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Article

Cellulose Nanofiber Lamination of the Paper Substrates via Spray Coating – Proof of Concept and Barrier Performance

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Abstract: Cellulose nanofibre (CNF) is a biorenewable and biodegradable nanomaterial and belongs to fibrous based carbohydrate polymers applied in the fabrication of various functional materials such as coating, nanocomposite, flexible electronics substrates and biomedical devices. Recently, CNF can be used as coating material for papers and paperboards to replace synthetic plastics, wax and aluminum foil which is not recyclable and also a threat to environment. The coating of CNF on the paper substrates enhances their barrier and mechanical properties. Spray coating is a newly proposed technique to deposit CNF on the paper and produce CNF laminates on the surface of paper to block their surface pores and allowing improve their barrier performance against water vapor, air and oxygen. Various concentration of CNF was sprayed on various paper substrates such as newsprint papers, packaging paper (brown paper) and blotting papers. The air permeability of CNF laminated paper substrates is completely impermeable against air. The SEM micrograph reveals that the surface pores in the paper substrates are filled with sprayed CNF and formed a barrier film as a laminate on the paper substrates. As a result, a considerable drop in the air permeability of the paper substrates was observed. Given this correspondence, spraying of cellulose nanofiber on the paper substrates allows the improvement of barrier performance and proof of concept for coating CNF on the paper and paperboard.

Keywords: Cellulose nanofibre (CNF), Spraying, Air permeability, and Mechanical properties

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1. Introduction

Generally, synthetic plastic materials are being used as packaging materials for various conventional applications. These synthetic plastic materials have an excellent barrier potential against air, water vapor and oxygen. However, these materials give a threat to environment such as worst recyclability and biodegradability. Conventional practice, aluminum foil and synthetic plastic layers are used as barrier coating for paper and paper board. Synthetic plastic materials and the aluminum are renewable and these composites are not susceptible for recyclability. In order to overcome this problem, biobased fibrous material is required to improve the barrier performance as well as minimize disposal or recycle problems [1].

Figure 1 shows the necessary of biobased coating on the paper and paperboards. Paper and paperboard are cellulose macrofibre based substrates having large surface pores. Because of these large surface pores, poor barrier performance was achieved [3]. As discussed above, the barrier performance of the paper and paper board will be enhanced by coating with wax or synthetic plastics or extrusion with aluminum foil. However, these approaches are not ecofriendly and poor recyclability. Recently, biobased coatings of paper and paperboard are a novel technology and improve the barrier potential of these substrates. Cellulose is one of the predominant fibrous carbohydrate polymers and bio-renewable, biodegradable and abundantly available in nature and potential feedstock for the development of various sustainable functional materials such as coatings, films and membranes on an industrial scale for production [4]. The cellulose based coatings on the paper and paper board solves the limitations such as recycling, disposal and incineration of waste[1].

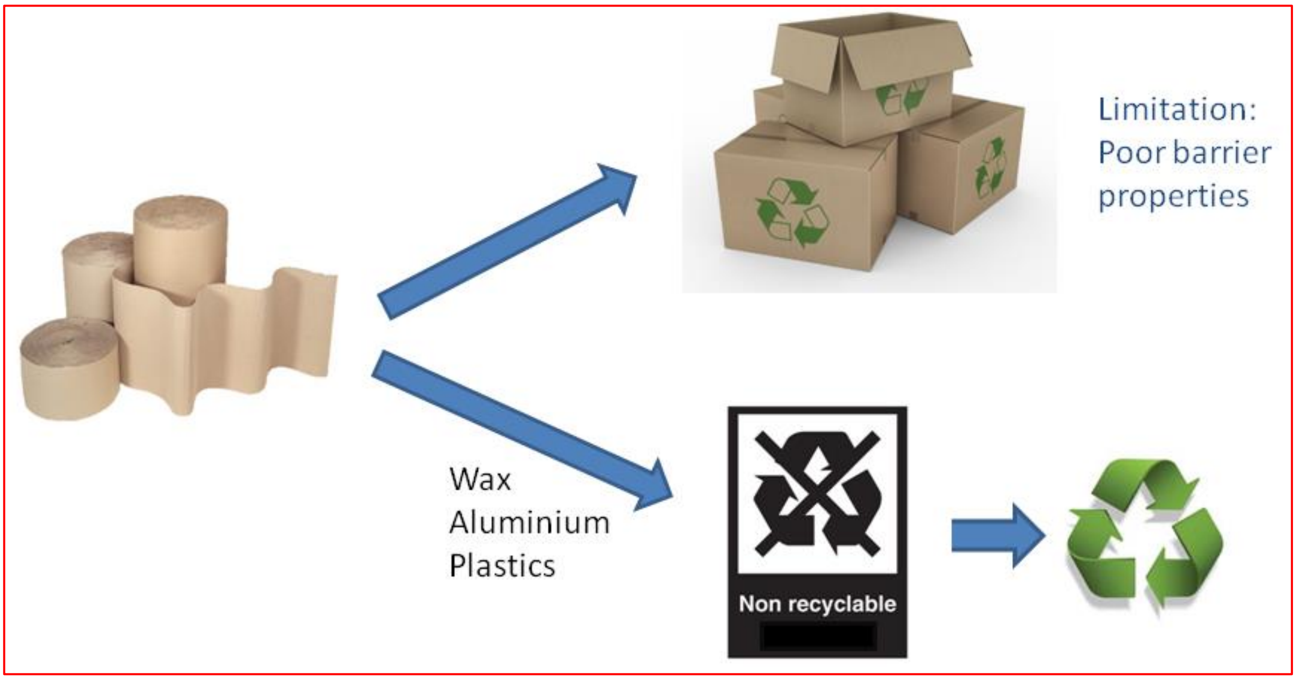

Figure 1. Necessity of CNF coating on the paper substrates [2]

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 delaminating 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 micrometers in length [5, 6]. Moreover, having a smaller dimension and a larger surface, cellulose nanofiber is a great opportunity to be developed more functional materials for various applications [7]. These Cellulose fibrils at micro/nano scale are used to functionalize paper substrates by coating or to make freestanding sheets/films and nanocomposites [8].

Cellulose nanofibre is a novel material derived from cellulose macrofibre and produced by disintegration and delamination of cellulose fibrils from various pulps such as wood, potato tuber, hemp and flax. The diameter of cellulose nanofibre varies from 5 to 100 nm and their length in several microns. Lowest reduction of diameter of CNF gives highest surface area. Cellulose nanofibre can be used as potential biomaterial for fabricating functional materials [4, 9-15]. Cellulose nanofibres are used to coat paper substrates for enhancing their barrier and mechanical properties [16].

Cellulose nanofibre also denoted as micro fibrillated cellulose (MFC), nano-fibrils, micro-fibrils, nanocellulose and nano-fibrillated cellulose (NFC). The processing of cellulose nanofibre from wood via various chemical, enzymatic, and/or mechanical treatments was achieved.CNF has high aspect ratio, high specific strength, flexibility, large specific surface area, and thermal stability, combined with biodegradability and good biocompatibility for developing tissue engineering scaffolds. These properties of CNF allows for a wide range of applications, such as nanocellulose film [8], reinforcing phase in composite materials [17], barriers in packaging [11, 18], rheology modifiers for suspensions [19], filters for virus removal and water treatment technologies [20, 21], flexible platforms for biomedical applications [22] and printed electronic applications [23].

It has been proved that the films/sheets and its nano composites made from cellulose nanofibre and coated with fiber substrates increased the barrier and mechanical properties [24]. Due to outstanding multifunctional barrier properties such as oxygen and water transfer rate, it has the potential for application of packaging materials for foods [11, 25, 26].

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 via various coating process. The previous studies confirmed that cellulose based coating on the paper based substrates substantially improved their barrier and surface properties [10, 25, 27]. 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. Figure 2 shows different coating processes for paper applications and their details are updated in Table 1 in the supplementary information.

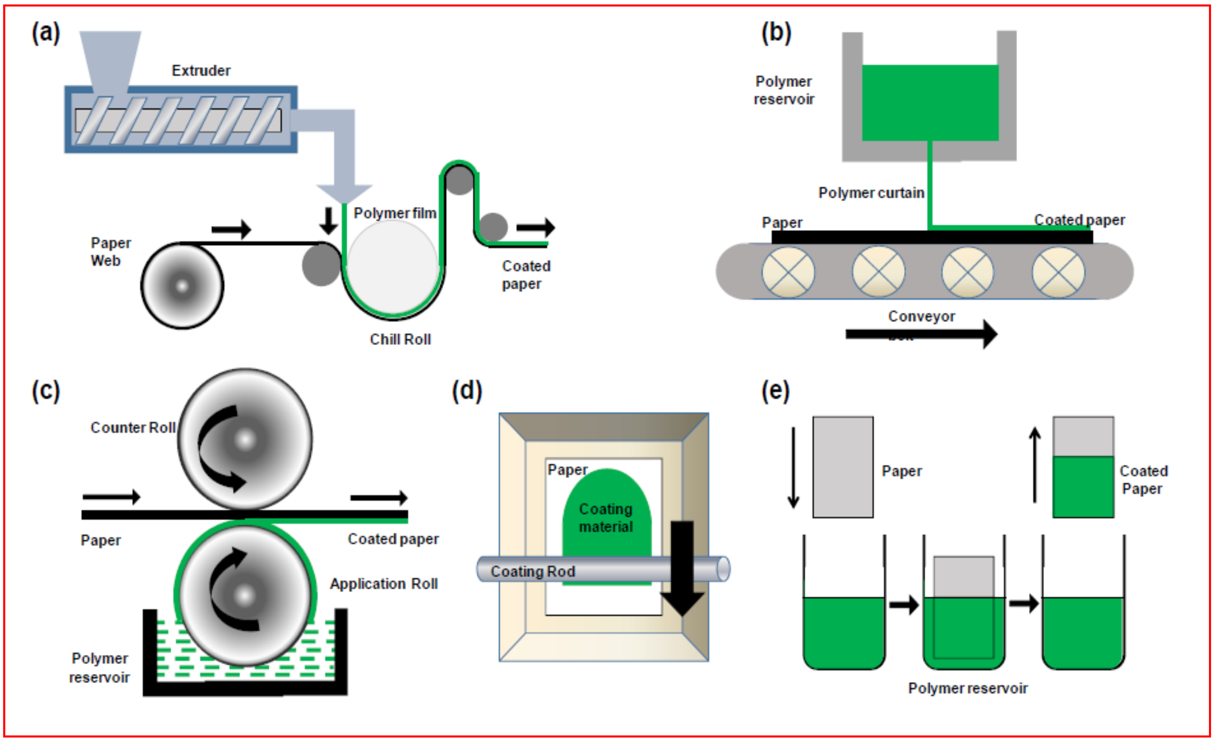

Figure 2. Different coating processes for paper applications, (a) extrusion coating; (b) curtain coating; (c) size press coating; (d) bar coating; and (e) dip coating. (36)

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 paper substrates, and solvent-free application. However, it has shortcomings in the coating performance such as low coat weight, thickness, instability of the polymer during melting stage, coating speed and efficiency. High coat weight is required to achieve the necessary barrier properties. It is only suitable for coating of thermoplastic polymers. Given that cellulose nanofiber is not thermoplastic it can only be suitable as a coating formulation by either dissolving cellulose nanofiber in a suitable solvent (*i.e.*, solvent coating/casting), or dispersing the polymer in solvent (*i.e.*, dispersion coating) [28, 29].

In dispersion and solvent coating methods, low coat weights around 10g/m^2 can be used to achieve the barrier layers of the paper substrates, but sometimes two layers are mandatory to coat to eliminate the surface pinholes and achieve a sufficient water vapour barrier 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 (MFC) 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 [24].

Curtain coating is where a uniform coating is applied and found sufficient to cover the entire surface. This method of coating produces a barrier layer with better gas and water vapour barrier properties. In size pressing, the coating is not covering 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[30]. Dip Coating is the quick testing performance of coating at laboratory scale. However, the coating thickness of the paper substrates is difficult to control and hence always find practical application at the laboratory scale [1]. Due to its film forming capacity, cellulose nanofibre could be used as coating layer on the paper substrate 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 MFC coat weight barely reached to 4 g/m^2 from ten successive MFC layers on the paper substrate. The bar coating of MFC on the paper board was found not to substantially enhance its barrier properties, however did increase stiffness while reducing compressing strength [31, 32]. 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 [33].

Micro-fibrillated cellulose (MFC) 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 MFC 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/m^2/day) [34].

Although above mentioned conventional processes offers some advantages, they poses serious limitations such these methods should as they are done in batches and/or are 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 CNF on the paper substrates [35] [36].

Spraying CNF suspension on the paper substrates is a novel method for increasing their barrier and mechanical properties [3, 37]. The common advantages of spraying were the formation of homogeneous layer and contour coating on the substrates [16, 38]. The handling of high CNF suspension in spraying is much higher than vacuum filtration which is conventional process for paper making and laminating/coating on the paper. Spraying process is capable of handling a higher initial solid content compared to filtration, reducing the amount of water that has to be removed in subsequent drying. The barrier performance of the spray coated CNF on the paper substrates are not explored so far. This paper deals about the spray coating of CNF on various paper substrates as proof of concept and the evaluation of barrier potential of CNF laminated paper substrates [16].

This work mainly focus on development of spray coating method for tailoring the barrier performance of paper substrates via CNF lamination, optimize CNF suspension consistency for spraying CNF on the paper substrates, the air permeability of CNF laminated paper substrates, giving this laboratory scale proof of concept into scale up for spray coating CNF on the papers [39].

Table 1. Coating of CNF on the paper substrates using various methods [39]

Type of Cellulose	Substrate	Methods	Function	Coat Weight	WVTR (g/m^2 day)	OTR or Air Permeability
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
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 8 g/m^2	NA	0.3 nm/Pa s. 0.2 nm/Pa s 0.009 and 0.0006 cm^3 µm/ (m^2 day kPa)
Micro-fibrillated cellulose	calendared paper (41 gsm)	Bar Coating Size Pressing	-	7 g/m^2 4 g/m^2	NA	786 ± 166 nm/Pa.s 4856 ± 1717 nm/Pa s.
Micro-fibrillated cellulose	Card board (300)	Bar coating	-	17±1 g/m^2	NA	0.18±0.01 cm^3/m^2 pa.s
Nanocellulose	Fibre based substrates	Foam Coating	Tailoring the surface properties of the sheet and Functionalization	0.3 -2 g/m^2	NA	NA
Micro-fibrillated cellulose	Composite paper	Forming and Dewatering-Filtration	MFC composite Paper	NA	NA	NA
Nano-emulsified Nanocellulose	Addition of the Nano emulsified Nanocellulose	Vacuum Filtration	Nanocellulose sheet	NA	NA	$2.75*10^{-08} \pm 0.9*10^{-8}$ K(m^2)
Micro-fibrillated cellulose	Porous Paper substrate	Spray Coating	Barrier and Mechanical Properties Enhancement	6 g/m^2	NA	Drastically Reduced
Graphite Carbon Black Micro –Fibrillated cellulose	Wet Paper Substrate	Spray Coating	Electrode	NA	NA	NA

2. Materials and Methods

The nomenclature for cellulose nanofiber has not been reported consistently in the literature. As well as cellulose nanofiber (CNF), it is also called micro-fibrillated cellulose (MFC), cellulose nano-fibrils, cellulose micro-fibrils, nano-fibrillated cellulose (NFC) and Nanocellulose (NC). In this paper, we use CNF as the generic term for the cellulose nanomaterials used. The CNF used was supplied from DAICEL Chemical Industries Limited (Celish KY-100S) at 25% solids content. DAICEL CNF (Celish KY-100S) has cellulose fibrils with an average diameter of ˜ 73 nm with a wide distribution of fibre diameter, a mean length of fibre around 8µm and an average aspect ratio of 142 ± 28. DAICEL KY-100S is prepared by micro fibrillation of cellulose with high-pressure water. The crystallinity index of DAICEL cellulose nanofiber was measured to be 78%. CNF suspensions were prepared using by diluting the original concentration of 25 wt. % to 0.25 wt. % to 1.5 wt. % with de-ionized water and disintegrating for 15,000 revolutions at 3000 rpm in a disintegrator [39]. The paper substrates used for coating study are newsprint paper, blotting paper and brown paper.

2.1. Evaluation of Viscosity for CNF suspension

The viscosity of the cellulose fiber suspension is evaluated to find the sprayable concentration of CNF suspension. CNF sample was used at consistencies ranging from 0.25 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 [39].

2.2. Spraying cellulose nanofiber suspension on the paper substrates

Cellulose nanofiber 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 nanofiber on the paper substrates. 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 pass to form a layer. The spray coated sheet is dried in the air drying under standard laboratory conditions. The experimental set is shown in Figure 3.

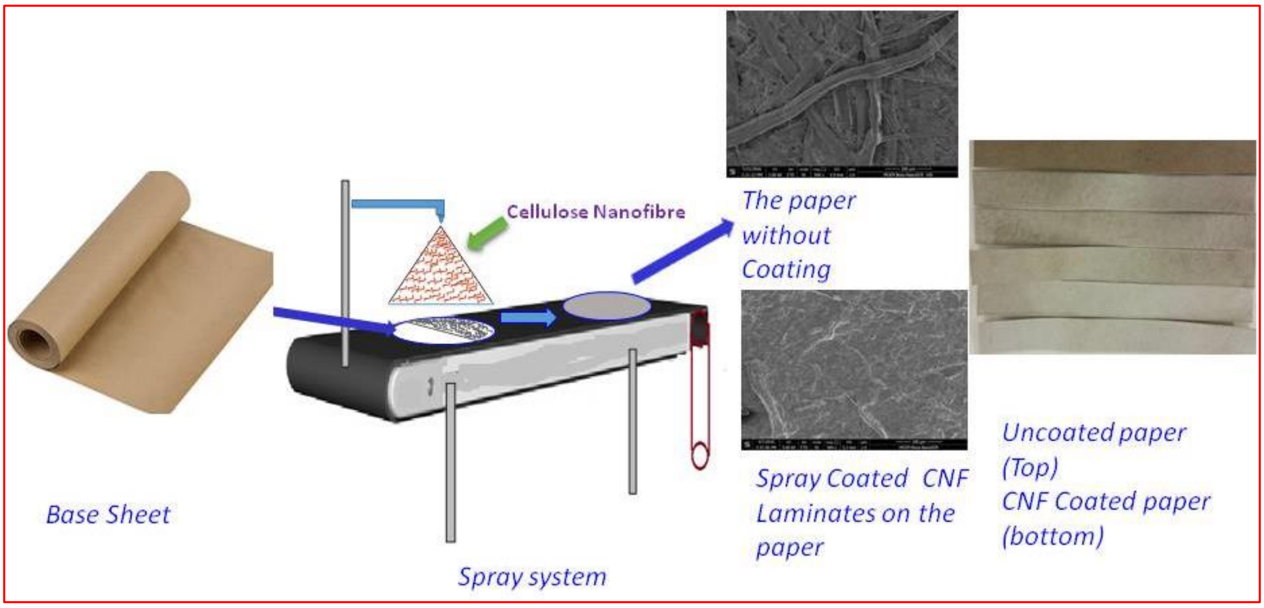

Figure 3. Spray coating experimental system for coating CNF on the paper substrates

2.2.1. Drying of spray coated CNF laminates on the paper substrates

The spray coated CNF on the paper substrates were dried in the open air with specific care in the standard laboratory conditions. The dried CNF layers on the paper substrates used for various characterizations such as surface topography, basis weight, thickness, barrier properties and mechanical properties.

2.3. SEM Investigation of Spray coated CNF on the paper substrates

2.3.1. Sample Preparation

The spray coated paper (4mm X 4mm) is fixed on the metallic stab using carbon tape and blowed with Nitrogen to remove the any dust or any loose material on the sample and then coated with Iridium with a maximum thickness of 10μm. Moreover, the iridium coated samples are blowed off with Nitrogen to remove any dust and loose materials on the sample before loading into the FEI-NOVA Nano SEM 450 [3].

2.3.2. Parameters for Scanning Electron Microscopy

Cellulose nanofibre is a biodegradable and delicate material in nature and highly susceptible to high accelerating voltage. Therefore, the parameters for collecting micrograph are optimized. The surface morphology and topography of the spray coated paper was characterized using FEI–NOVA Nano SEM 450.

Mode 1: This mode is used for collecting the low resolution micrograph at 100 μm and this micrograph is ideal for investigating the survey of the surface of the cellulose nanofibre coated paper substrates and the roughness of the coated surface. The optimized parameters for high voltage and spot size are 3 KV and 2.00 respectively. The working distance and aperture size are 5 mm and 6 (30 mm).

Mode 2: This mode is used for collecting the micrograph at 1μm and 10μm (high resolution (UHR) imaging) and this micrograph is ideal for investigating the fibre orientation and size of the fibres and pores in the surface of the spray coated surface. The optimized parameters for high voltage and spot size are 3 KV and 2.00 respectively. The working distance and aperture size are 5 mm and 6 (30 mm).

2.4. Basis weight of the CNF Coating on the paper substrates

The basis weight (g/m^2) of spray coated CNF laminates on the paper substrates was calculated by dividing the weight of the coated sheet, after 4 hours drying in the oven at a temperature of 105 °C, by the paper area.

2.5. Thickness of the CNF coating on the paper substrates

The thickness of the spray coated CNF laminates on the paper substrates was determined using a Thickness Tester Type 21 from Lorentzen & Wettre AB, Stockholm, Sweden. The thickness was evaluated at fifteen points and averaged. The thickness was measured according to TAPPI T 411, 2015.

2.6. Barriers Properties of Spray coated CNF laminates on the paper substrates

Air Permeability

The air permeance of dried CNF coated paper substrate was measured with an L&W air permeance tester with an operating range from 0.003 to 100 μm/Pa.S. The mean value of air permeance evaluated from 3 different areas of each CNF coated laminated paper was reported. The Technical Association of the Pulp and Paper Industry (TAPPI) standard T 460 is used to measure the air permeance of the CNF coated paper substrates.

3. Results and Discussion

Spraying CNF on the paper substrates is a novel method for improving the barrier performance of the paper substrates [3, 37]. However, CNF suspension is a Non Newtonian fluid and comes under the category of "pseudo plastic behavior (Shear thinning)" and spraying CNF suspension is a challenging task in fluid flow phenomena [42, 43]. The viscosity of the CNF suspension is estimated via a dip cup method for spray coating on the paper substrates. When CNF solid content increase in the watery suspension, their viscosity is also increased [44].

3.1. Estimation of Sprayable Concentration of CNF

Figure 4 reveals the viscosity of CNF suspension evaluated via Brookfield dip cup method. This method decides the viscosity of CNF suspension to be sprayed. This result confirm that the low CNF suspension consistency gives watery suspension and easy to spray on the paper substrates. The viscosity of CNF suspension increased with fibers content in the suspension [42, 43].

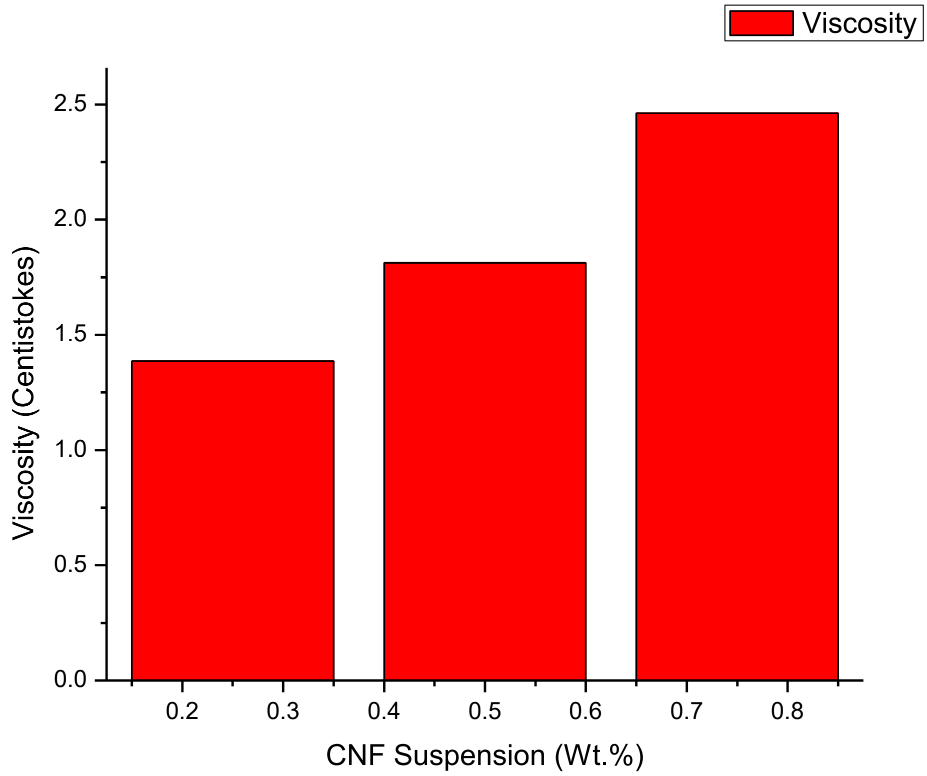

Figure 4. Viscosity of CNF suspension using Brookfield dip cup Method

Figure 5 shows the viscosity of CNF suspension evaluated via dip cup method. As discussed earlier, the viscosity of CNF suspension increases with fiber content in the suspension. In this plot, below 1 wt. % of CNF suspension shows the watery suspension and easy to spray on the paper substrates. However, the watery suspension does not wet the paper substrates easily and poor adhesion between the cellulose nanofibrils and paper substrates. Above 1 wt.% of CNF suspension, the viscosity becomes thick and completely shows non Newtonian behavior and challenging for spraying the suspension. 1.5 wt. % is a good formulated suspension CNF consistency for spraying on the paper substrates and CNF shows well adherence on the paper substrates. Above 2 wt. %, CNF suspension shows solid suspension and hard to spray via a domestic spray gun [44]. The reengineering of spray system can handle high suspension consistency to coat the paper and it will increase the barrier performance of CNF lamination on the papers [45].

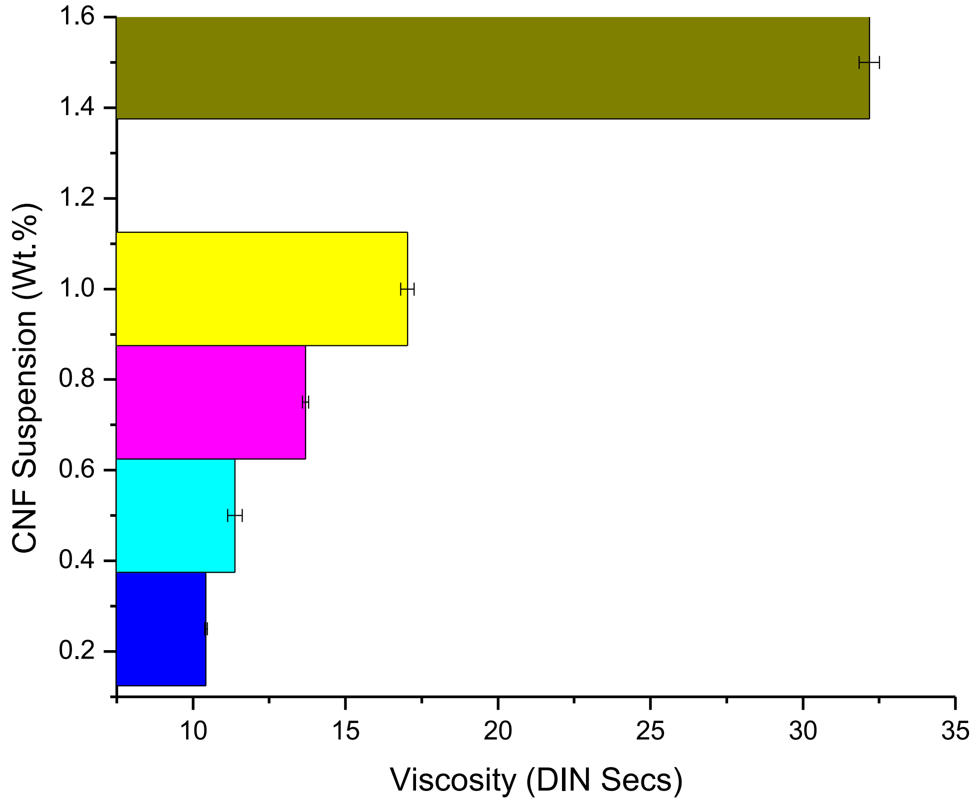

Figure 5. Viscosity of CNF suspension using dip cup Method

3.2. CNF laminates on the paper (Visual Observance)

Figure 6 and Figure 7 show the spray coated CNF laminates on the brown paper. Figure 6 shows the wet CNF lamination on the paper substrates confirming that the spraying CNF covers the paper surface completely. The spraying process allows the proper distribution of cellulose nanofibrils on the paper surface. Figure 7 shows the dried CNF laminates on the paper substrates confirming that there were fillings of surface pores on the paper substrates by cellulose nanofibre. The coat density increased with CNF wt. % suspension sprayed on the paper substrates [3].

Figure 6. Spray Coated Wet Laminates of Cellulose nanofibre on the paper

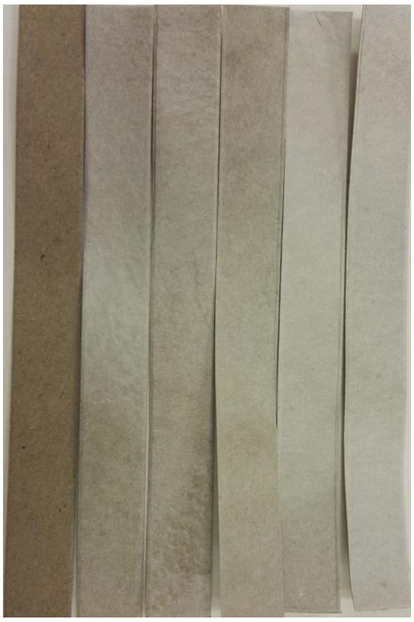

Figure 7. Dried Spraycoated CNF laminates on the paper

3.3. Barrier Properties of CNF coated paper substrates

Figure 8 reveals the effect of spray coated CNF laminates on the air permeance of various paper substrates. The graph really shows that the spraying of CNF suspension on the paper substrates drastically reduce the air permeance of the sheets. The effect of paper substrates and their structure also play a major role in this process and adhesion between CNF and paper surface and surface pores in the paper surface controls their air permeance. The air permeance of uncoated blotting paper is >12.39μm/Pa.S and coated with 0.25 wt % CNF coating on the blotting paper give a reduction of air permeance to <2.48μm/Pa.S. It is confirmed that CNF fills the surface pores on the blotting paper which is the reason for reduction of air permanence. It was observed for all types of paper substrates when coat with CNF. Spraying of CNF fibers at lower concentration results the reduction of air permeance through CNF fills surface pores of the paper substrates. CNF films were formed on the paper substrates when spraying of CNF suspension at higher concentration performed on the paper substrates. It was shown in the Figure 7 confirming that increase CNF coating on the paper would increase the coat density on the paper through the formation of CNF film which acts as barrier against air and water vapor.

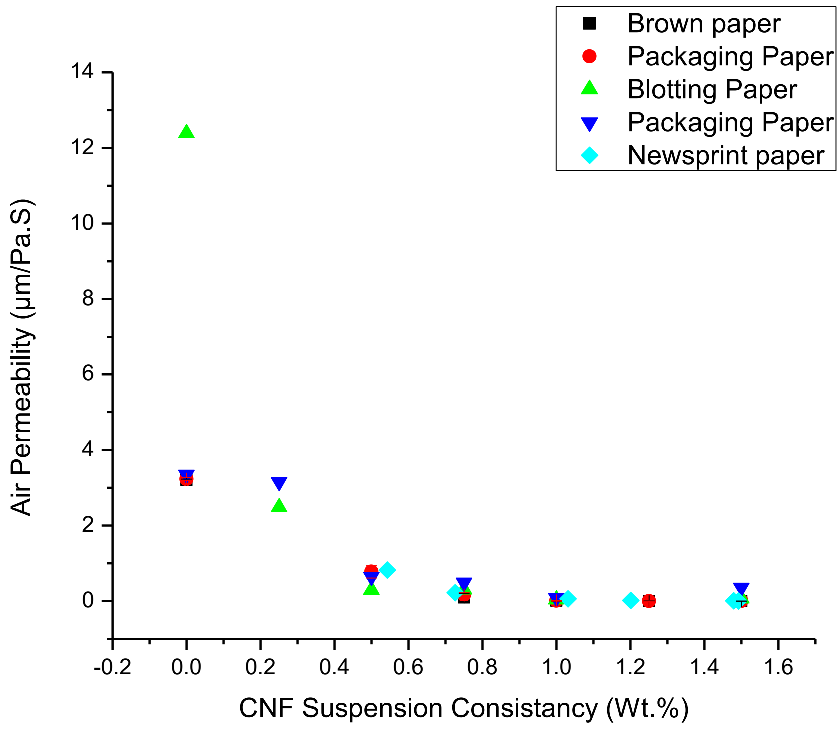

Figure 8. Plot between CNF suspension consistencies versus Air permeability of the CNF coated sheet.

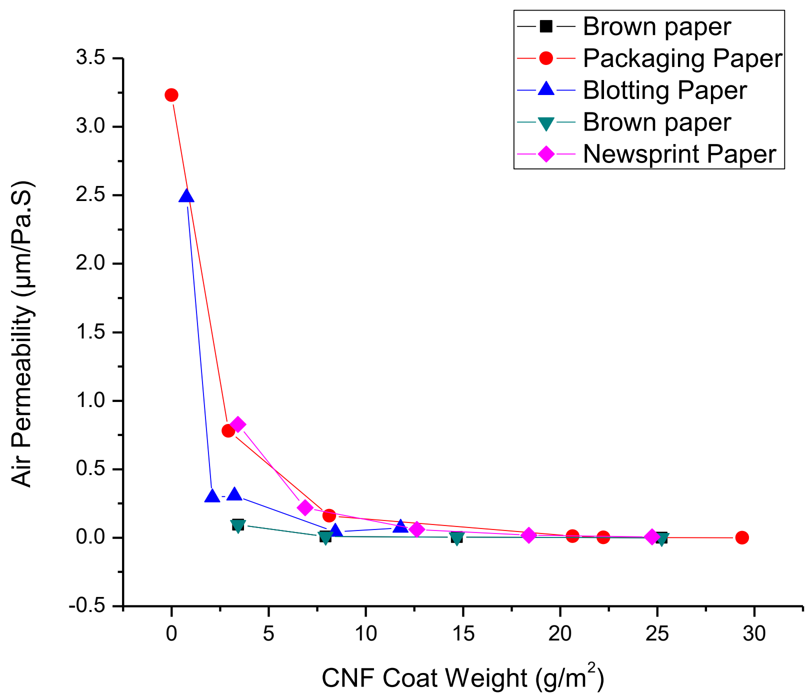

Figure 9. Plot between CNF coat weights versus Air permeability of the CNF coated sheet.

Figure 9 shows the effect of CNF coat weight on the air permeance of paper substrates. Figure 9 is the replication of Figure 8 and plotted between air permeability of the paper substrates and CNF coat weight. At lower coat weight, CNF filled the surface pores of paper substrates. As a result, the air permeances of the CNF coated sheet were stared to reduce from the initial value. When increase the coat weight via spraying of high CNF concentration on the substrates, the CNF film were formed on the paper substrates and acted as barrier against air and other gaseous substances.

3.4. Basis weight and Thickness of the CNF Coat Paper Substrates

Figure 10 shows the plot between CNF coat weight and CNF coat thickness. The plot concludes that there is directly proportional between CNF coat weight and CNF thickness. CNF Coat weight and thickness on the paper substrates can be tailored by varying the CNF suspension concentration. Unlike Vacuum Filtration, Spraying has no limitation in the handling of either low CNF concentration or high CNF concentration for coating on the paper substrates. In the case of vacuum filtration, handling high CNF concentration is a real challenge and consumes high dewatering time. Spraying has an operation time of less than a minute and its operation time was independent of CNF suspension concentration [44, 45].

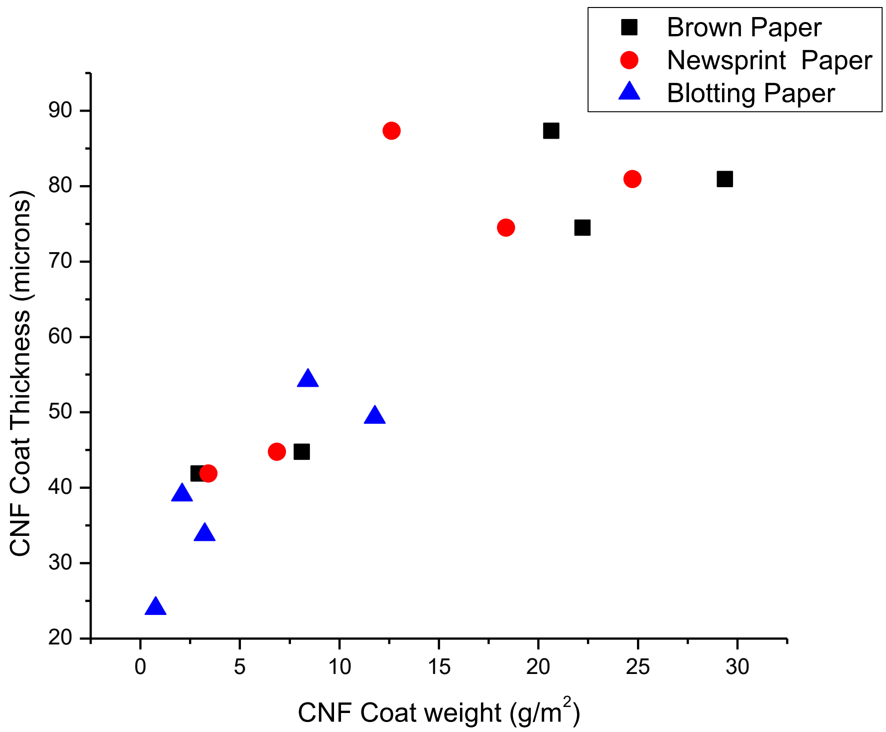

Figure 10. Plot between CNF coat weight and CNF coat thickness

3.5. Surface Roughness of CNF coat on the paper substrates

Figure 11 shows the plot between surface roughness (ml/min) and CNF suspension consistency. Spraying of CNF on the paper substrates increase the surface roughness of the CNF laminates on the paper substrates. At lower CNF suspension consistency, less cellulose nanofibrils coated on the surface of paper substrates. The lowest CNF coating gives low surface roughness of the CNF laminated paper substrates. When increase coat density via spraying of high CNF suspension on the paper substrates, their surface roughness of the sheet were elevated. An important quality of the coated paper is surface roughness which is also an influencing property in barrier performance and their mechanism remains obscure. In addition to that, surface roughness of the coated paper substrates plays a major role in the printability [46].

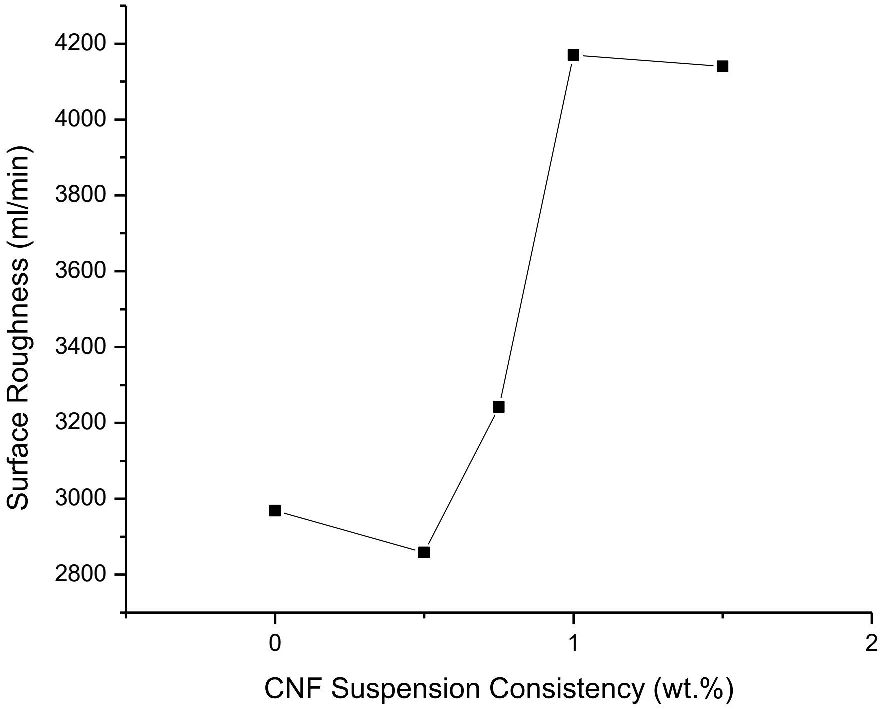

Figure 11. Plot between surface roughness (ml/min) and CNF suspension consistency

3.6. Mechanical Strength

Figure 12 shows the mechanical performance of the CNF laminated packaging paper. The plot informs the CNF coating on the paper substrates increasing their mechanical strength via cellulose nanofibrils with paper substrates [47]. At low coat weight, the tensile index (TI) was increased and cellulose nanofibrils were well adhered to the paper substrates. At lower coat weight, the plastic mechanical behaviors of CNF laminated paper substrates have been observed. The tensile index was decreased and also fluctuated at higher coat weight of CNF and showed brittle behavior of coating at higher coat weight. The adhesion between CNF and paper substrates were poor at higher coat weight and formed a CNF film on paper substrate and easily peeled from the paper surface due to high coat weight [38, 46].

Figure 13 shows the specimen breakage during the evaluation of mechanical strength. As we discussed earlier, the CNF films are formed on the paper surface at higher coat weight. During the measurement, the film can be tore first and then paper substrates were broken. At this condition, CNF film gives a separate stress –strain data apart from the stress –strain curve of the paper substrate. Due to poor adhesion between CNF layer and paper surface and brittle nature of high coat weight of CNF on the paper, the layer was peeled from the paper surface and either CNF layers breaks first or paper substrate breaks during the tensile strength evaluation [38, 46].

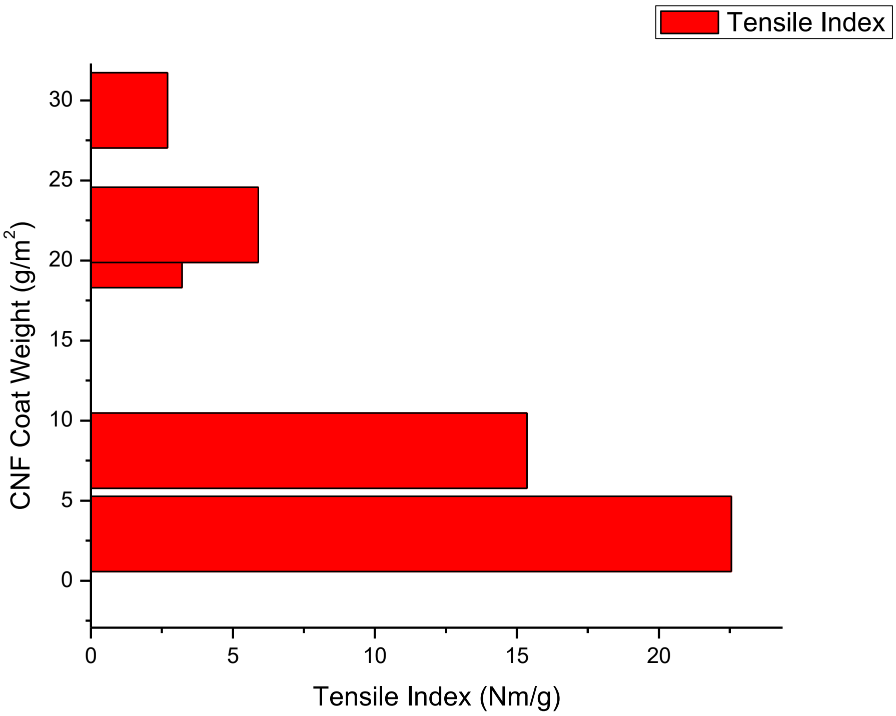

Figure 12. Mechanical Strength of CNF laminated paper sheet

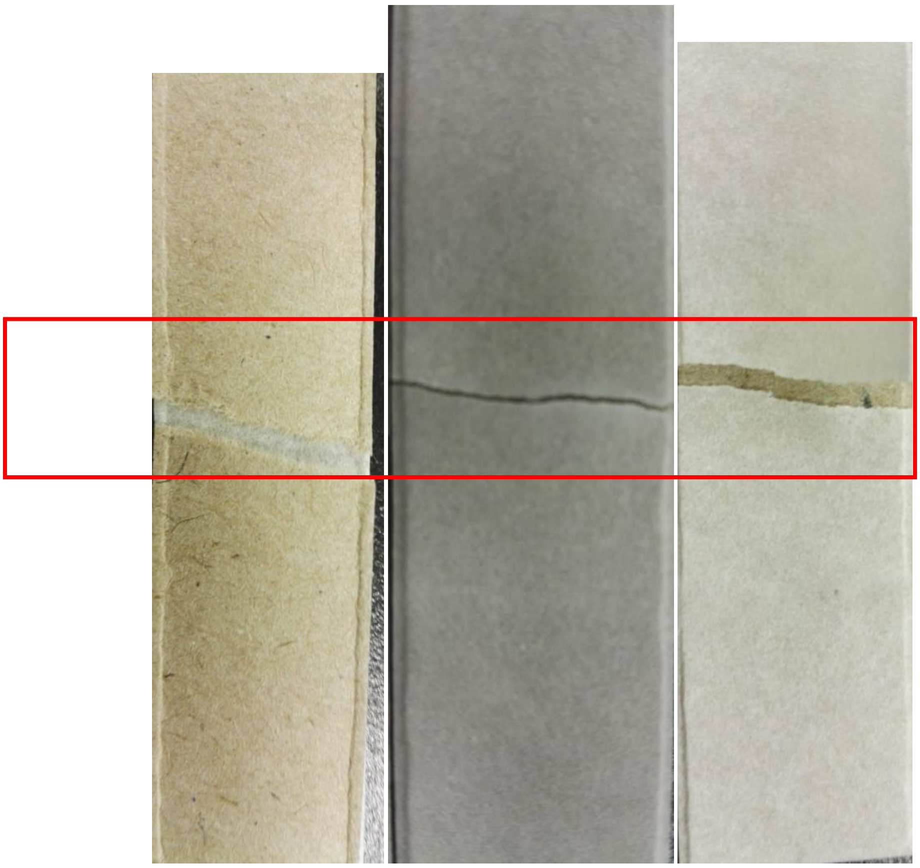

Figure 13. Sample Breakage during Mechanical Testing. Sometime the breakage of CNF layer will be first and then paper substrate.

3.7. SEM Micrographs

Figure 14 shows the SEM micrographs of the uncoated packaging paper confirming that the surface pores of the paper are opened. The openings of surface pores in the cellulose matrix (paper) are the main reason for elevating the air and gaseous transport. The barrier properties of the packaging paper can be elevated by the coating of CNF with paper surface. During coating process, the surface pore can be closed and allowed for increasing the barrier performance of paper substrates. In the high magnification of SEM Micrographs, there is an aggregate of CNF suspension on the paper substrates. It was formed due to accumulation of fibers from spray gun. An advantage of coated aggregates on the paper substrates is a creation of tortuous pathway in CNF lamination. As a result, air and other gaseous molecules diffuse across the paper in a longer way [18].

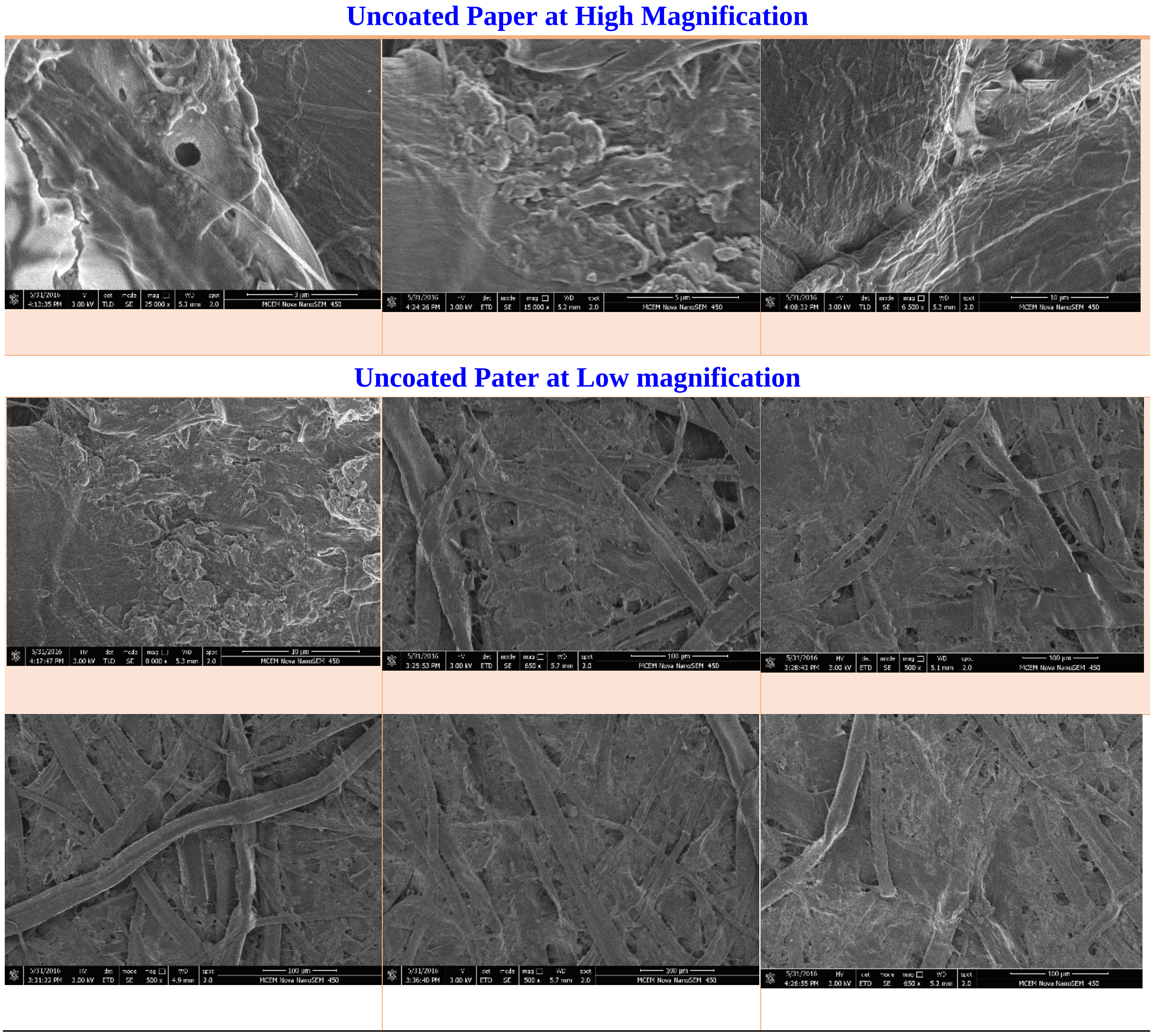

Figure 14. SEM Micrographs of Packaging Paper (Uncoated). The high magnification image shows the particles of cellulose clumped with the micro fibres in the surface of the uncoated sheet. The low magnification confirms the presence of the cellulose interconnected fibres with various size of surface pores.

Figure 15 shows the SEM micrographs of CNF laminated packaging papers.CNF fills the surface pores of the paper and formed the film on the paper surface. This film can be acting as barrier against air and gaseous molecules. The SEM micrographs confirm the formation of uniform CNF layers on the paper and there is an absence of pinholes on the coated surface. The coated surface has rough and porous with a considerable surface roughness due to fiber distribution on the CNF coating [3].

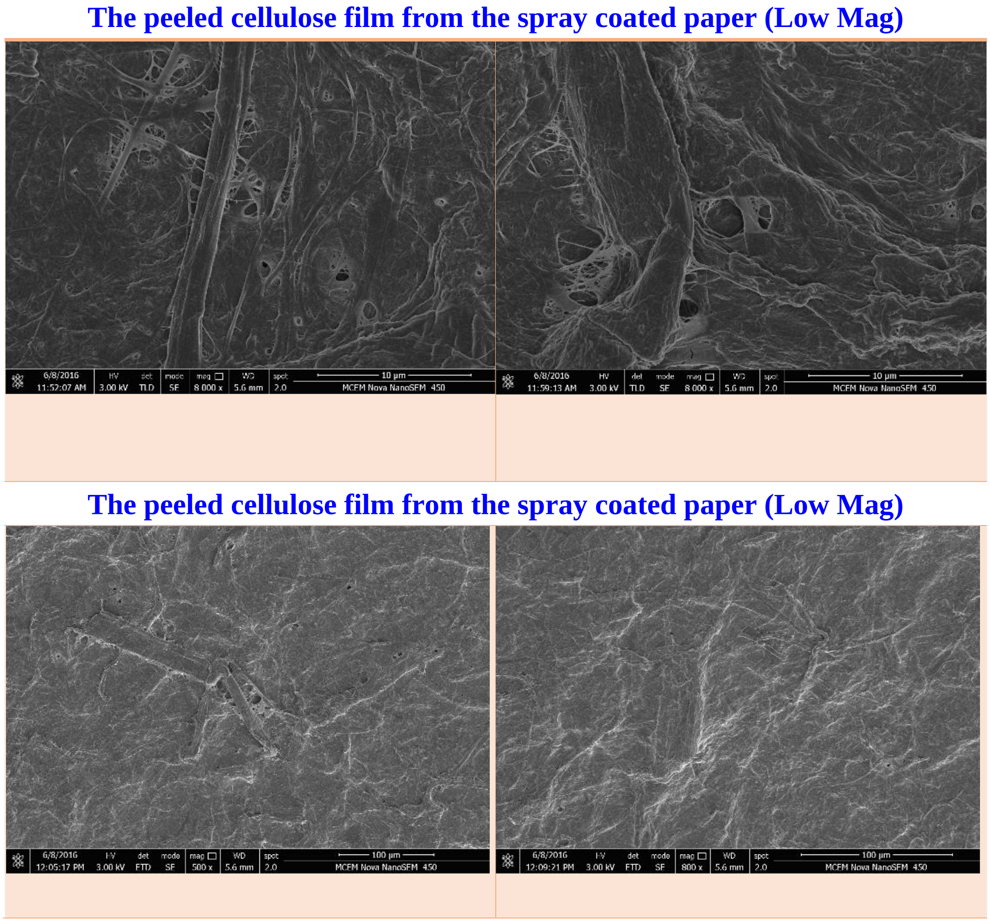

Figure 15. SEM micrographs of CNF laminated Packaging Papers. The SEI image of the peeled cellulose film from the base sheet at High and Low magnification. The cellulose film has surface roughness due to the presence of difference size in fibers.

Figure 16 shows SEM micrographs of coated paper with CNF varying from 0.25 wt. % to 1.00 wt. % CNF. The 0.25 wt. CNF coated sheet confirms that the partial closure of surface pores on the papers with sprayed CNF. The 0.25 wt. % CNF suspension is watery and when spraying this concentration on the paper substrates, there was wetting and poor adherence of the suspension resulting the poor fill of the surface pores. The 0.5 wt. % is also bit watery suspension and sprayed on the papers and resulted in the partial fillage of CNF in the surface pores. The 0.75 wt. % and 1.00 wt. % of coating CNF on the paper gives a promising results and complete coverage the surface pores and formed a barrier film on the paper. The coating of CNF on the paper substrates with either 0.75 wt. % and 1.00 wt. % CNF suspensions would be optimum concentration for spray coating. At these concentrations, the viscosity of CNF suspension would be sprayable in the professional spray coating system. Another advantage of these concentrations is better adherence of CNF into the paper substrates and better wettability of the paper substrates.

Adhesion and wettabilty of CNF suspension not only depends on the CNF solid concentration and also on the types of paper substrates. The paper substrates used are newsprint paper, packaging paper and blotting paper. Newsprint paper and blotting paper were highly capable of absorbing water than the packaging paper. During the spraying CNF on newsprint papers, the newsprint paper are highly shrinkable when CNF suspension wets the paper.

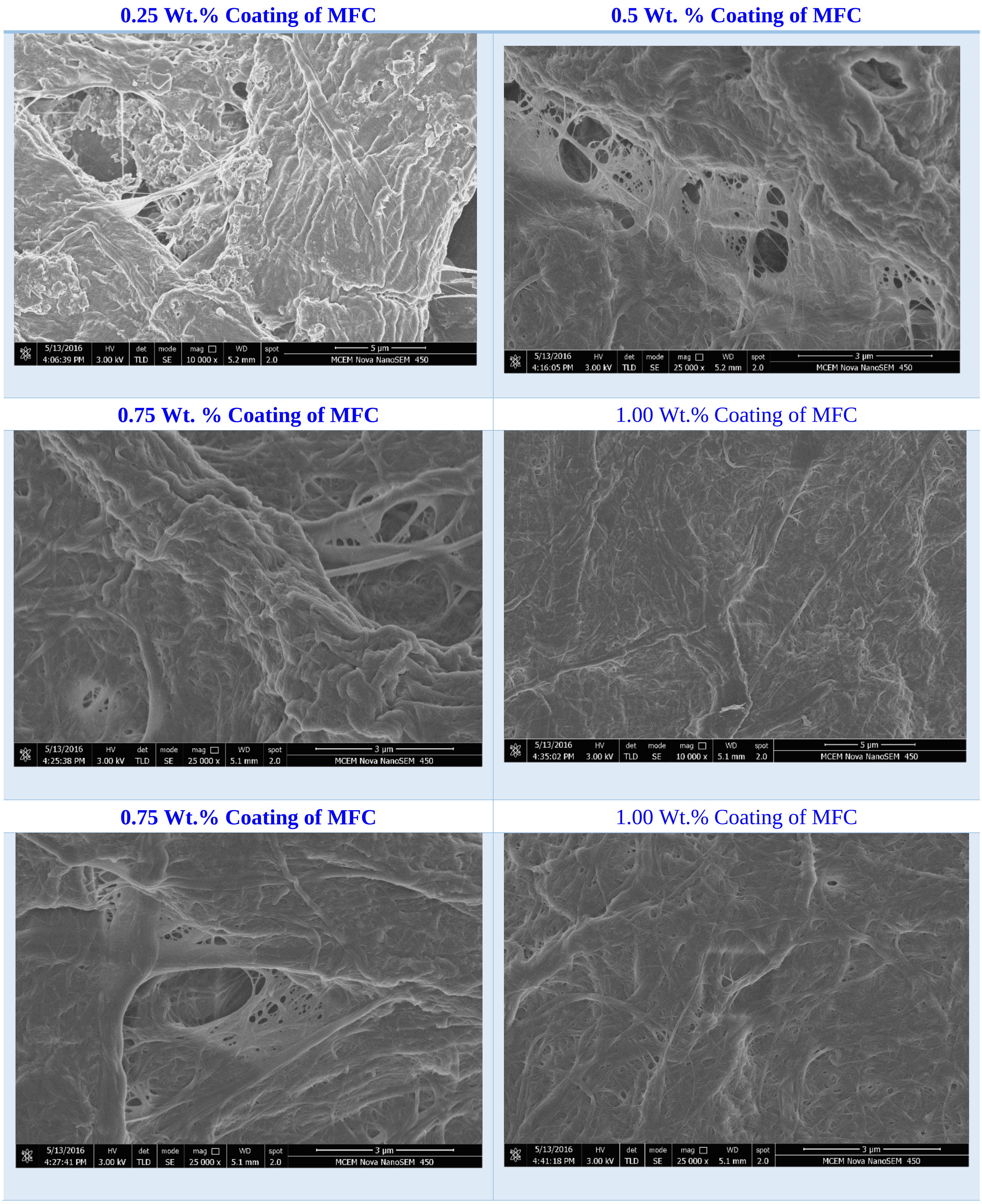

Figure 16. SEI Micrograph of the spray coated paper. These are rough images of spray coated paper and confirm the presence of cellulose fibrils and various size of the pores in the surface of spray coated sheet.

SEM Micrographs

Figure 17 reveals the SEM micrograph of spray coated CNF laminates on the paper substrates at high and low magnification. High magnification of SEM micrograph confirms the CNF layers completely cover the paper surface and CNF fibrils interacting with cellulose fibers in the paper. In addition to that, the surface pores were closed by spray coated CNF fine droplet from the spray gun in the spraying process. Low magnification of SEM micrograph reveals the complete fibrous structure in the form of matrix with CNF fibres.

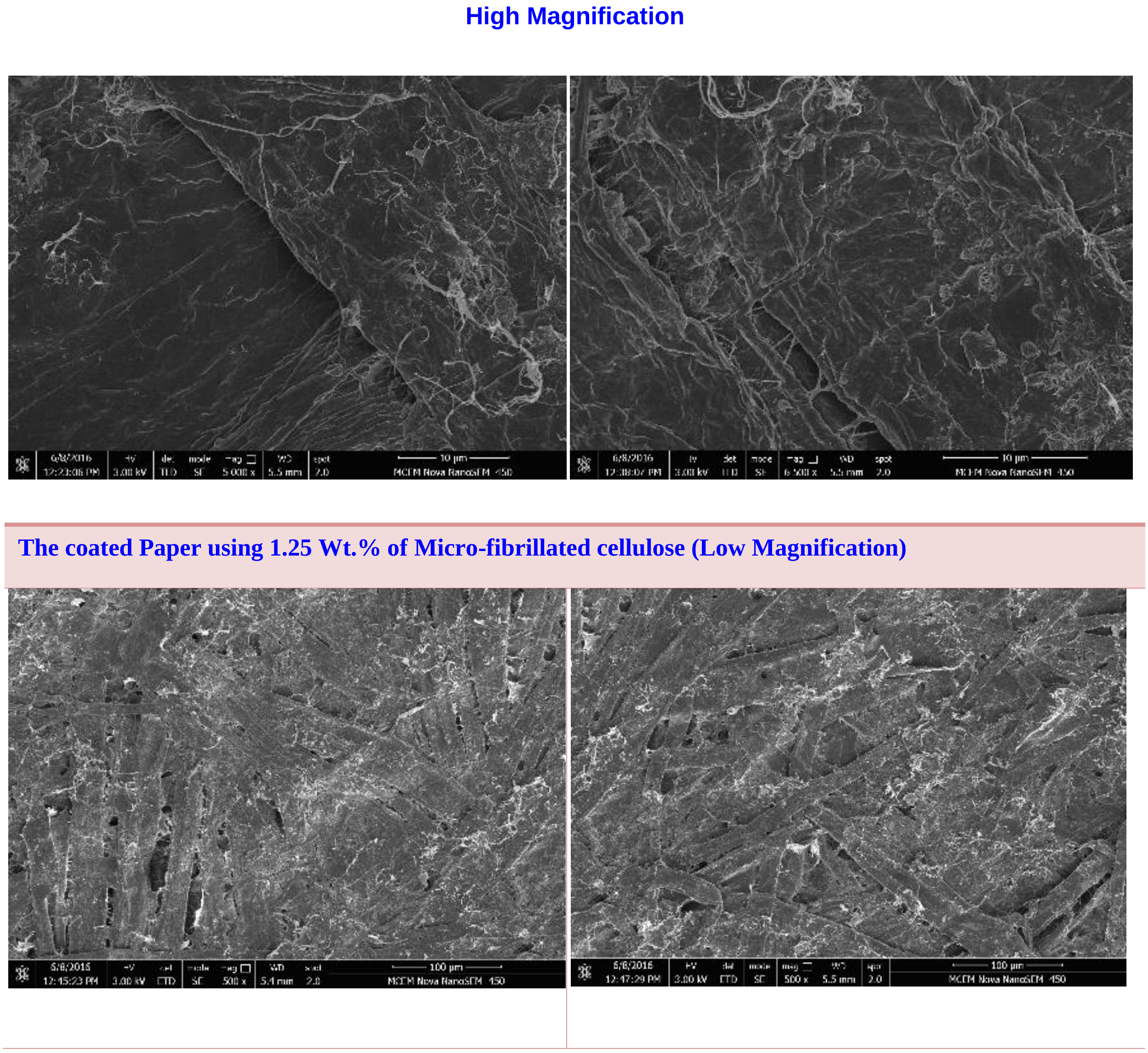

Figure 17. SEI Micrographs of the spray coated paper at High and Low magnification. The high magnification image shows the coating coverage of the surface of the paper substrates. The surface of the coated base sheet shows different size of the cellulose fibers. SEM micrographs reveal the closure of surface pores on the paper by cellulose nanofibres.

3.8. Recommendations for Further Improvement

Raw Cellulose nanofibre which has fibril diameter of 70 nm was used from spraying for production of CNF laminated surface on the paper substrates. This partially homogenized CNF can create good barrier layers on the paper substrates. However, due to fibril size, the expected barrier performance is not achieved. So that, the reduction of fibril size via high pressure homogenization can be performed and then the spraying of homogenized CNF on the paper substrates increased barrier performance of the CNF coating on the paper substrates via forming smooth layers which has lowest surface roughness. Reducing fibrils in CNF suspension increase the viscosity of the suspension and dilute it and increase easiness for spraying.

Homegenization is a mechanical process of fibrillation of cellulose microfibre or cellulose nanofibre (diameter >70nm) into nanocellulose fibres having an average diameter of 20 nm. Therefore, spraying homogenized CNF on the brown paper substrates gives better reduction in air permeance and enhances the barrier performance of homogenized CNF laminated on the packaging paper. The barrier performance of the sheet can be improved with spraying of homogenized CNF on the paper [48].

Figure 18 shows the effect of homeginized cellulose nanofibre on the air permeance of CNF laminated paper. The air permenace of dry uncoated brown paper is 3.075 μm/Pa.S. In dry paper, the surface pores were not opened fully due to dryness of cellulose fibrils. While wetting the sheets via spraying pure distilled water, the cellulose fibrils are loosened and pores are widened and allowing more amount of air. This is why that the air permenace of the wetted sheet elevated to 3.562 μm/Pa.S from 3.075 μm/Pa.S. When spraying 0.75 wt.% unhomogenized CNF on the brown paper, the air permeance of CNF laminated paper was 0.239 μm/Pa.S. In this condition, CNF fills the surface pores of the paper and reduce the air permeability of the coated sheet. When spraying 0.2 wt.% homogenized CNF on the brown paper, the air permenance of the homogenized CNF laminated paper was less than 0.003 μm/Pa.S and perfectly impermeable against air and other gaseous substances.

During homogenization, microfibers are fibrillated or delaminated into nanofibres having diameter 20 nm. When spraying homogenized CNF, CNF forms film on the paper and covers the surface pores on the sheet. Homogenized CNF has better film forming capacity than raw CNF. Film formation was performed throught the hydrogen bond between neibhour fibrils. This is why that homenized CNF laminates on the paper is completely impermeable.

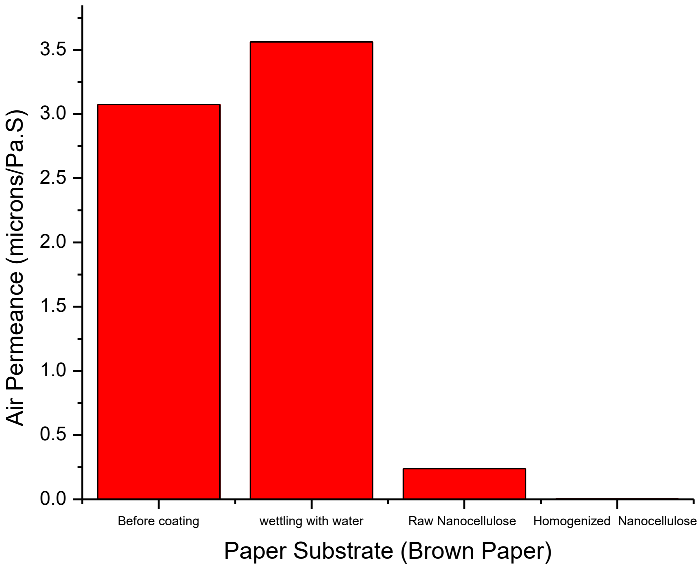

Figure 18. Effect of Homogenized cellulose nanofibre on the barrier performance of brown paper. The air permeance of the brown paper before coating, wetting with water via spraying, coating with raw cellulose nanofibre and coated with homogenized cellulose nanofibre via spraying were evaluated.

3.9. Scalability

Based on laboratory investigation on spraying CNF on the paper substrates, the proof of concept was developed and barrier performance of the paper substrates improved via spraycoated CNF lamiates. This method is worthy for scale up and can be attained via roll to roll coating methods. Figure 19 shows dow web coater similar to roll to roll coating.The spray system can be mounted to spray CNF on the paper web and Infra red dryer in dow web coated dry the wetted sheet. This will be model for scale up the spray coating process.

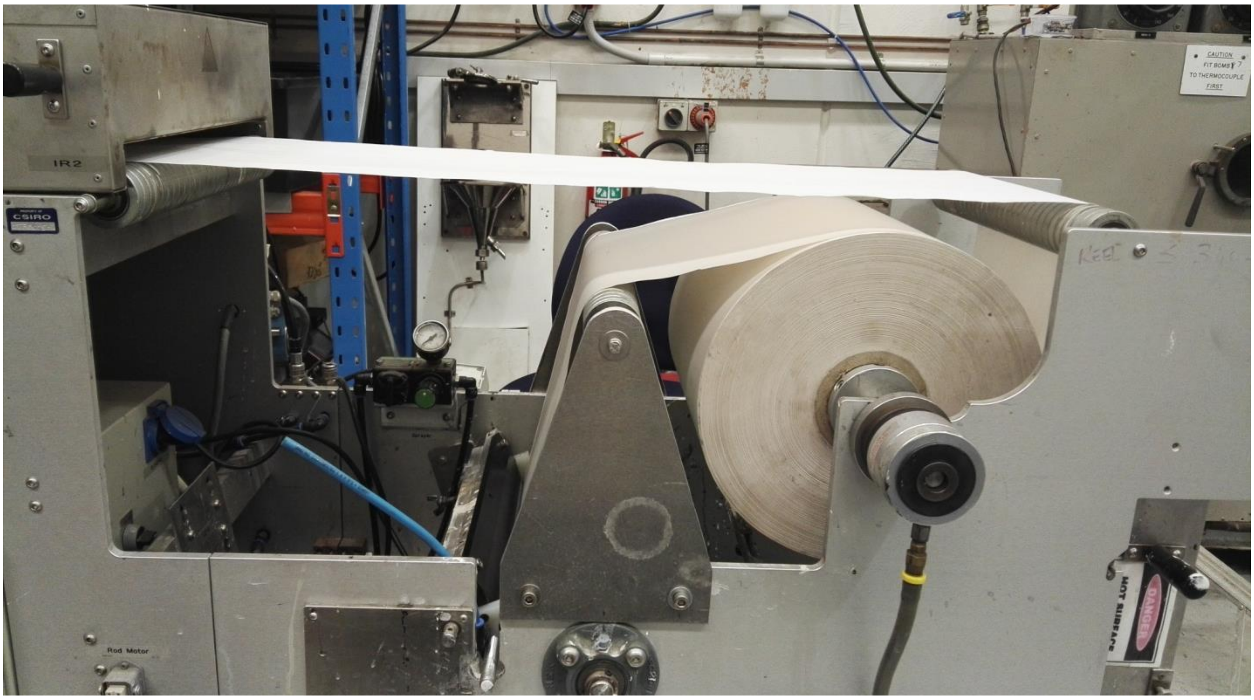

Figure19. Dowweb coater for Scale up of spray coating process.

4. Conclusion

Spraying CNF on the paper substrates is a novel concept to forming either wet thin or thick barrier layers on the substrates. The operation time for wet laminating CNF consumes less than 1 min and drying the CNF laminates takes min 24 hours under standard laboratory conditions. The CNF layer on the paper substrates was tailored by simple adjusting CNF suspension concentration in the spraying conditions. As a result, the thickness of CNF barrier layers was tailored and barrier performance was elevated based on the coat weight and thickness on the paper substrates. From this study, spraying is a feasible method for producing barrier layers on the paper substrates and worthy method for industrial scale up.

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Conflict of Interest

None

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