properties of the cellulose nanofibre sheet prepared via different CNF suspension of cellulose nanofibre.

2.5. Research Gap

The literature reveals that spraying of cellulose nanofibre has been shown as a potential method to produced cellulose nanofibre layers on the base sheet to tailor its barrier and mechanical properties and to produce various cellulose nanofibre functional sheets and to replace sheet forming method. The following research gaps are observed and will be investigated through this research:

- The uniformity and surface topography of the spray coated cellulose nanofibre sheet in comparisons with sheet prepared via vacuum filtration is not understood.
- Similarly, the barrier and mechanical properties of spray coated cellulose nanofibre sheet in comparisons with the cellulose nanofibre sheet prepared via vacuum filtration is not understood.
- What range of materials can be produced and how can the process be controlled to produce sheets to the required properties. How does spraying of different suspension concentration of cellulose nanofibre affect the properties of the sheet?
- What is the effect of forming the cellulose nanofiber-inorganic composites by spraying to improve barrier properties and mechanical properties of the nano-composite?
- The spray coated process could be adapted to make continuous or standalone sheets to replace the conventional vacuum filtration process.

2.6. Rapid preparation of Cellulose nanofibre film by spray coating method

2.6.1. Introduction

This research describes a novel, highly efficient method for the laboratory production of cellulose nano-fibre sheets by spraying cellulose nanofibre directly either on to circular steel plates or various fibre base substrates to produce barrier materials. The cellulose nano-fibre sheets formed in this way then can be subsequently dried in air under restraint without having to separate the sheet, maximising the rate at which the sheets can be produced. In this work, the quality of the sheets formed was compared, as measured by the variation in thickness, and compare it to sheets formed by filtration.

Micro-fibrillated cellulose (CNF) supplied from DAICEL Chemical Industries Limited (Celish KY- 100S) was used to prepare films. CNF sample was used at consistencies ranging from 0.5 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 CNF suspension was evaluated by the flow cup method which evaluates the process of coating fluid flow through an orifice to be used as a relative measurement of kinematic viscosity expressed in seconds of flow time in DIN-Sec.

2.6.2. Preparation of Micro-fibrillated films through spray coating and vacuum filtration methods:

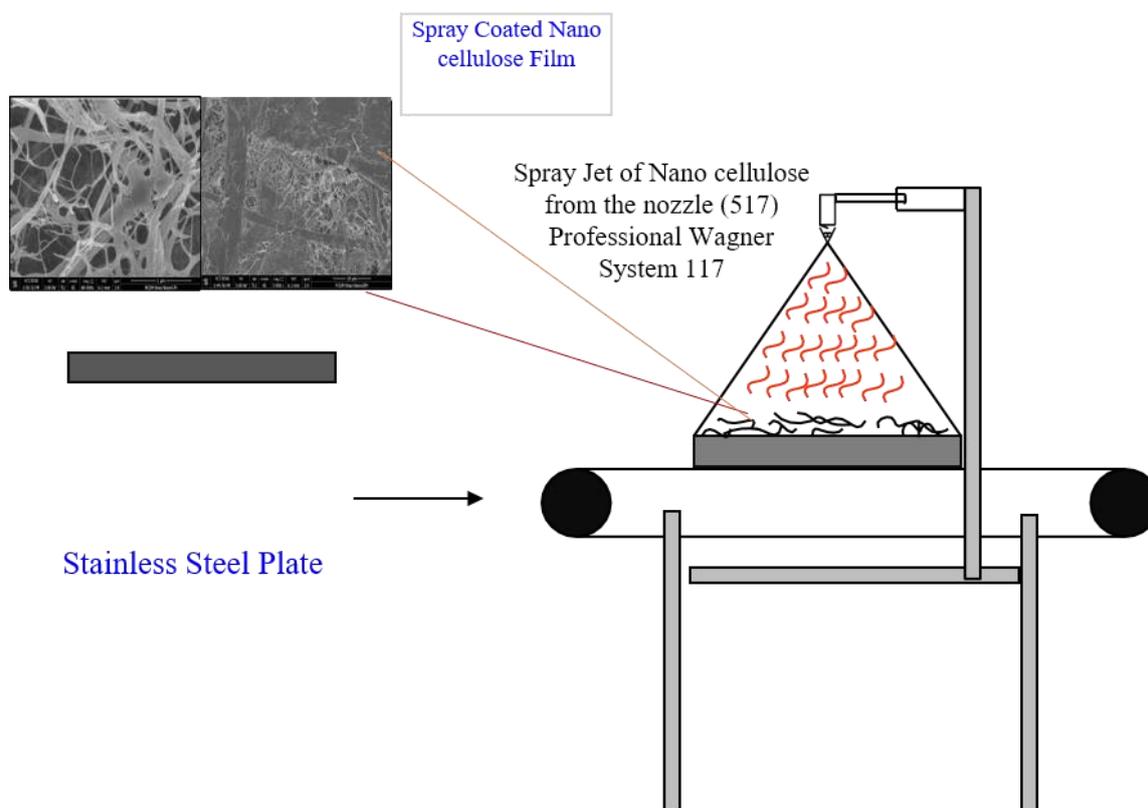


Figure 3. Experimental Set up for Lab Scale Spray Coating System for Preparation of Nano cellulose Film.

After spraying, the film on the plate was dried under restraint at the edges for at least 24 hours. The CNF film can then be readily peeled from the stainless steel plate and stored at 23°C and 50% RH for further testing. For comparison, nanofiber films were also prepared using vacuum filtration method as reported in [10]. In brief, CNF suspension with

0.2 wt. % concentrations was poured into a cylindrical container having a 125 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 drum drier for around 10 minutes. 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 micro fibrillated cellulose sheet was calculated by dividing the weight of the sheet, after 4 hours drying in the oven at a temperature of 105 °C, by the sheet area.

2.6.3. Evaluation of Thickness Distribution and Thickness Mapping

The Micro fibrillated sheet thickness was measured utilizing L&W thickness analyser (model no 222). The circular CNF sheets were divided into six regions and measure thickness in six location of each region. The thickness mapping of centre rectangular region of the circular sheet are done by plotting contour plot using Origin Pro 9.1. The visual explanation is given in the [Figure 4](#). The thickness of the sheets in six location of each region is measured and averaged. A 4 cm square section in the middle of each sheet was tested for thickness variation by measuring a matrix of 6 X 6 evenly spaced points for thickness mapping. The information on thickness mapping is added as supplementary information. The mean thickness of all the sheets is plotted against the suspension concentration of cellulose nanofibre. The mass of the film per unit area is evaluated for various concentration of cellulose nanofibre sprayed on the stainless steel plate.

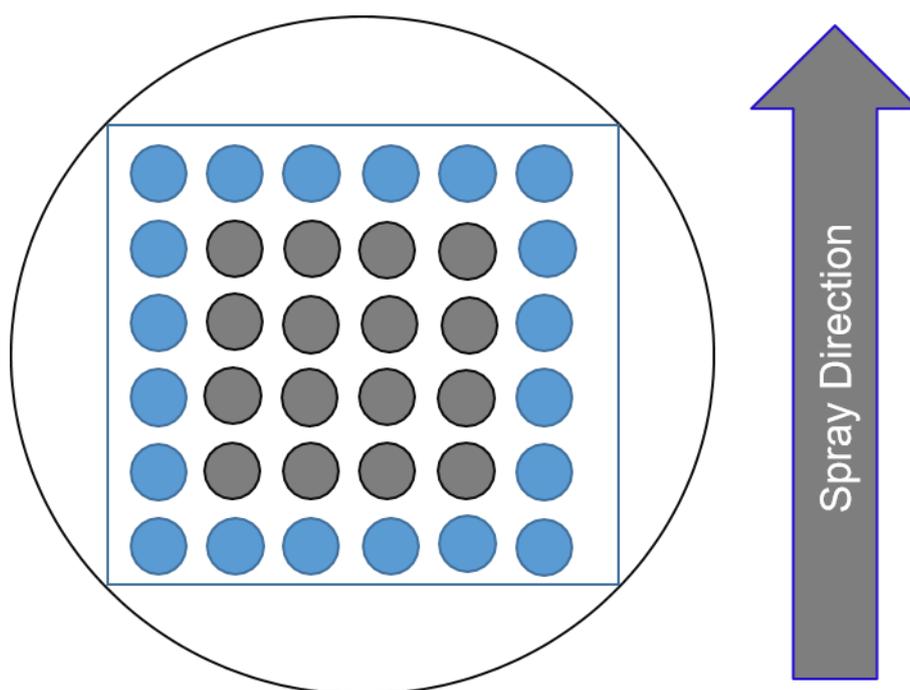


Figure 4. Mapping of thickness of the micro-fibrillated sheet. The thickness is measured in the centre region of the sheet. The square section of centre part of the sheet is used for contour plotting. The grey point of thickness used for mapping to confirm the uniformity of the sheet.

2.6.4. Surface Topography of Nano fibrillated Sheets

The surface morphology and topography of the iridium coated nano-sheet prepared at a conveyor speed of 0.32 cm/sec are performed with FEI Novo SEM. The images of both surface of the CNF sheets are captured at magnification from 1 μm to 100 μm in secondary electron mode-II of FEI Novo SEM. Furthermore, the surface roughness of both sides of the film at nanoscale is evaluated by atomic force microscopy.

3. Result and Discussion

Effect of suspension concentration on the viscosity of cellulose nanofibre is given in Figure 5. It increased with solid/ fibre content in the suspension. The efflux time < 30 sec confirms the sprayable concentration of cellulose nanofibre for coating operation. The viscosity of 1.5 wt. % CNF suspension is 32.18 ± 0.94 DIN Sec predicted by dip cup method. It is quite challenging to predict the efflux time and viscosity of cellulose nanofibre suspension beyond the concentration of 1.5 Wt. %. It is reported that cellulose nanofibre suspension could form a gel like structure and behave shear thinning rheology even at low concentration of CNF in the suspension. The viscosity of cellulose nanofibre suspension increase with concentration of fibers content [44]. The rheological properties of CNF suspension is influenced by fibre morphology, orientation and aggregation. It is also reported that the viscosity of suspension increases with fibre aspect ratio and becomes substantially higher for high suspension concentration [45]. When the CNF suspension concentration is higher than 2.00 wt. %, CNF suspension has lost its fluidity, becomes like stiff gel and also viscosity is higher than 32.18 DIN Sec after disintegration of fibres. Onwards of this concentration above 2 wt. %, CNF suspension behaves as a viscoelastic fluid and formation of network of entangled cellulose fibrils which causes gel-like behaviour [46,47]. The spraying high solid content suspension is really challenging because more chance of clogging the nozzle. Furthermore, the high shear force is required to pump and spray the high fibre content of the slurry.

Effect of suspension concentration on Viscosity of Cellulose nanofibre

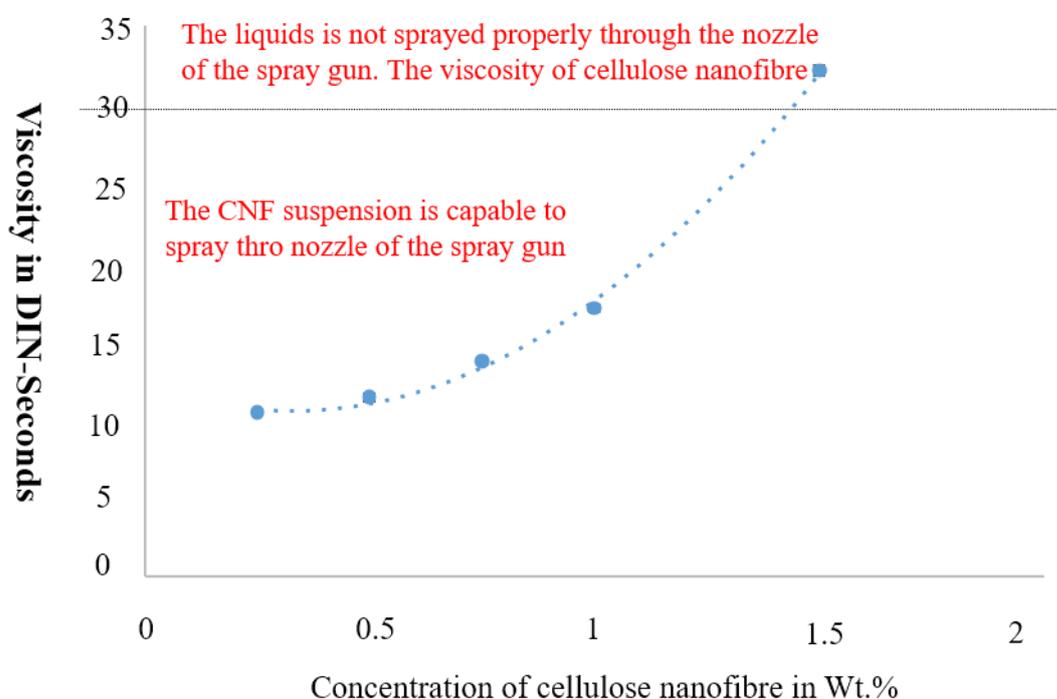


Figure 5. Viscosity of cellulose nanofibre suspension using dip cup method

The stable and homogeneous films were prepared with various concentrations of CNF suspension via spray coating technique as described in the experimental section. The operational range for spraying cellulose nanofibre suspension was between 1.0 wt. % and 2.0 wt. %. Below 1 wt. %, the suspension was too dilute and flowed over the metal surface producing an uneven film difficult to peel from the plate after drying. Above 2% wt., the

suspension become too viscous to spray. The lower and upper limits, corresponded to suspension viscosities of 17.0 ± 0.6 to 32.2 ± 0.9 DIN sec, respectively. Figure 6 shows the effect of cellulose nanofibre suspension concentration on the basis weight of the film and mean thickness of the film. Each point is the average of 4 replicates with the error bars providing the standard deviation. Both sheet basis weight and thickness increased approximately linearly with increasing cellulose nanofibre suspension concentration. Basis weight range from 52.8 ± 7.4 to 193.1 ± 3.4 g/m² by spraying suspension with concentration of 1.0 and 2.0 wt. %, respectively; film thickness were $83.9\pm 13.9\mu\text{m}$ and $243.2\pm 6.6\mu\text{m}$ for the lowest and highest consistencies.

Effect of Suspension Concentration of Thickness and Basis weight of the NFC film:

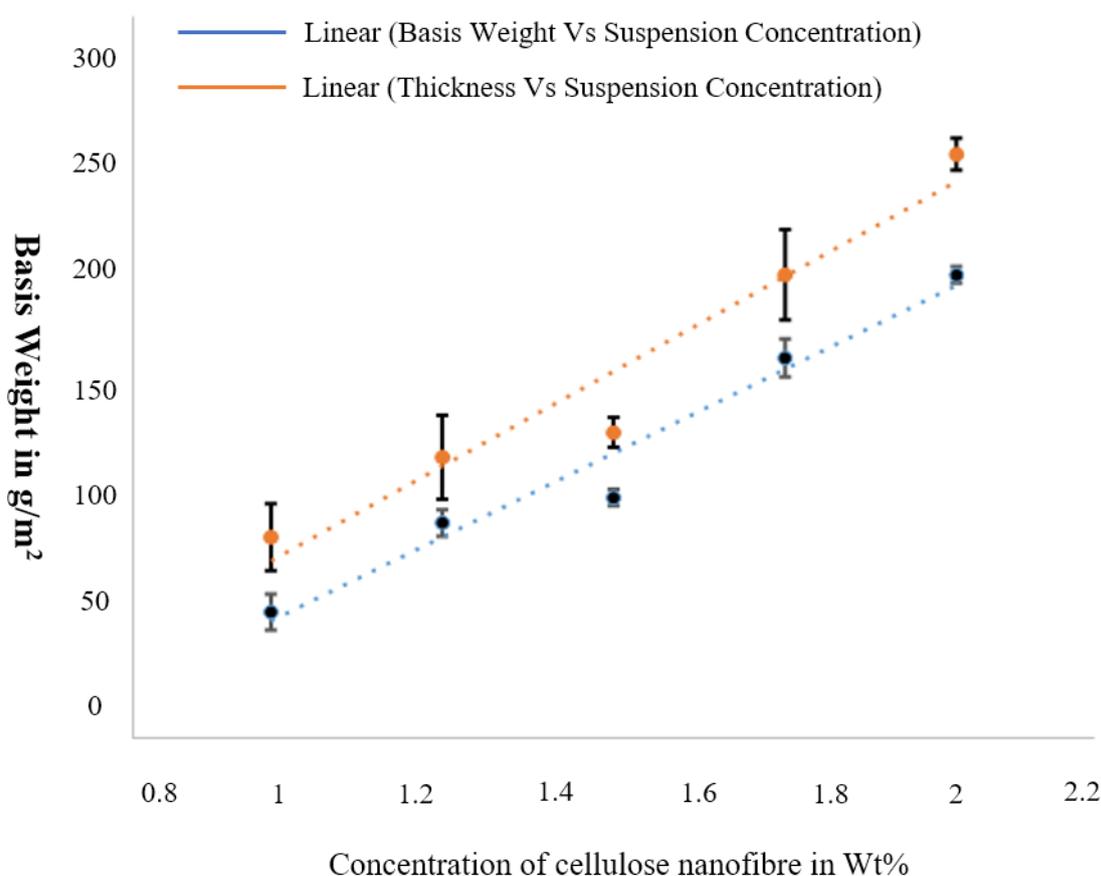


Figure 6. Effect of suspension concentration on the basis weight of the nano cellulose film prepared using spray coating technique at a constant velocity of 0.32 cm/sec.

Figure 7 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 sheet prepared by spray coating and vacuum filtration are almost identical at 100.5 ± 3.4 g/m² and 95.2 ± 5.2 g/m², respectively. The spray direction was from bottom to top. Compared to spray coating, vacuum filtration required a much higher dewatering time of 15 minutes to produce the sheet.

When compared to the sheet made from vacuum filtration, the spray coated micro – fibrillated cellulose sheet is slightly thicker, even when correcting for the slight difference in basis weight. The apparent density of the spray coated sheet and sheet prepared via vacuum filtration were 793 and 834 kg/m³, respectively. In addition, there is a somewhat wider distribution of thickness for the spray- coated film. The thickness of the CNF film

sheet prepared via vacuum filtration process and spray drying were $113.4 (5.4) \mu\text{m}$ and $127.1 (12.1) \mu\text{m}$, respectively. The numbers in brackets give the standard deviation of the distribution of measured thickness. The measured standard deviations of thickness for each sheet were normalized by the average thickness. For the thinnest, lowest basis weight sheets made at 1.0 wt. % consistency, the normalized value was $52.8 \pm 7.4 \text{g/m}^2$, in comparison to a value of $193.0 \pm 3.4 \text{g/m}^2$ for the sheets made at 2.0 wt. % consistency. 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.

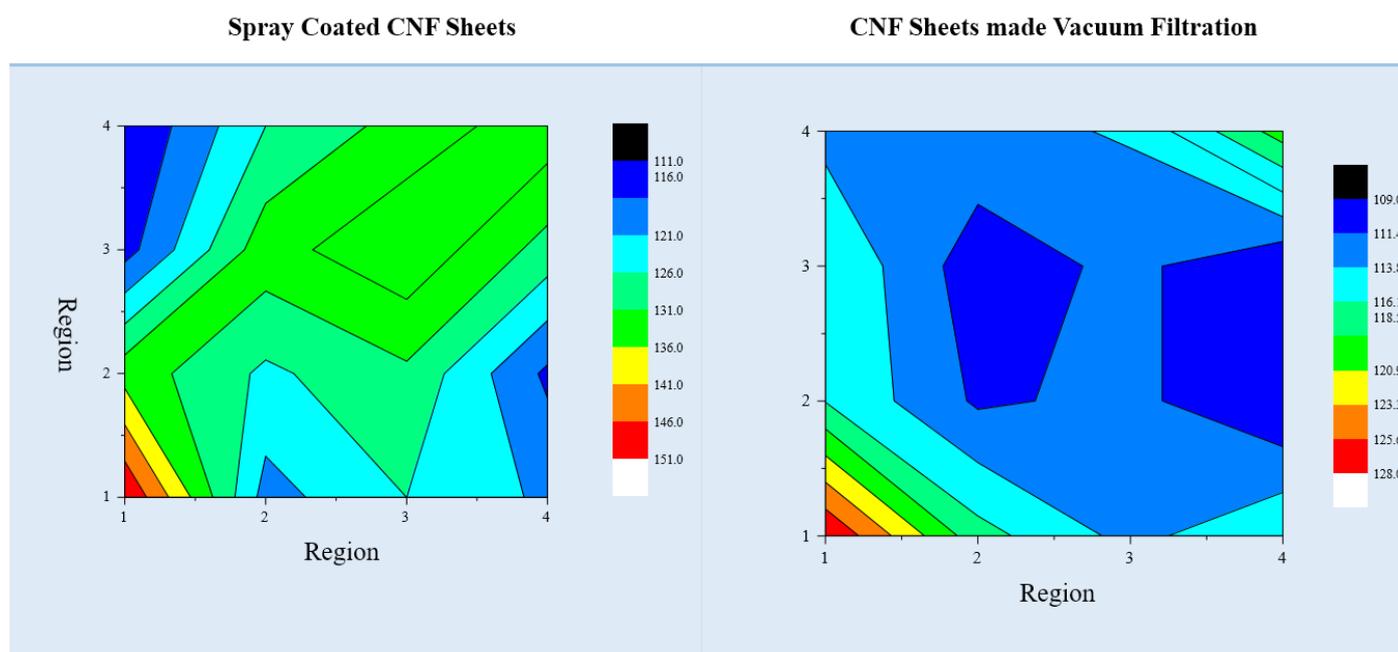


Figure 7. Thickness Distribution of the cellulose nanofibre sheets –Spray coated at Conveyor velocity of 0.32cm/sec and Vacuum Filtration

Figure 8 shows the surface morphology and topography of both sides of the spray coated micro- fibrillated cellulose sheet investigated by scanning electron microscopy and atomic force microscopy (AFM). 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 in the sheet surface as it dried. Visually the smooth surface of the sprayed film has a glossy, shiny appearance. Roughness was quantified from the AFM images. The RMS roughness of the rough side is 414.0 nm for $10 \mu\text{m} \times 10 \mu\text{m}$ film area and 51.4 nm for $2 \mu\text{m} \times 2 \mu\text{m}$ film area whereas the surface roughness of the glossy side in root mean square (RMS) is only 81.1 nm for $10 \mu\text{m} \times 10 \mu\text{m}$ film area and 16.7 nm for $2 \mu\text{m} \times 2 \mu\text{m}$ film area. AFM measurements of the sheet prepared by filtration are given in the Supplementary information and show both sides had a surface roughness of 417.7 nm (Side 1) and 330.8 nm (Side 2) at an inspection area of $10 \mu\text{m} \times 10 \mu\text{m}$, which is approximately the same as the rough side of the sheet prepared by spray coating. The results reported in this investigation confirm that a laboratory scale spraying of various concentration of micro-fibrillated cellulose on a stainless steel plate is viable for the rapid preparation of micro-fibrillated cellulose sheet with basis weight ranging from 52.8 ± 7.4 to $193.1 \pm 3.4 \text{g/m}^2$. The basis weight of the sheet was readily controlled by the concentration of micro-fibrillated suspension sprayed on the stainless steel plate at a constant velocity of conveyor. In our investigation on spraying, the processing time was 50.2 seconds to spray 15.9 cm diameter sheets, independent of the

basis weight from 52.2 to 193.1 g/m². The quickest time reported in the literature for sheet formation with filtration was from work in the research group (Varanasi and Batchelor 2013), where 2.8 minutes was required for filtering a low basis weight of 56.4 g/m², formed from 0.6 wt. % suspension. In contrast the 95.1 g/m² sheet formed at 0.2 wt. % made for the work in this paper took 15 minutes to filter, with filtration time exponentially increasing with sample basis weight. After filtering, the micro-fibrillated sheets can often be difficult to separate from the filter, taking additional time to complete the transfer to the blotting paper without destroying the sheet. Drying the filtered sheet then requires repeatedly manually feeding the sheet into a rotating drum dryer until dry, with the overall process taking at least 10 minutes from the start of filtration. In the spray coating method, the drying time for nano cellulose sheets in ambient conditions is from 24 hrs to 48 hrs, which is reduced to 30-60 minutes when drying in an oven at 105°C. However, while the total time to prepare and dry a sheet is longer with spray coating a stainless steel plate, the key strength of the method is the reduction in operator time. Leaving aside, the preparation of the cellulose nanofibre suspension, which is common for the two methods, preparing 10x100 gsm sheets requires less than 9 minutes of operator time with spraying compared to 220 total minutes with filtration.

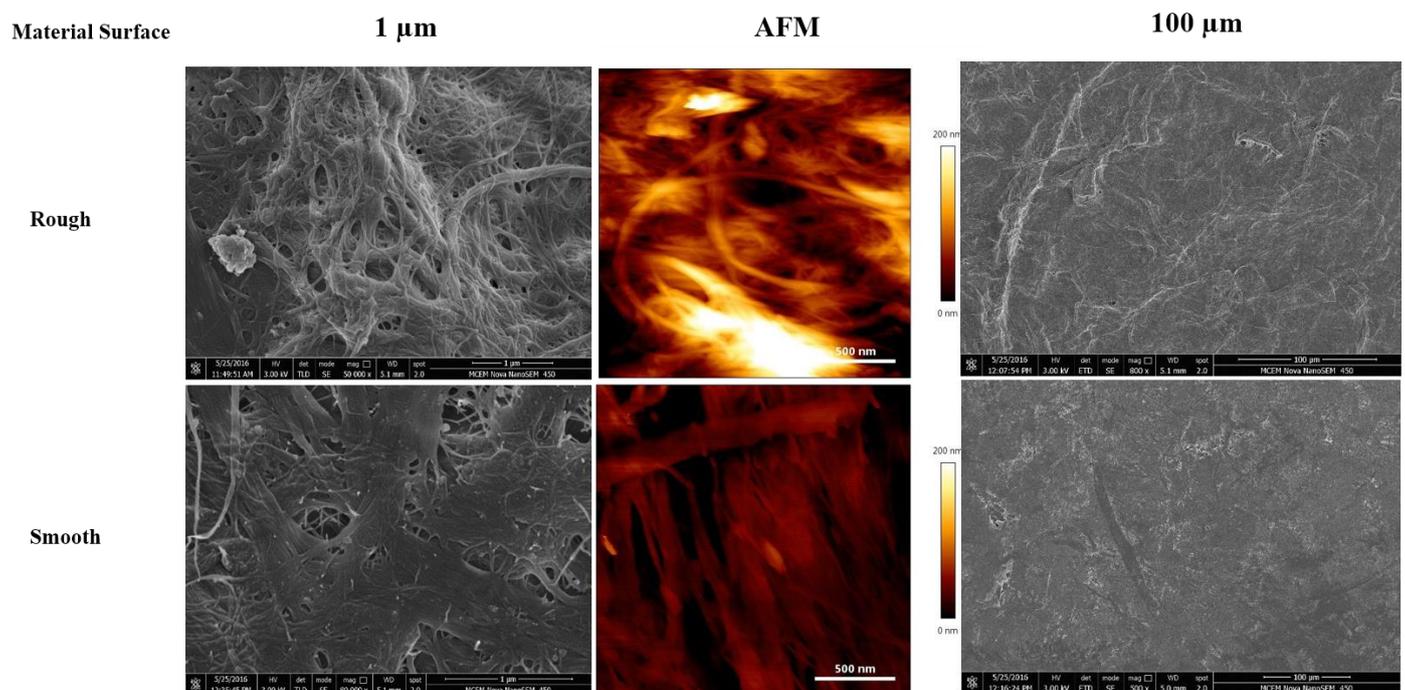


Figure 8. SEM image of the cellulose nanofibre sheet – Rough and Smooth surface and AFM Image of the both sides of the CNF Film.

The [Figure 9](#) explains about the effect of the velocity of the conveyor on the basis weight of the cellulose nanofibre sheet prepared by spray coating process and how it does influence on the spraying time of cellulose nanofibre on the stainless steel plated indirectly and as a consequence, the basis weight of the sheet is varied from 45 to 100 g/m². The figure confirms that the basis weight of the cellulose nanofibre sheet is controlled by the velocity of the conveyor.

Mechanical and Barrier Properties of Spray Coated Cellulose nanofibre sheet: Optimization of Velocity of the conveyor

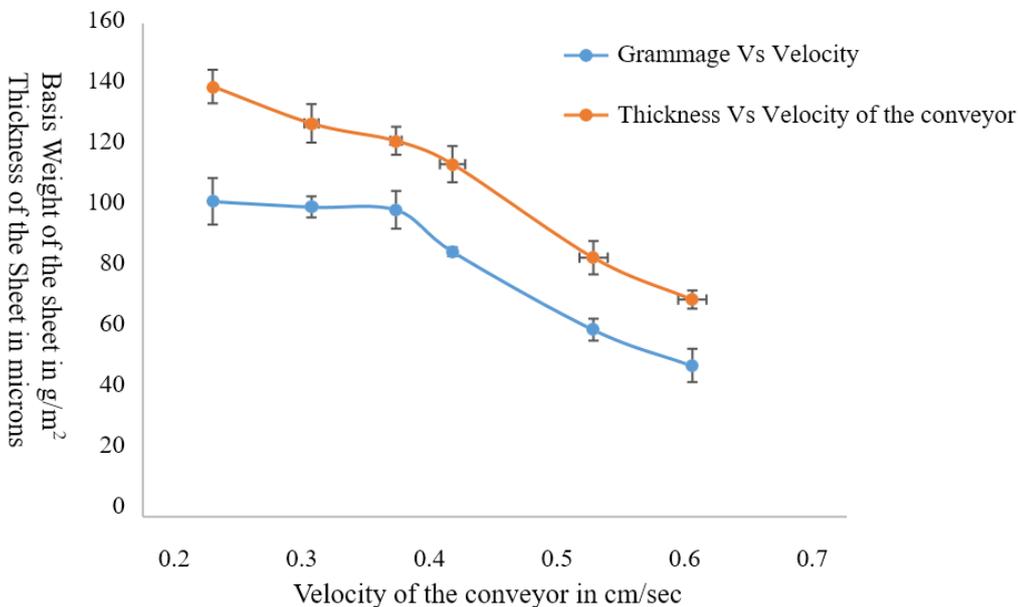


Figure 9. Effect of the velocity on the basis weight of the CNF sheet and **Figure 3**– Effect of Velocity of the conveyor on thickness of the spray coated shee

Figure 10 and **11** shows the effect of velocity on the uniformity of free standing CNF film. These figures conclude that the uniformity of the film can be increased at lowest velocity. At lowest velocity, more CNF suspension deposited on the base surface forms thick and uniform films.

Formation Test for Spray coated sheet at Different Velocity of the Conveyor

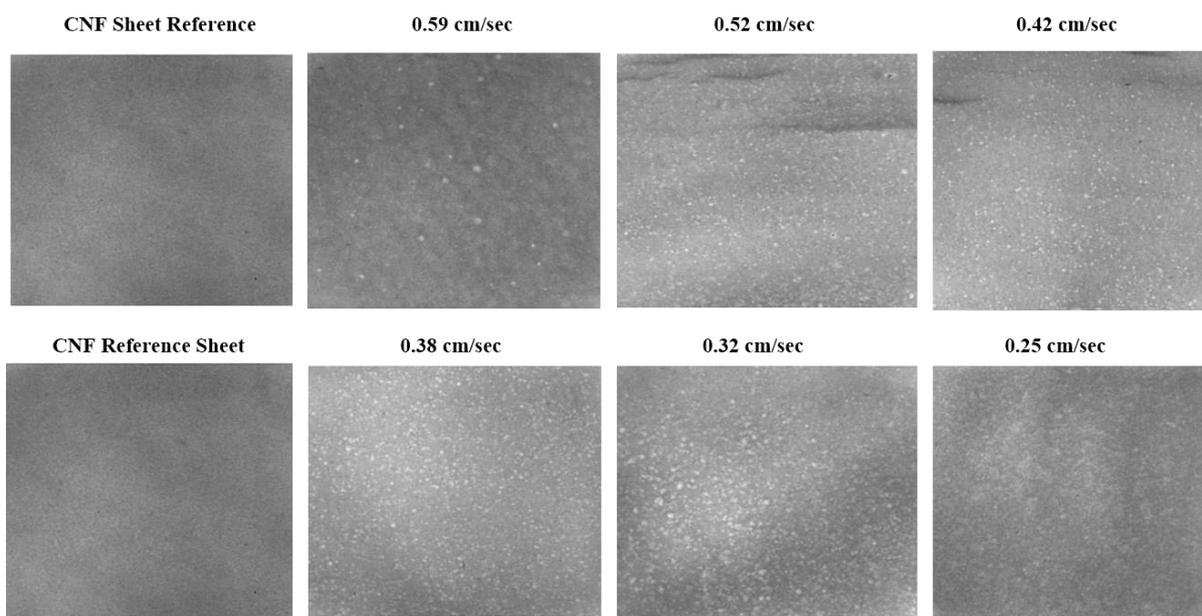


Figure 10. Uniformity of the spray coated sheets prepared at various velocity of the conveyor

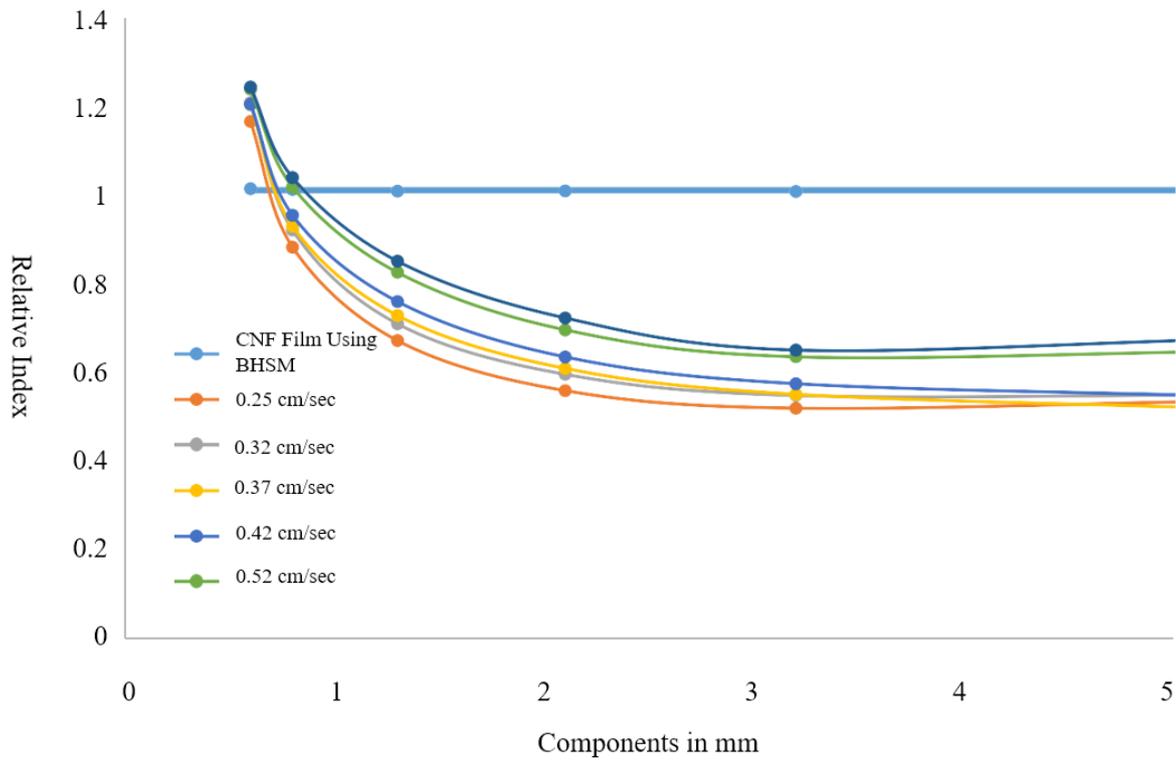


Figure 11. Formation test of Spray Coated sheet prepared at various of velocity of the conveyer

Figure 12 and 13 the effect of CNF suspension consistency on the uniformity of the film. The CNF suspension consistency increase the uniformity of the film also increased.

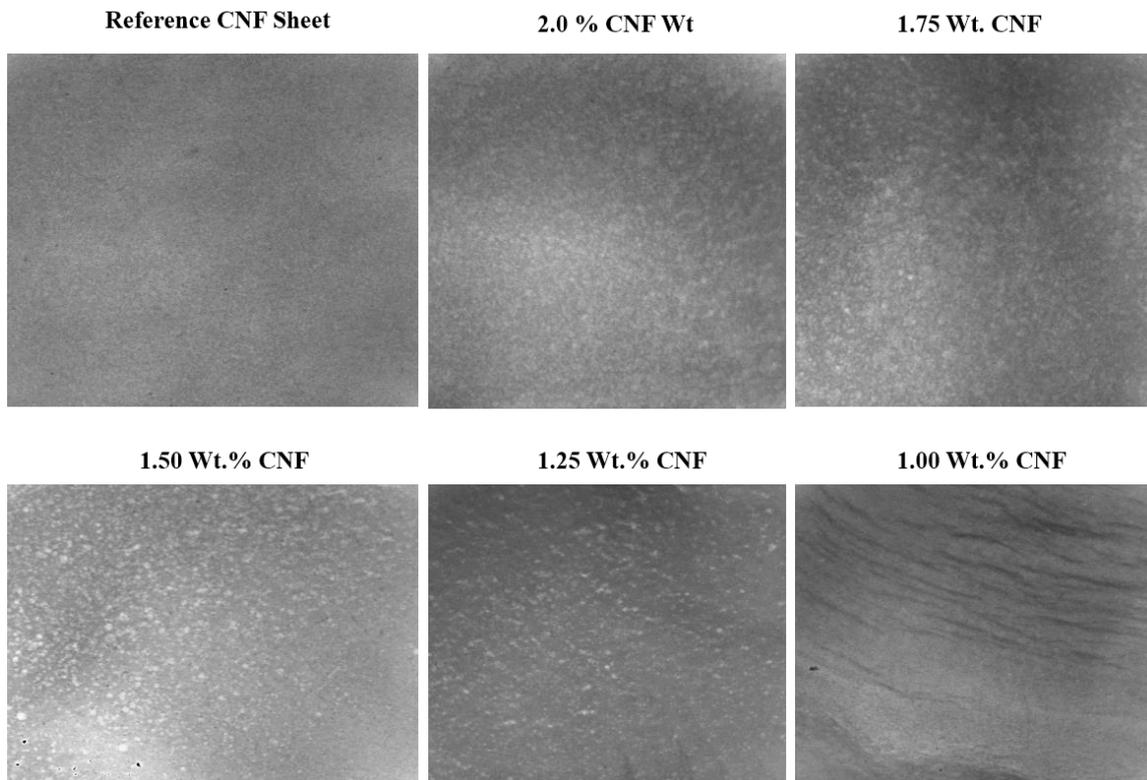


Figure:12. Uniformity test of spray coated paper prepared different suspension of CNF

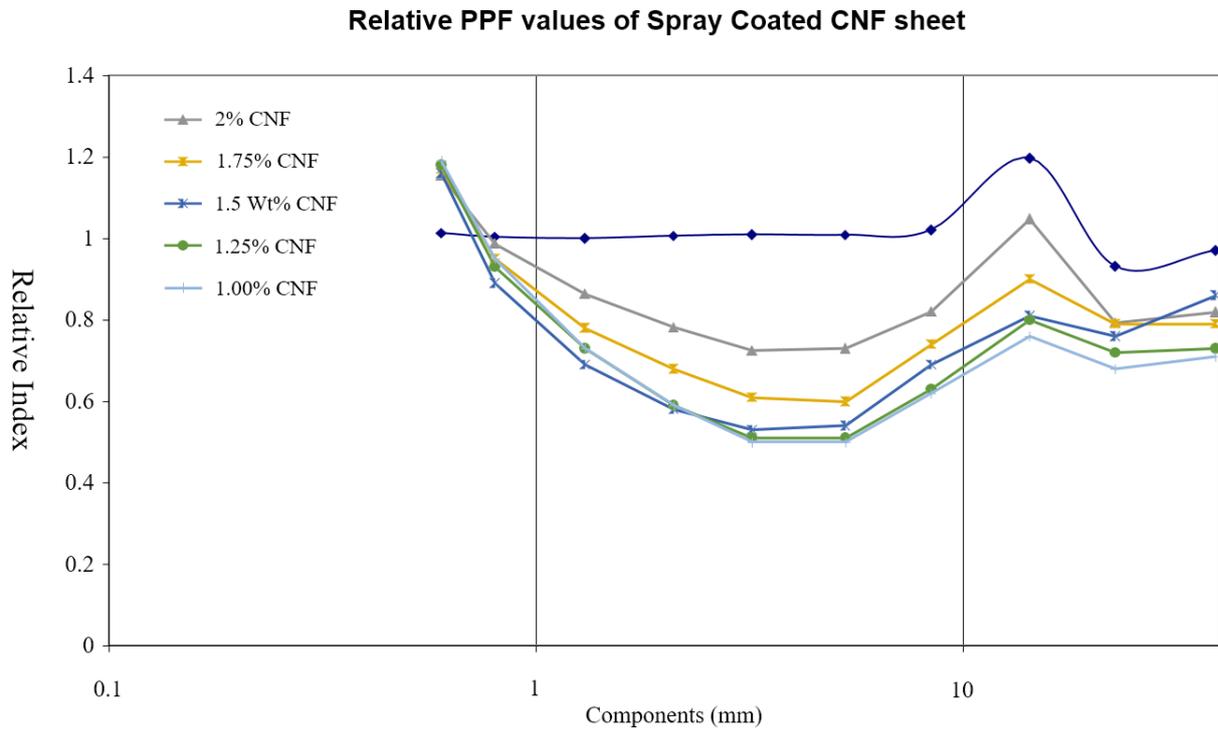


Figure:13. Formation Test of Spray Coated sheet made by different suspension of CNF

Effect of Suspension concentration on apparent density of the sheets:

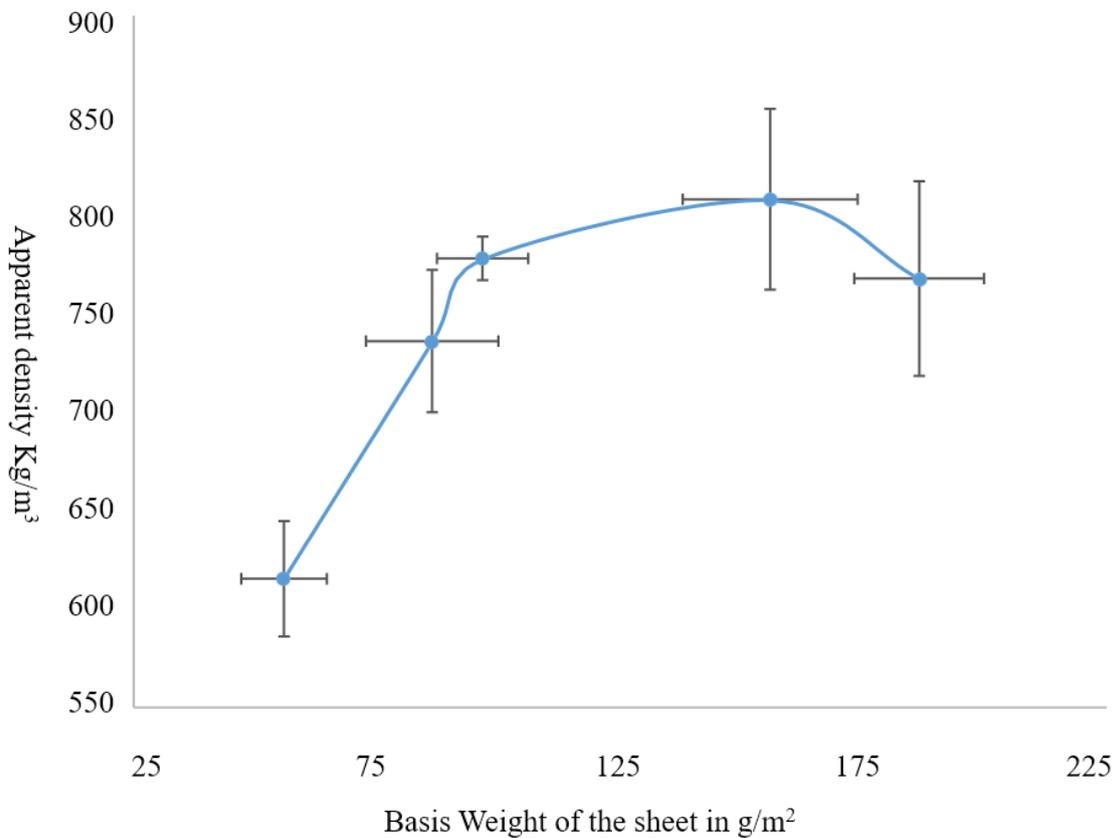


Figure 14. Effect of suspension concentration on apparent density of cellulose nanofibre sheet.

The Figure 14 explains the effect of suspension concentration of cellulose nanofibre sprayed at constant velocity of the conveyor on the stainless steel plate on the apparent density of the cellulose nanofibre sheet. The apparent density of the cellulose nanofibre sheet increased with the suspension concentration sprayed on the stainless steel. The apparent density of the sheet increased through increasing thickness of the sheet and basis weight of the sheet. The figure investigates the effect of the basis weight of the cellulose nanofibre sheet prepared via spraying on the stainless steel plate on the apparent density of the sheet. The apparent density of the sheet linearly with basis weight of the sheet up to 96.6g/m² and then it is almost constant in apparent density of the sheet.

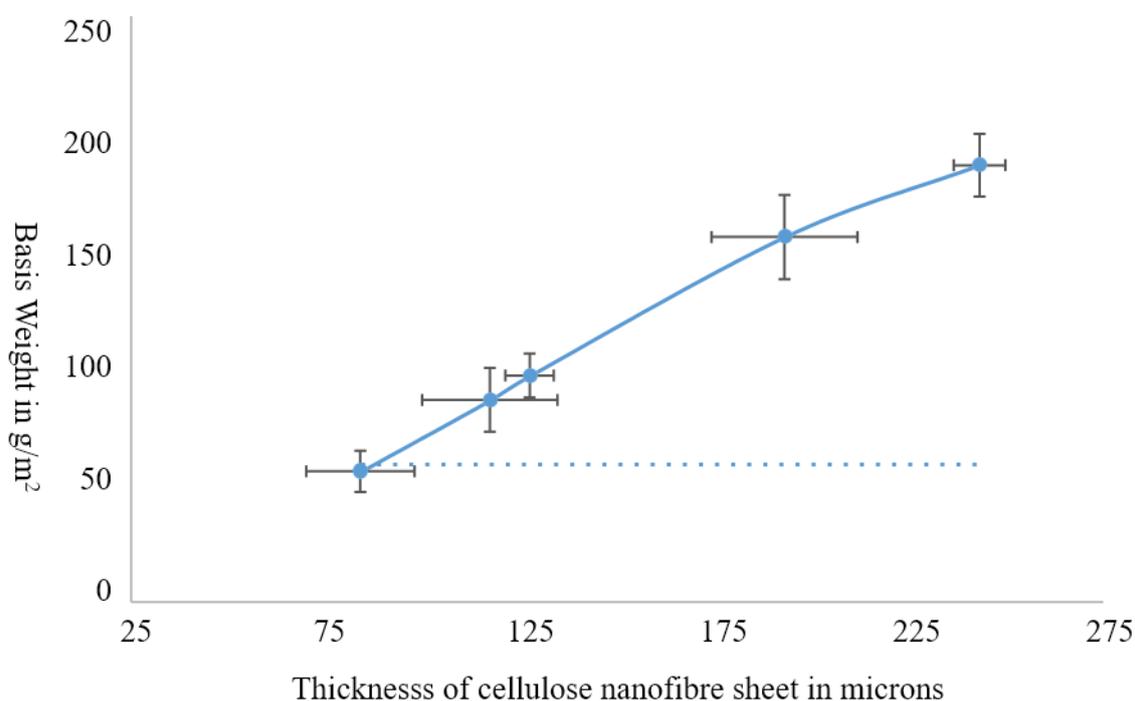


Figure 15. Effect of thickness of the cellulose nanofibre sheet on the basis weight

The Figure 15 investigates the effect of thickness of the nano cellulose sheet prepared by suspension concentration from 1.0 wt.% to 2.0 wt.% sprayed on the stainless steel plate and evaluated its basis weight of the sheet. The plot between thickness of the cellulose sheet and basis weight of the sheet is a linear relationship.

Barrier Properties of the cellulose nanofibre sheet:

The barrier properties of the cellulose nanofibre sheet are evaluated by measuring the air permeability of the sheet and water vapour transmission rate of the cellulose nanofibre sheet.

Air Permeability of the CNF Sheets

The air permeability of the cellulose nanofibre sheets prepared via spraying at various velocity of the conveyor and different concentration of CNF suspension are impermeable. The effect of velocity of the conveyor does not influence on the barrier properties of the sheet. The air permeability of the cellulose nanofibre sheet is < 0.003 $\mu\text{m}/\text{Pa.S}$.

Mechanical Properties of the spray coated sheet

The tensile index of the spray coated sheet increased with increasing its basis weight(as shown in Figure 16).

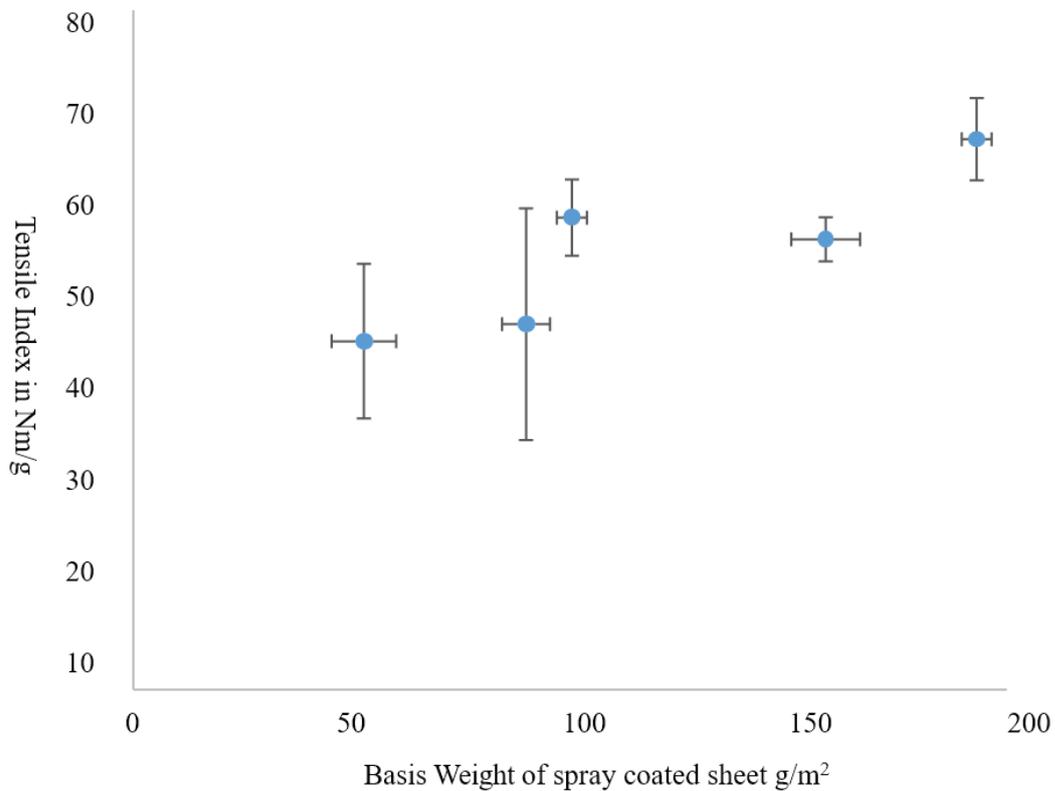
Influence of Suspension concentration on Mechanical properties of spray coated CNF Sheet:

Figure 16. Tensile Index of the spray coated sheet.

The young's modulus of the spray coated CNF sheet increase with the suspension concentration of cellulose nanofibre sprayed on the base surface(as shown in [Figure 17](#)).

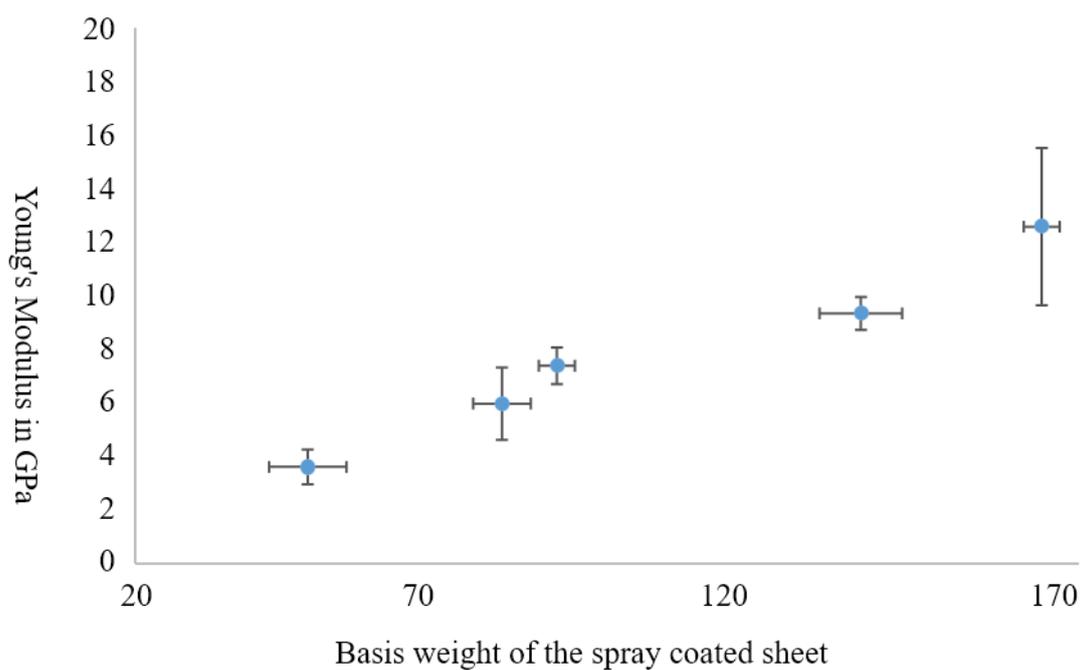


Figure 17. Young's modulus of the spray coated sheet

The tensile index of the spray coated sheet altered when the velocity of the conveyor is varied(as shown in [Figure 18](#)).

Effect of the velocity of the conveyor on tensile properties of the sheet:

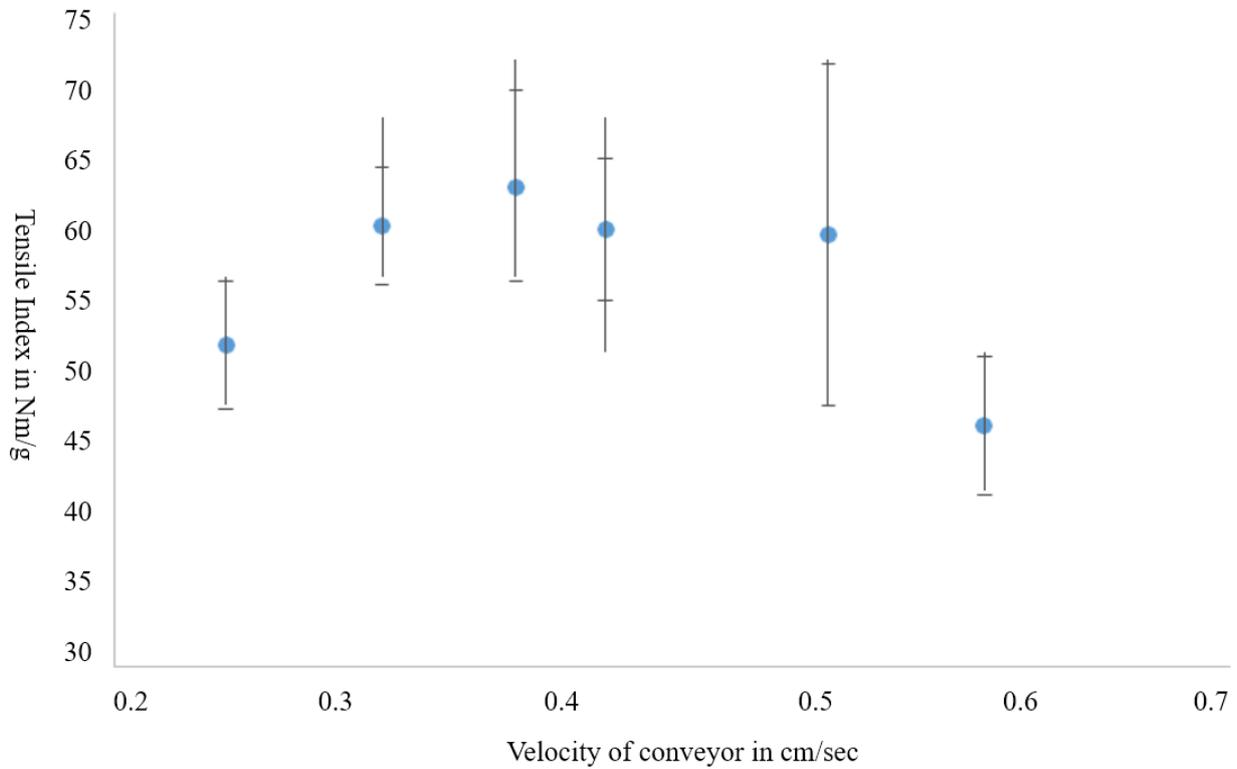


Figure 18. Influence of conveyor velocity on Tensile Index of the spray coated sheet.

The young's modulus of the spray coated CNF sheet increase with decrease velocity of the conveyor in the experimental set up(as shown in [Figure 19](#)).

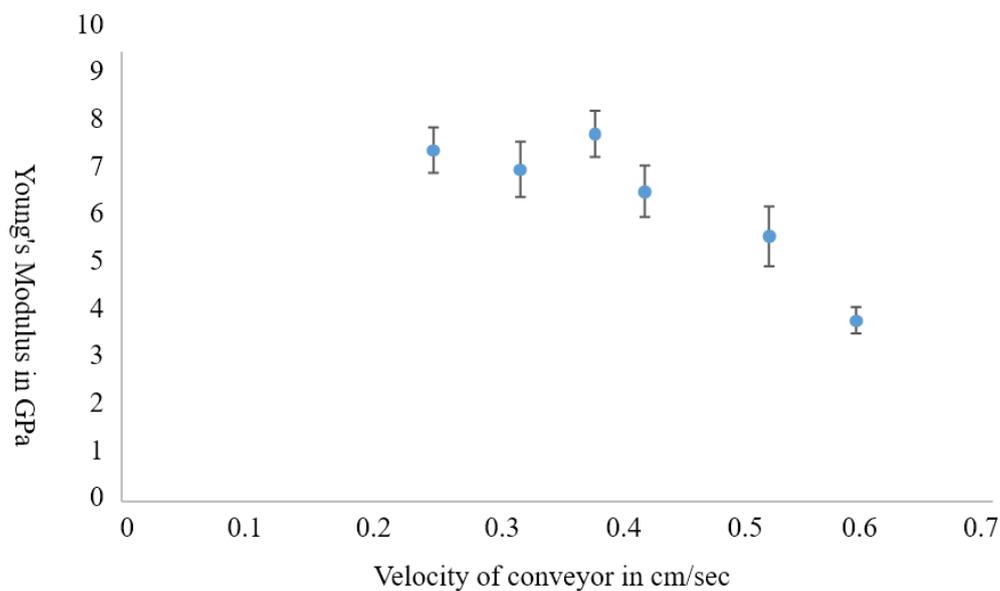


Figure 19. Influence of Conveyor Velocity on Young's Modulus of the spray coated sheet

Zero Span Test for Spray Coated Micro fibrillated sheet:
 Influence of the Suspension concentration: (as shown in [Figure 20](#))

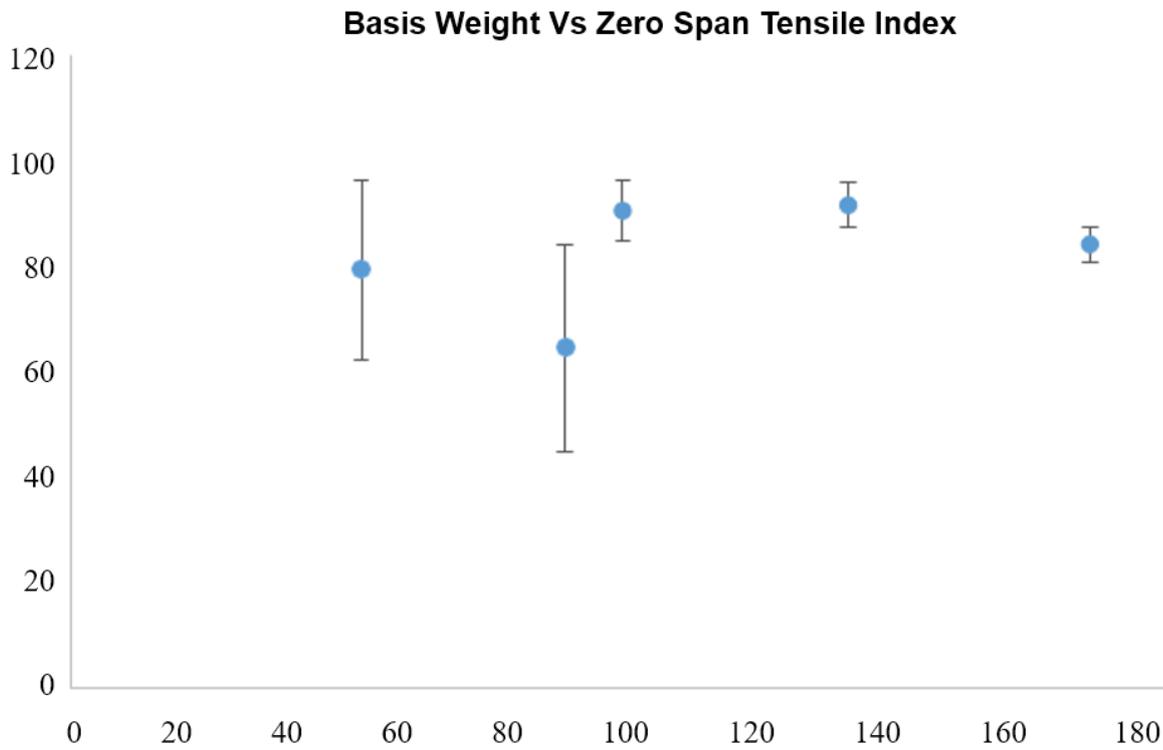


Figure 20. Zero span test of spray coated sheet prepared by different concentration of CNF.

Influence of Velocity of the conveyor: (as shown in [Figure 21](#))

Basis Weight Vs Zero Span Tensile Index

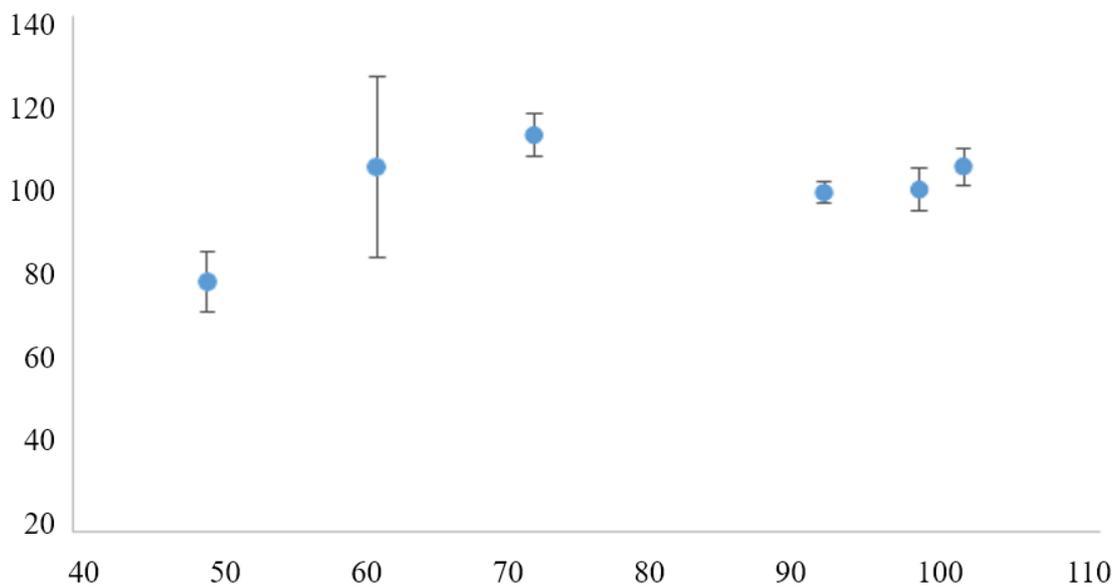


Figure 21. Influence of velocity of conveyor on the spray coated sheet.

The Figure 20 and 21 shows the zero span tensile indexes increased with the suspension consistency of CNF and decreasing the velocity of the conveyor.

Stress and Strain Curve for Spray Coated Cellulose nanofibre Sheet:
 Influence of suspension concentration: (as shown in Figure 22)

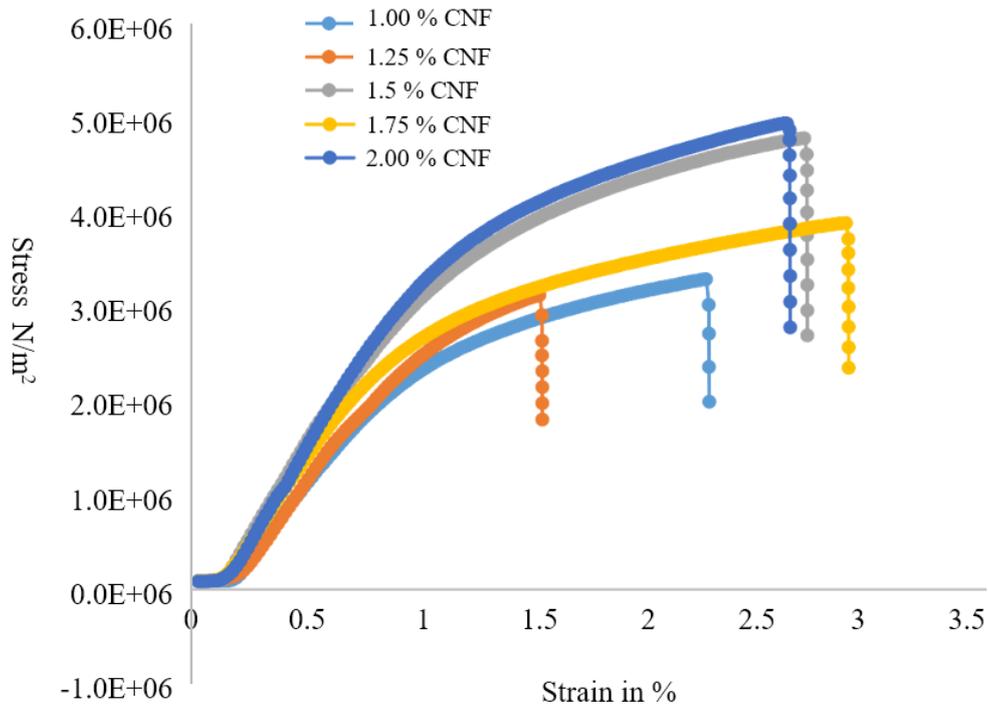


Figure 22. Stress and strain curve for CNF Film

Effect of velocity of the conveyor: (as shown in Figure 23)

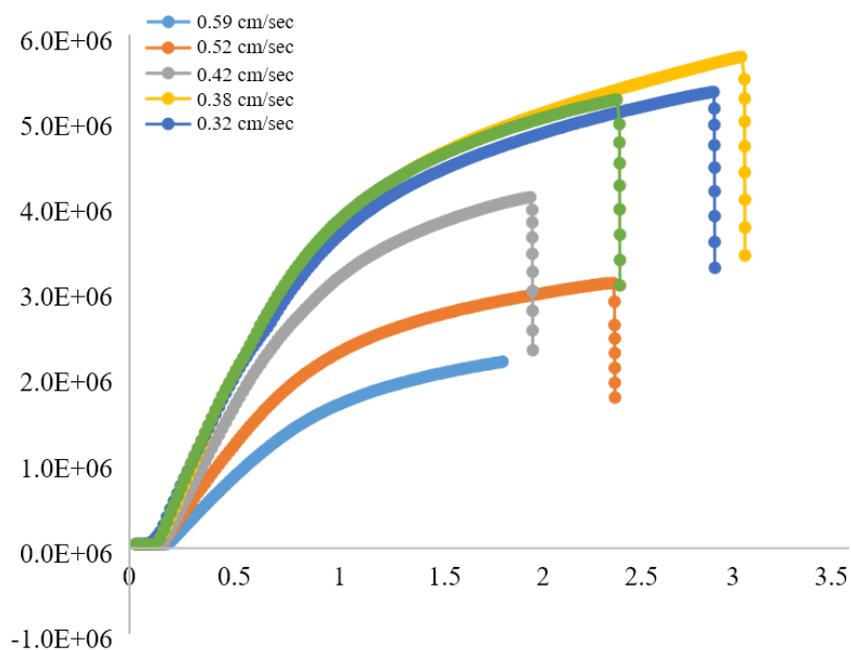


Figure 23. Stress and strain curve for CNF Film

Figure 22 and 23 shows the stress and strain curve for pure cellulose nanofibre film prepared via spraying. Figure 22 reveals that the strength of the film increased with increased CNF concentration. The sheet produced from lower CNF suspension concentration has flimsy in thickness and contains mark of ripples on the sheet. The sheet has very strong and good mechanical strength once the higher CNF suspension concentration sprayed on the steel plate. The optimization of conveyor's velocity is another parameter for controlling CNF film properties. Figure 23 confirms the effect of conveyor's velocity on the stress – strain curve of the CNF films. At lower conveyor speed, the cellulose nanofibres are deposited large on the stainless steel plate. The film has well in strength when the film fabricated via spraying 1.5 wt. % CNF on the plate kept in a moving conveyor at a velocity of 0.32 cm/sec. At higher velocity, the CNF are less deposited on the steel plates and the sheet becomes very flimsy after drying and lowest strength.

4. Summary

Spraying of micro-fibrillated cellulose suspension onto a polished stainless steel surface to make smooth films with a basis weight ranging from 50 to 200 g/m², simply by adjusting the suspension consistency, is an efficient technique at laboratory scale. This method confirms the faster formation of the sheet within a minute on the solid surface. 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.

4.1. Spray coating of cellulose nanofibre on the base sheet

The spraying cellulose nanofibre on the base sheet (Brown paper -Packaging material) could boost their barrier properties. Initially, the spraying of cellulose nanofibre on the packaging paper using domestic spray gun is performed. The spray coated brown paper is characterized for evaluation of performance of laboratory scale spray deposition method. Based on the laboratory scale performance of coating, the spray coating is upgraded with Professional spray gun integrated with Dow web coater for continuous process coating.

4.1.1 Materials and Methods

Micro fibrillated cellulose (CNF) supplied from DAICEL Chemical Industries Limited (Celish KY-100S evaluation) was used for spraying operation for coating purpose. The domestic spray gun is used for spraying cellulose nanofibre on the base sheet. The spray pattern is elliptical and the distance between spray nozzle and paper substrate is 20±2 cm. The coating of cellulose nanofibre on the paper substrate is one layer. The spray coated sheet is dried in the air drying under standard laboratory conditions.

4.1.2. Results and Discussion

Effect of Suspension Consistency on basis weight:

The Figure 24 and Figure 25 shows the effect of suspension concentration on the coat weight. Using lab scale spray coating, the maximum of 25-35 g/m² on the base sheet is spray coated with concentration of 1.5 wt. % of Micro fibrillated cellulose. At this concentration of spray coating of CNF on the base sheet, it forms film over the surface and this film acts as barrier materials.

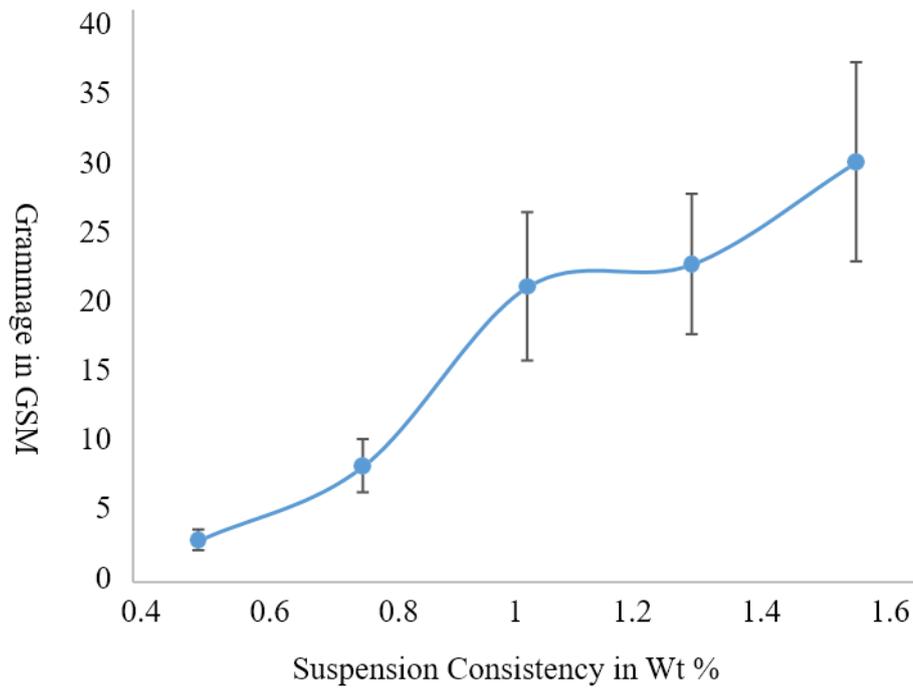


Figure 24. Plot of coat weight on the base sheet against suspension consistency

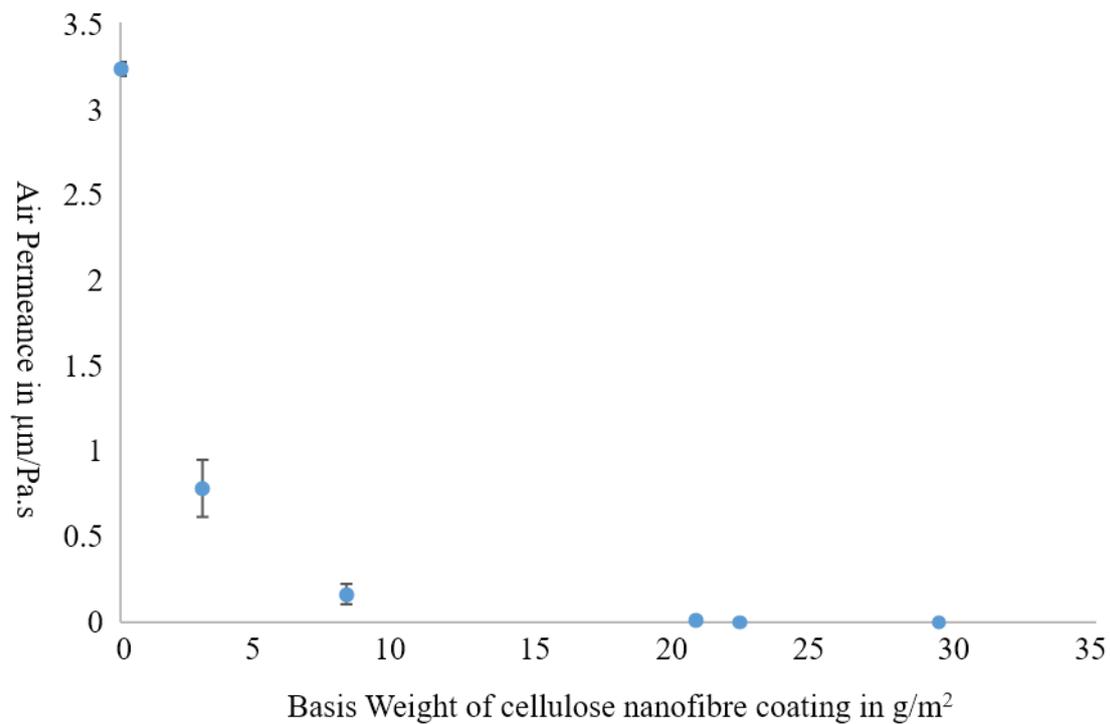


Figure 25. Plot between air permeance vs coat weight

The [Figure 26](#) shows the micrograph of the spray-coated paper with 1.25 Wt. percentage of the micro-fibrillated cellulose at low magnification. The micrograph (100μm) shows the deposited cellulose fibres clumps and fibres on the surface of the base sheet. It also confirmed the different size of the fibre entangled with cellulose fibres clumps on the surface. Moreover, the micrograph (100μm) confirms the complete

coverage of micro-fibrillated cellulose coating formulation on the base sheet. When compared to the micrograph (100 μm) of the uncoated paper, the coated paper showed that the coating formulation filled many surface pores and void space between the cellulose fibres.

SEM Studies on Coated Surface:

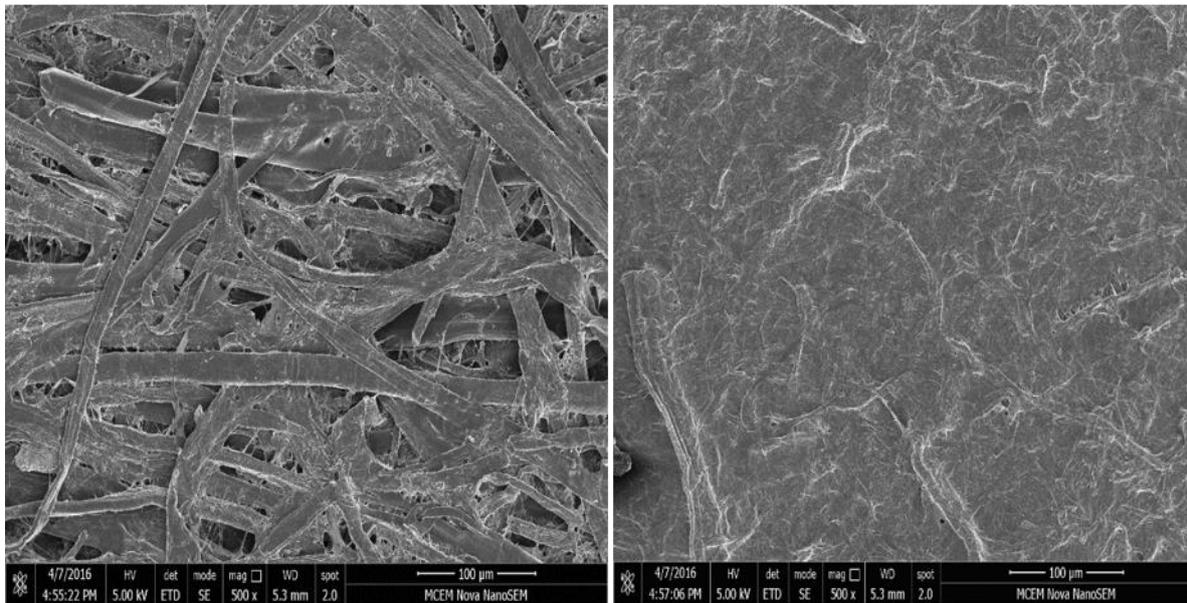


Figure 26. Micrograph of coated and uncoated paper

4.2. Continuous web-spray system

Scale Up from Laboratory Scale to Continuous Process

The spray coating of micro-fibrillated cellulose on the stationary paper using domestic spray gun confirmed promising results. However, these experiments have to be carried out batch wise. The integrated Dow web coater with professional Wagner spray system is developed for preparing similar spray coated material in a continuous mode.

Experimental Setup and Trial Run

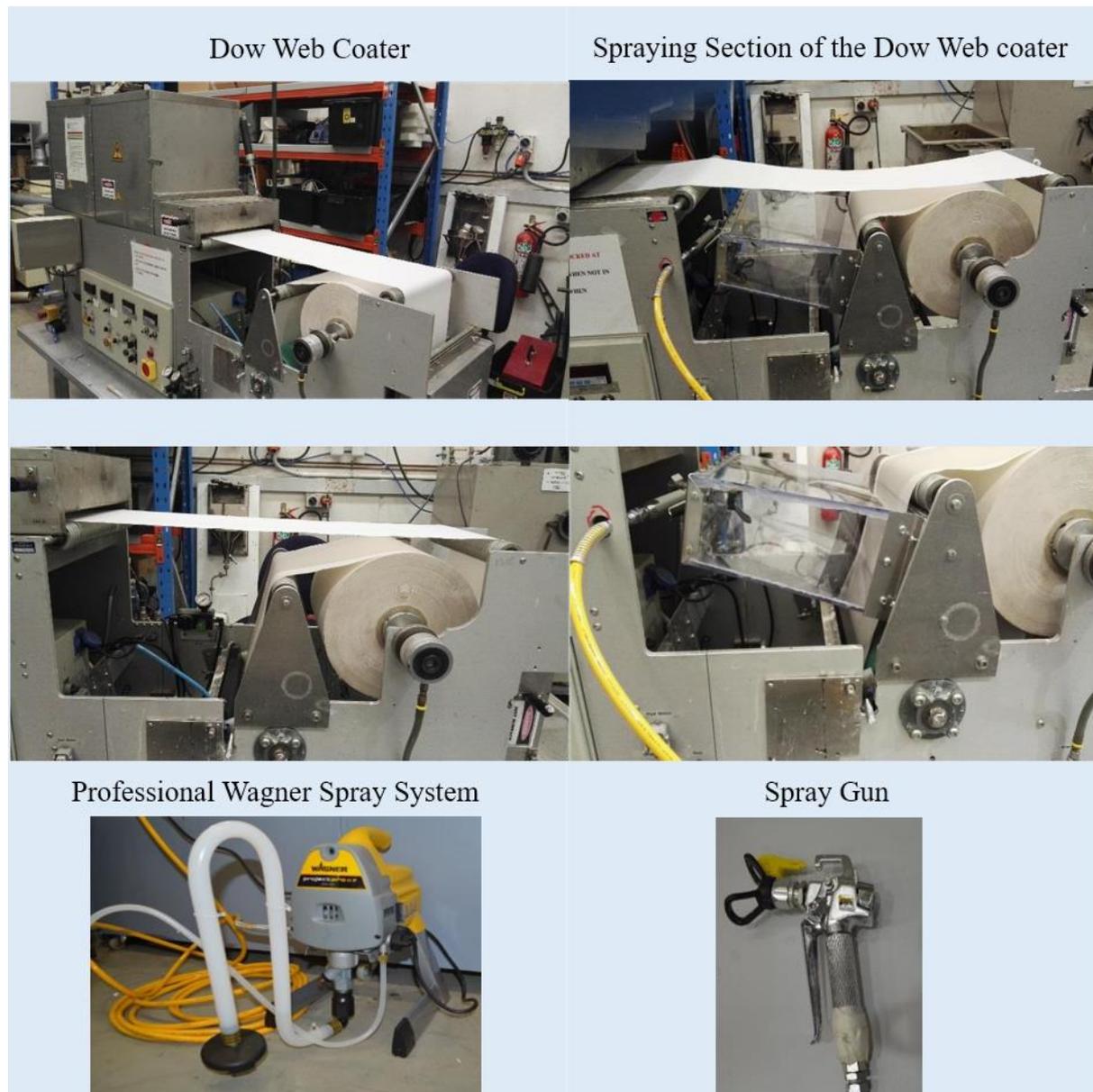


Figure 27. Components of Dow Web Coater integrated with Spray System

4.2.1. Preliminary Results

The suspension (CNF) sprayed on the base sheet is 1.5 Wt. % using this integrated Dow web coater with spray system. The CNF suspension from 0.5 to 1.00 Wt. % is also sprayed on the base sheet, due to continuous movement, the coating fluid is not stagnant on the base sheet and poor adsorption of the brown paper.

4.2.2. Limitations in the experimental set up

In the experimental setup for continuous process coating, the spray coated paper is stick to the other side of the paper when rewinding in the Dow web coater. It affect the coating surface on the base sheet. This problem arises due to the improper drying of the coated sheet in the dow web coater. Another limitation is dripping of the coating fluid

from the base sheet due to moving from downward to upward in the Dow web coater. The spray gun is planned to locate on top of web near to the infrared heater 1 in the Dow coater. This rearrangement might help to prevent the dripping of coating fluid on the base sheet and coating could be retained on the base sheet.

4.2.3. Conclusion

The preliminary results reported in this section confirms that the spraying of cellulose nanofibre on the base sheet allows the complete retention of cellulose nanofibre. The laboratory spray coating confirms that this techniques enhanced the barrier properties of the base sheet. For continuous spray coating of cellulose nanofibre on the base sheet, the dow web coater integrated with professional spray gun is used. In this experimental setup, the speed of the web controls the coat weight of cellulose nanofibre on the base sheet. Preliminary studies on dow web coater showed that spraying is a feasible technology to increase the barrier and mechanical properties of the base sheet.

4.2.4. Future Research

This project proposes to investigate the development of spray coating process for fabrication of various cellulose nanofibre based functional materials such as barrier layers, coating on the base sheet, nano composite with Nano clay and cellulose nanofibre crystal. When compared to the conventional method for developing cellulose nanofibre materials, spraying could provide contactless coating with substrate and a contour coat applied to uneven surfaces. Moreover, tear sensitive web materials could be coated with spray system and coating weight can be controlled by changing the web velocities. Spray coating is a contactless coating process. The topography of the substrate has no influence on the coating weight. On uneven surfaces a contour coat can be applied; a closed film can be achieved with a decreased amount of liquid. This could result in a reduction of costs and an improvement of quality. The lack of a metering coating gap leads to a decreased sensitivity for coating defects and a reduction of web breaks - even for very low coating weights.

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