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Concept Paper

Spray Coated Cellulose Nanofiber (CNF) Film as an Eco-Friendly Substrate for Flexible and Printed Electronics

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Abstract: Cellulose nanofiber is an eco-friendly nanomaterial used for fabricating various functional materials. It is an alternative for synthetic plastic and other petroleum derived materials. Due to demand of CNF film, fast and rapid method for fabrication of CNF film is required. A new method on spray coating to prepare smooth cellulose nanofiber (CNF) films was developed. In this method, spraying CNF suspension onto a smooth and polished metal surface was carried out and then allowed the spray coated wet film to dry in air under standard laboratory conditions. Spraying has notable advantages such as contour coating and contactless coating with the base substrate. The basis weight and thickness of the CNF film is tailorable by adjusting CNF suspension in spraying process. CNF film prepared via spray coating has unique two-sided surface roughness with the surface in contact with the base substrate or metal side much smoother than the air-contact side. The surface roughness is one of the controlling parameter in the application of the CNF film as a substrate for flexible and printed electronics. The RMS roughness of the two surfaces investigated by Optical Profilometry [OP] was found to be 2087 nm on the rough side and 389 nm on the spray coated side, respectively. The spray coated CNF film has ultra-high smoothness on the side exposed to the polished stainless steel surface. The factors including the size of cellulose fibrils and surface smoothness of base surface that control the roughness of the film are currently being investigated and will be discussed in this chapter. The surface smoothness requirements for substrate applications in flexible and printed electronics will be discussed.

Keywords: Cellulose nanofiber, Spray Coating, Smooth Surface, Surface Roughness, RMS, Flexible Electronics and Printed Electronics.

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1. Introduction

Plastic substrates widely used in the development of flexible electronics and printed electronics. After consumption of these synthetic plastics, it became a threat to the environment as pollutants or solid waste. These plastic wastes are either not biodegradable or not recyclable into a useful product. This issue is a global problem about the disposal of synthetic plastics waste into the environment. To mitigate this issue, natural polymers are considered to be an alternative for synthetic plastics. Generally, natural polymers are biodegradable, ecofriendly to the environment and mainly renewable [1, 2].

Cellulose is the abundant biopolymer derived from pulps of various woody materials, grass and Cotton etc.[3], it is a carbohydrate bio-fibrous polymer composed of homo-polysaccharide linearly with β-D-glucopyranose units connected by β-1–4-linkages with cellobiose repeatdly and used as feed stock for production of paper and paper or card board. Paper was used as a base substrate for printing the electronics circuits or developing flexible electronics [2]. Paper is a cellulose macro fiber substrates consisting of large pores and highly susceptible to water vapour transmission and oxygen permeability [4]. Cellulose fibre is a hydrophilic polymer and the fibrils are highly susceptible to swelling due to water vapour transmission across the paper [5].

To mitigate this issue, Cellulose Nanofiber (CNF) is derived from the pulp of woody material via mechanical homogenisation, Chemical process such as Acid hydrolysis, Bioprocess – enzymatic process [6,7]. CNF is a nanomaterial which has eco-friendly, biodegradable and renewable and has notable properties such as high mechanical strength such high tensile strength, E-modulus, surface area, containing many hydroxyl groups for chemical modification the CNF [5]. CNF is a fibrous network and matrix offers good barrier performance against air, water vapour and oxygen and excellent tortuous pathway for increase the diffusion length for gaseous molecules and water vapour [8]. Due to these properties, CNF is a potential barrier material to replace the synthetic packaging material. In addition to that, CNF has low density, transparency and low thermal expansion properties used for developing various function materials [9].

Free Standing CNF film is one of the functional materials developed from the cellulose Nanofiber [10-12]. These films can be used as packaging material, membrane for water and water water treatment, a base substrate for functional electronics, food packaging material, and tissue engineering scaffolds and drug delivery vehicles for various biomedical applications [13]. Figure 1 shows the potential applications for cellulose nanofiber in various fields[14].

The preparation of cellulose nanofiber film is still challenging task and requires fast process for film fabrication. There are many methods available for fabrication of CNF films namely solvent casting, hot pressing, vacuum filtration etc.[15], Time consumption was more than 24 hours and poor uniformity of the CNF film via solvent casting is unresolvable issue. Vacuum filtration is the conventional process for paper making and CNF film fabrication. However, in this method, the time taken for dewatering from CNF suspension consumed from 30 mins to 24 hours and the draining time/dewatering time increased with CNF suspension consistency. It is a bottleneck for tailoring the properties of CNF film and scale up for large scale production [16].

Recently, Spraying is a flexible process in the fabrication of CNF film and ability to tailor the properties of the CNF film via simply adjusting CNF suspension consistency and few process parameters in the experimental prototype[17-19]. Moreover, the operation time for fabricating the film was less than a minute [10]. Spraying CNF suspension on the polished stainless steel plate produces the film with unique surfaces[12]. When CNF sprayed on the metal surface, the surface of the film adhered to the metal side was low in surface roughness and glossy and compact in the structure [10, 12, 20]. The shiny side of CNF film can be useful for the construction of functional materials such as OLED devices, flexible and printed electronics, and substrate for solar cells. The CNF film surface exposed to free air was rough and highly porous[20].

Figure 1. Application of Cellulose nanofiber films.

This paper deals on the spray coating for production of CNF films and surface roughness of the spray coated side of the CNF film. Additionally, the parameters controlling the surface roughness of CNF film can be elaborated and the role of surface roughness in the fabrication of flexible electronics substrate.

2. Materials and Methods

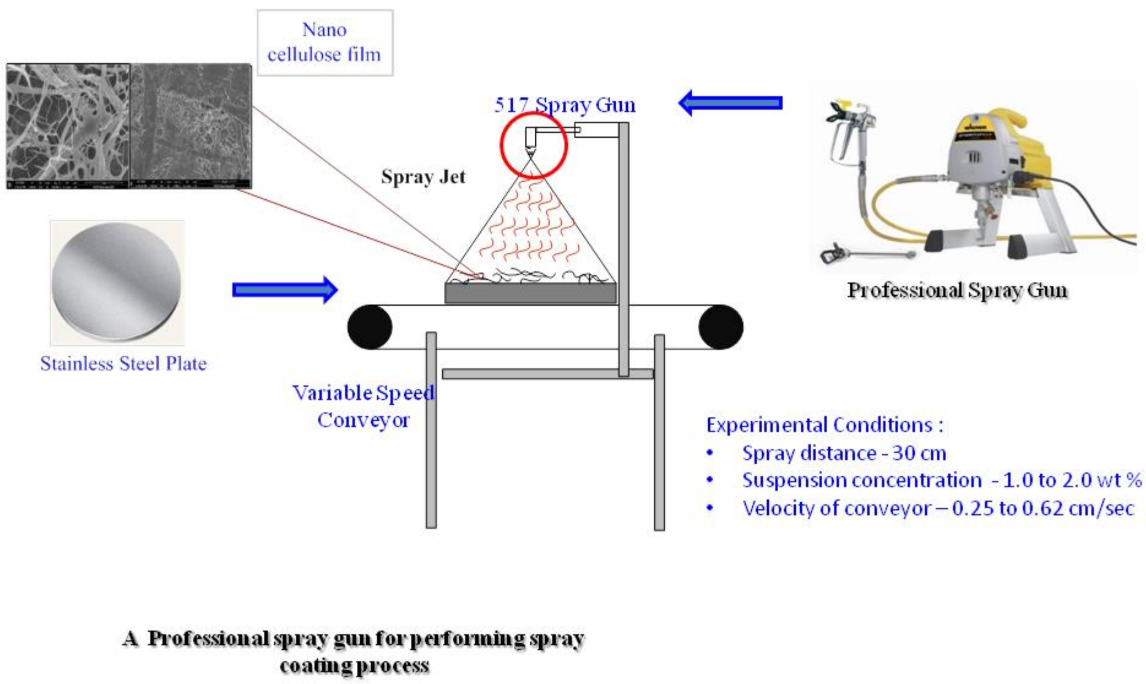

Figure 2. Spray coating experimental setup for fabrication of Cellulose nanofiber film.

Cellulose nanofibre (CNF) also called as nanocellulose, micro fibrillated cellulose, nano fibrillated cellulose, was bought from Diacel Japan Ltd. In this paper, CNF as the generic term for the cellulose nanomaterials was 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 fiber diameter, a mean length of fiber 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 1.5 wt. % with de-ionized water and disintegrating for 15,000 revolutions at 3000 rpm in a disintegrator [20].

2.1. Spraying cellulose nanofiber (CNF) suspension on the polished metal surface:

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 stainless-steel plate. The spray pattern is elliptical and the distance between spray nozzle and paper substrate is 20±2 cm. The coating of cellulose nanofiber on the stainless-steel plate 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 02. The spray coated CNF on stainless steel were dried in the open air with specific care in the standard laboratory conditions. The dried CNF films were used for various characterizations such as surface topography via scanning electron microscopy and surface roughness via atomic force microscopy and optical profilometry [20].

2.2. SEM Investigation of Spray coated CNF Film:

The spray coated CNF film (4mm X 4mm) is fixed on the 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. 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 CNF film was characterized using FEI–NOVA Nano SEM 450 [20].

2.3. Atomic Force Microscopy (AFM) and Optical Profilometry (OP)

The sample of CNF film was subjected to the measurement of surface roughness of the both sides of the film via AFM and OP. The images are processed via software for evaluation of surface roughness[20].

3. Results and Discussion

Spraying is a fastest process in the fabrication of CNF film and the properties of the film can be tailorable in this process by simply adjusting the suspension concentration and spray process parameters. The spray coated film has two unique surfaces namely the free surface which is exposed to air and spray coated surface which is compact and shiny [10, 20].

3.1. Cellulose Nanofiber Film:

Figure 3 and Figure 4 show the spray coated cellulose nanofibre films. The films are compact and have two surfaces namely the free surface and smooth surface. Thickness and basis weight of the films were tailored via adjusting CNF suspension and process parameters in the spray coating pilot prototype. However, these parameters do not influence on the surface roughness of the CNF films.

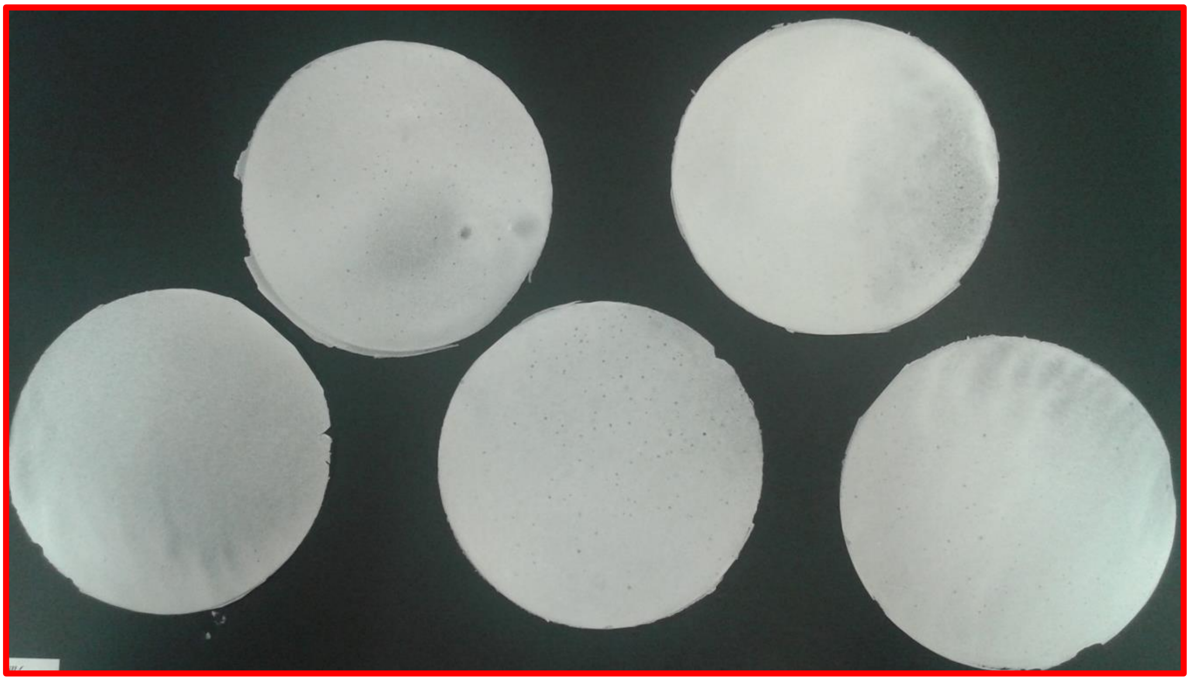

Figure 3. Spray coated Cellulose Nanofiber Film

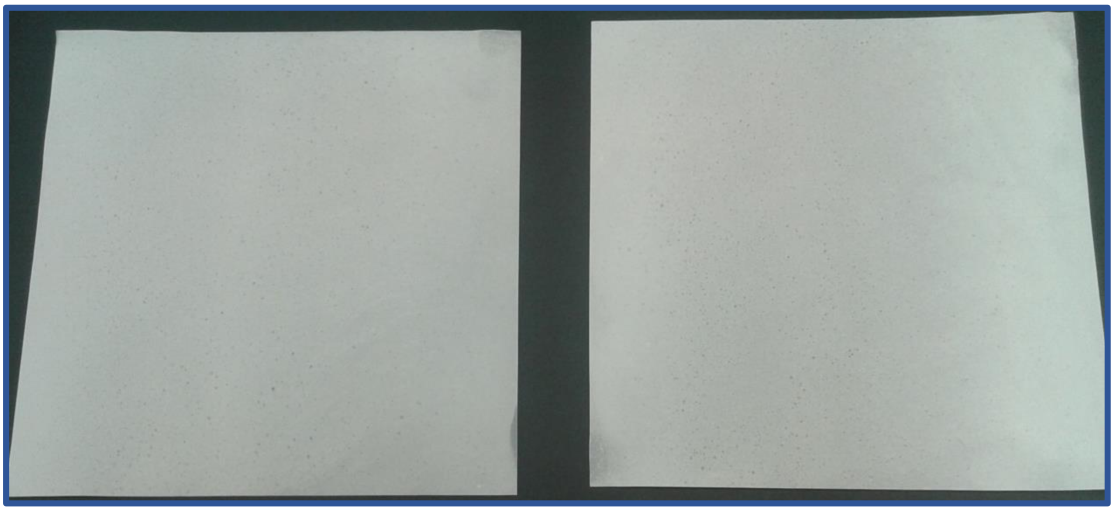

Figure 4. Spray coated Cellulose Nanofiber Film

3.2. Scanning Electron Microscopy (SEM) Images of CNF Film

Figure 5 and Figure 6 show the spray coated CNF film revealing that the film has two unique surfaces namely rough surface and smooth surface. The rough surface has highly porous and high surface roughness. The smooth surface of the CNF film was lowest roughness and glossy and compact film.

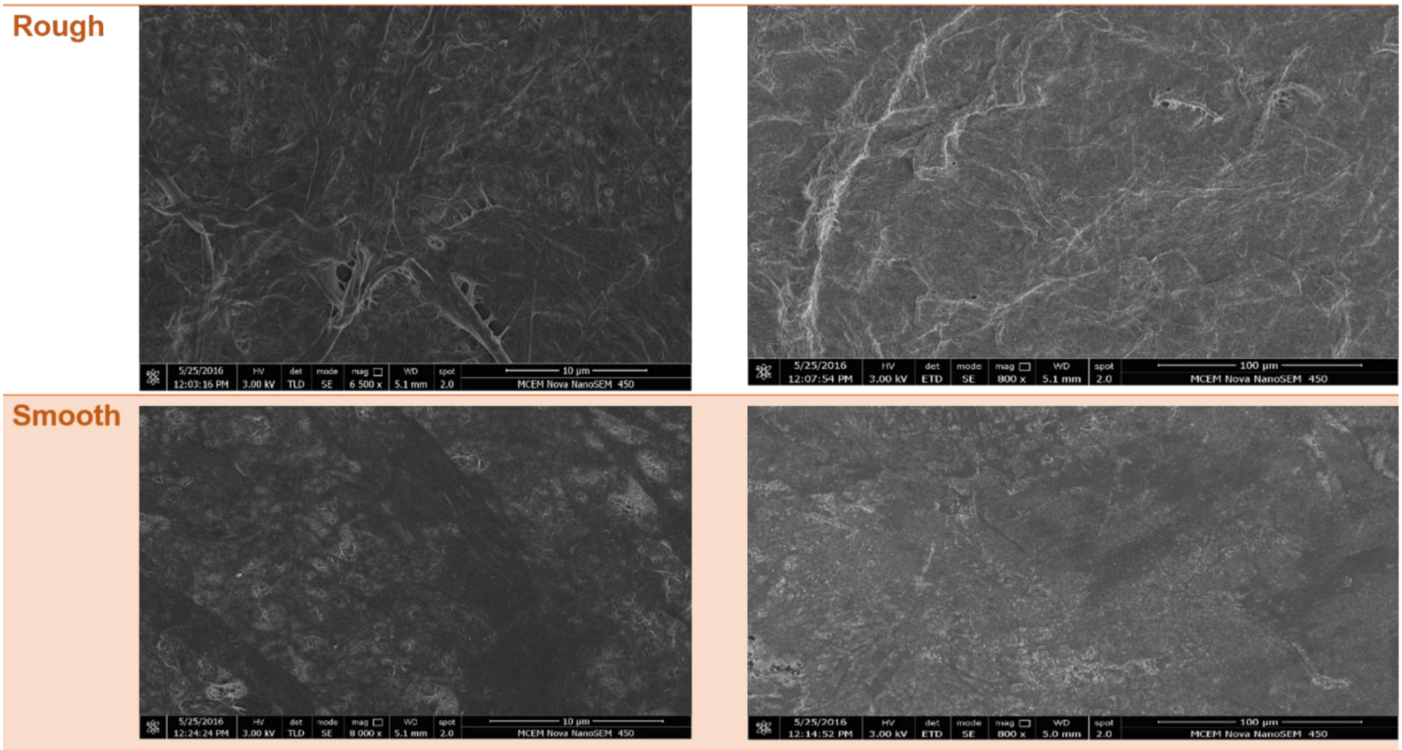

Figure 5. SEM micrographs of Cellulose Nanofiber Film

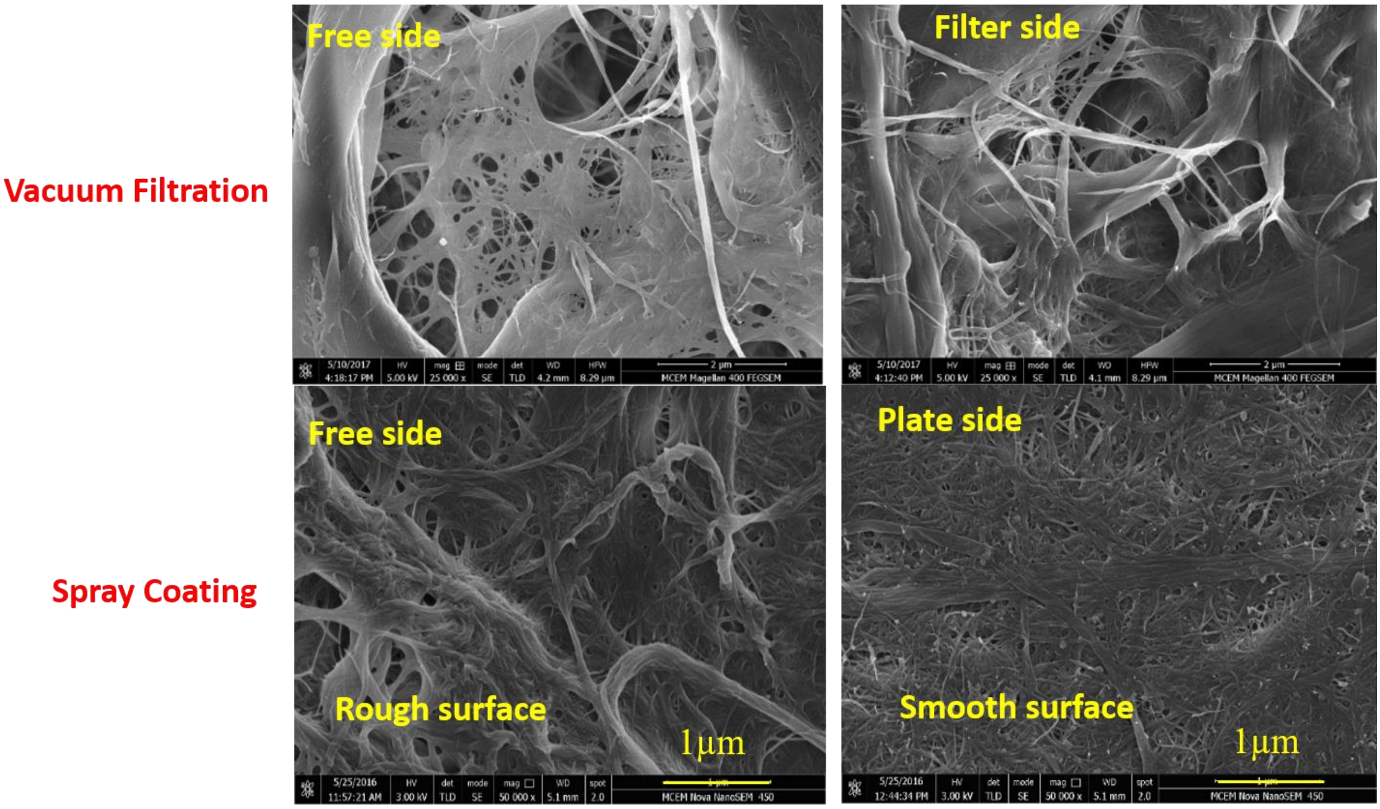

Figure 6. SEM micrographs of Cellulose Nanofiber Film- Comparison between Spray Coated CNF Film and Vacuum Filtered Film

Figure 7 shows the AFM micrographs of spray coated CNF film. The rough surface shows the porous and high roughness value. The spray coated side is very smooth and glossy and compact. In addition to that, the Polishness of the stainless steel was replicated on the CNF film.

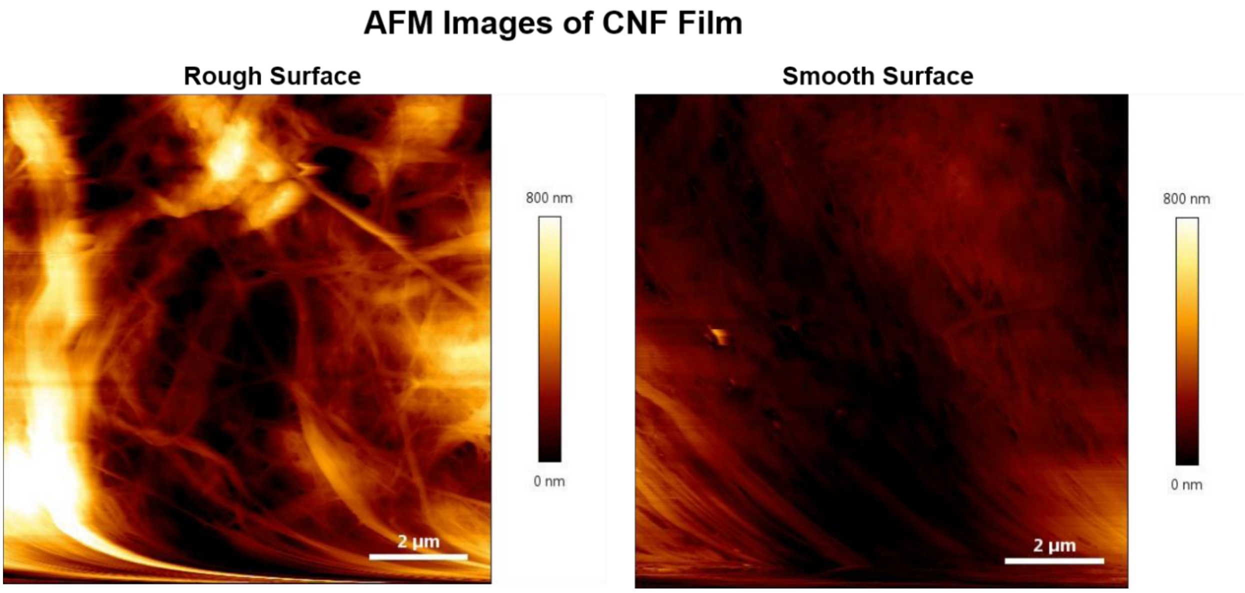

Figure 7. AFM images of Cellulose Nanofibre Film

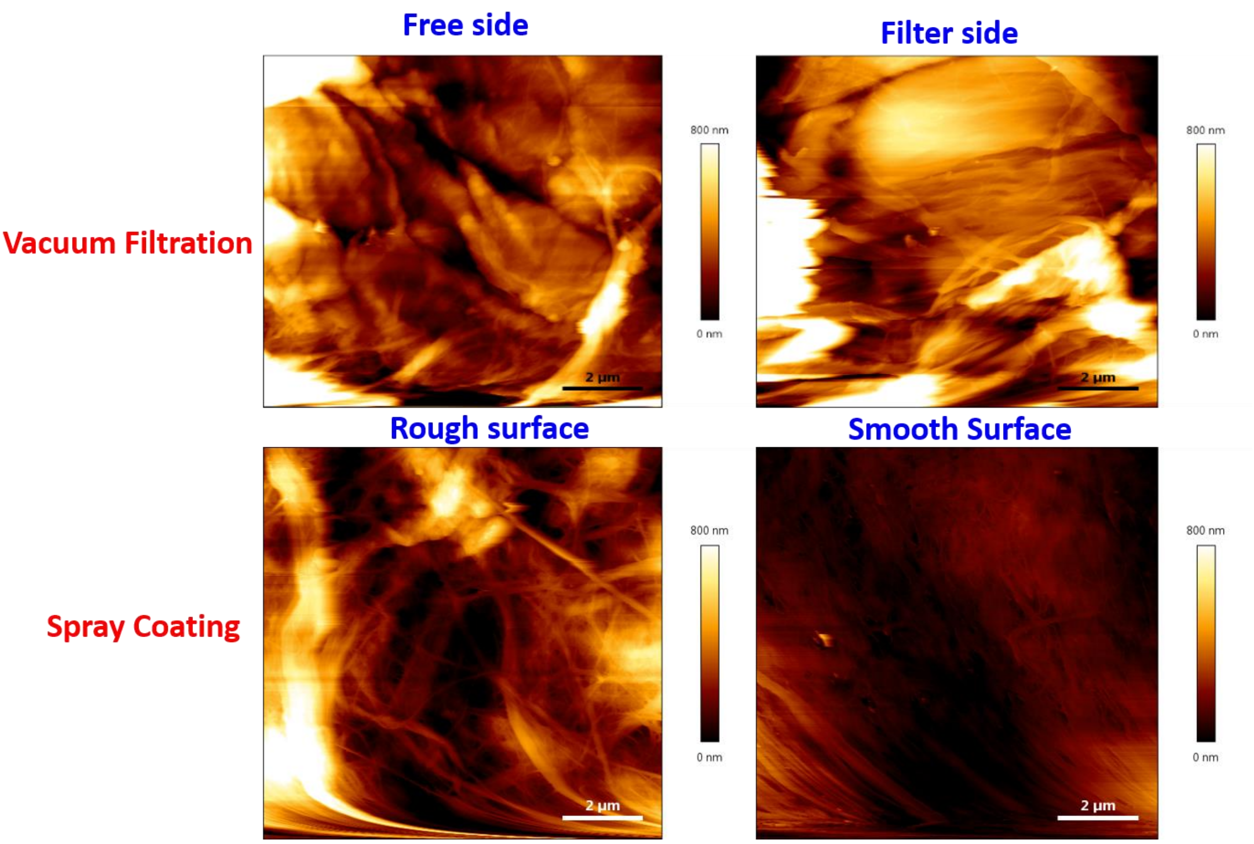

Figure 8. AFM images of Cellulose Nanofibre Film – Comparison between Spray coated CNF film and Vacuum filtered CNF film.

Figure 7 and Figure 8 show AFM images of CNF film prepared via spray coating and vacuum filtration. The AFM micrographs confirm that the smooth side of spray coated CNF film has low surface roughness and surface was smooth and compact in comparison with rough side of spray coated CNF film. In the case of film prepared via vacuum film, the free side and filter side of the CNF film were highly porous and almost same roughness.

Figure 9 shows the roughness data for CNF film prepared via spray coating and vacuum filtration. The RMS of rough side of the spray coated CNF film was evaluated to be ̃80 nm and the rough side of the Spray coated CNF film was 400 nm. When comparing these values with the film prepared via vacuum filtration, the free side's roughness was around 400 nm and filter side was 310 nm. The Figure 9 confirms that the spraying CNF on the polished metal surface produce the film with lowest surface roughness which is replicated from the stainless-steel plates. The mechanism of replication remains obscure.

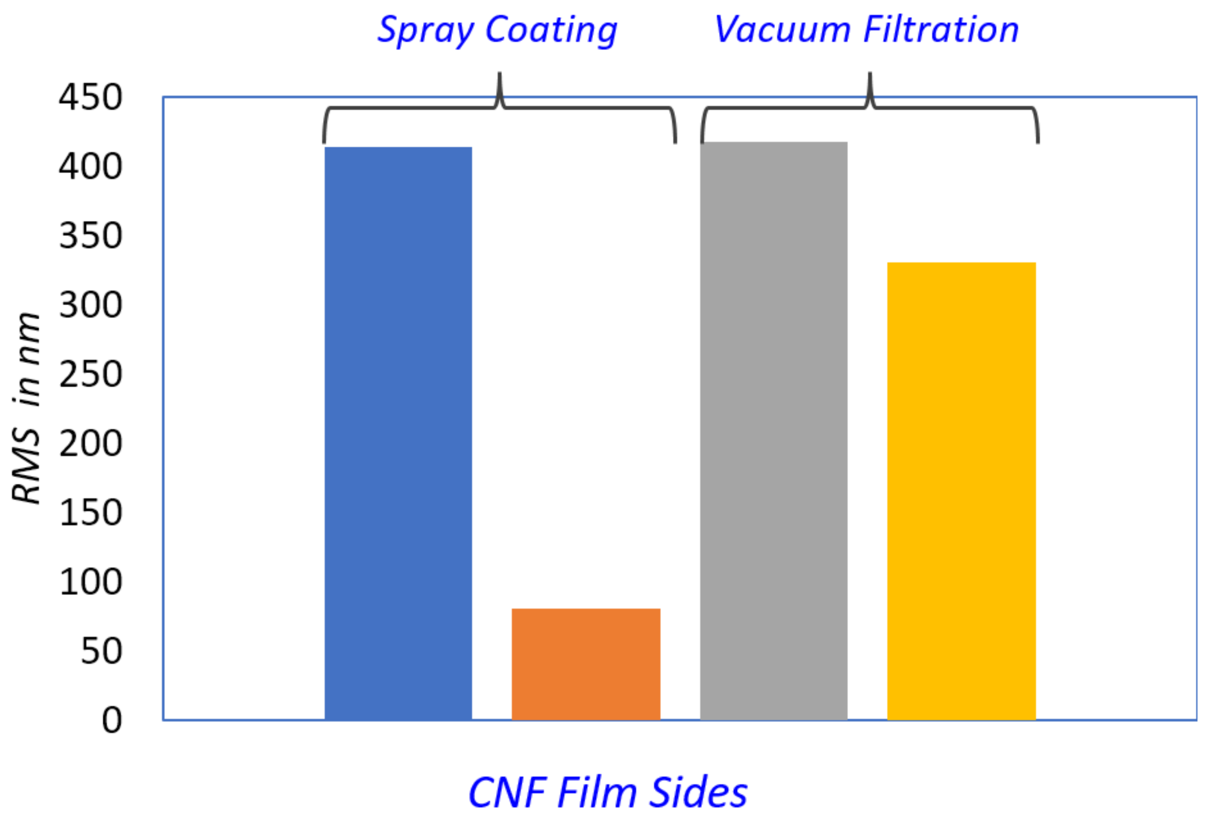

Figure 9. Roughness data for CNF Film

3.3. Optical Profiler Images of Cellulose Nanofiber Film:

Figure 10 shows the optical profiler images of CNF film prepared via spray coating and vacuum filtration. The RMS values are shown in the Figure 11.

Figure 11 shows the roughness of CNF film prepared via spray coating and vacuum filtration. CNF film from spraying process has lowest surface roughness especially film peeled from metal side has lowest surface roughness around 400 nm. The RMS of the CNF film prepared via vacuum filtration was found to be 2600 nm on filter side and 3750 nm on rough side.

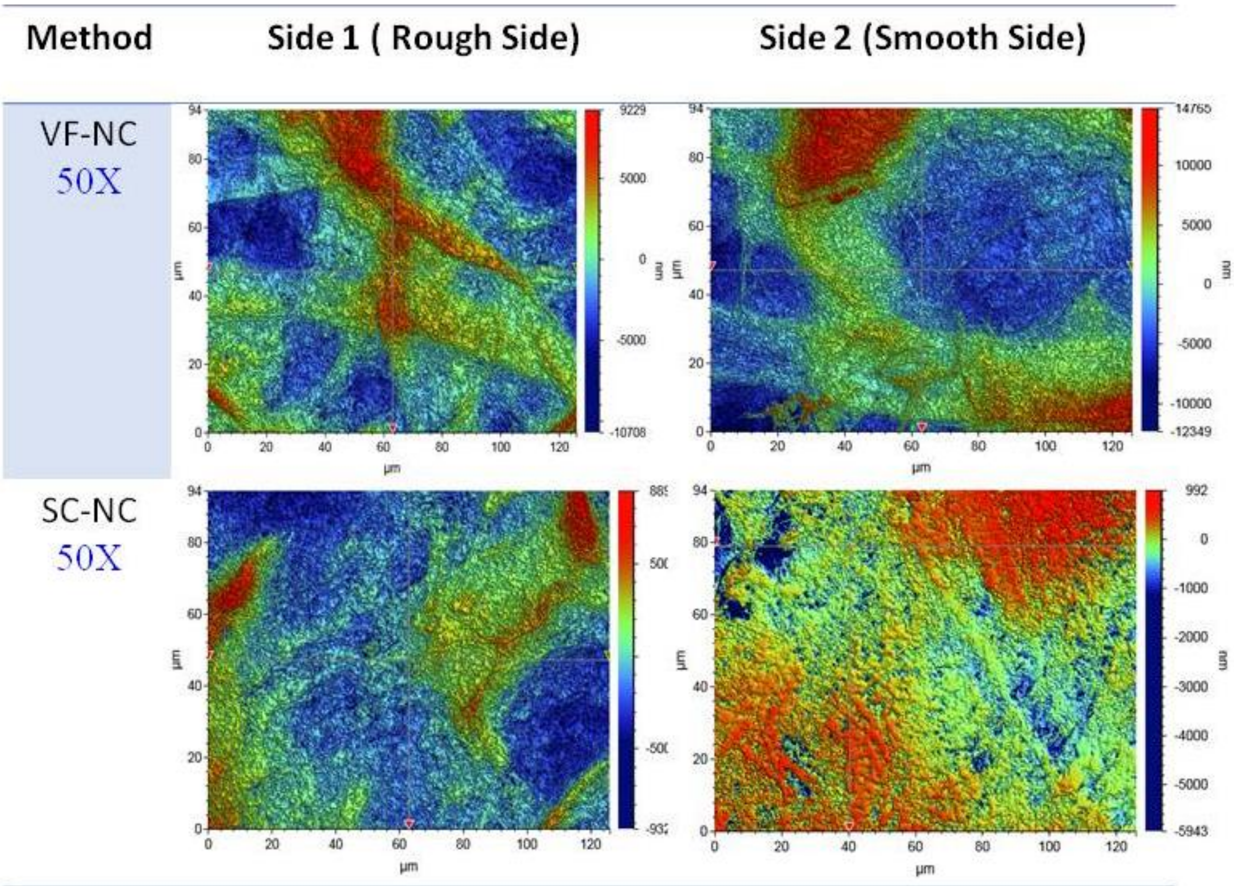

Figure 10. Optical profiler Images of CNF film (50X magnification)

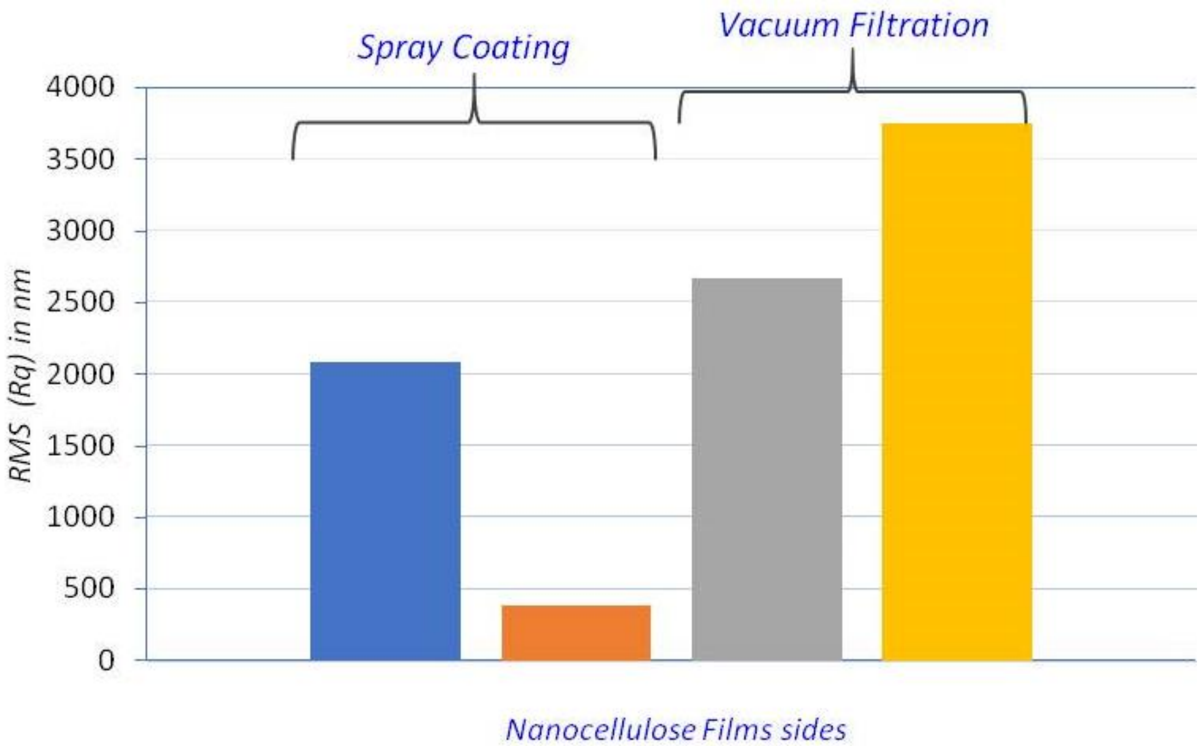

Figure 11. RMS values of CNF film

Figure 12 reveals the surface roughness of the CNF film prepared via spray coating and vacuum filtration. At lower magnification in optical profilometry, the surface roughness of the film was increased due to low magnification. The data was shown in Figure 13.

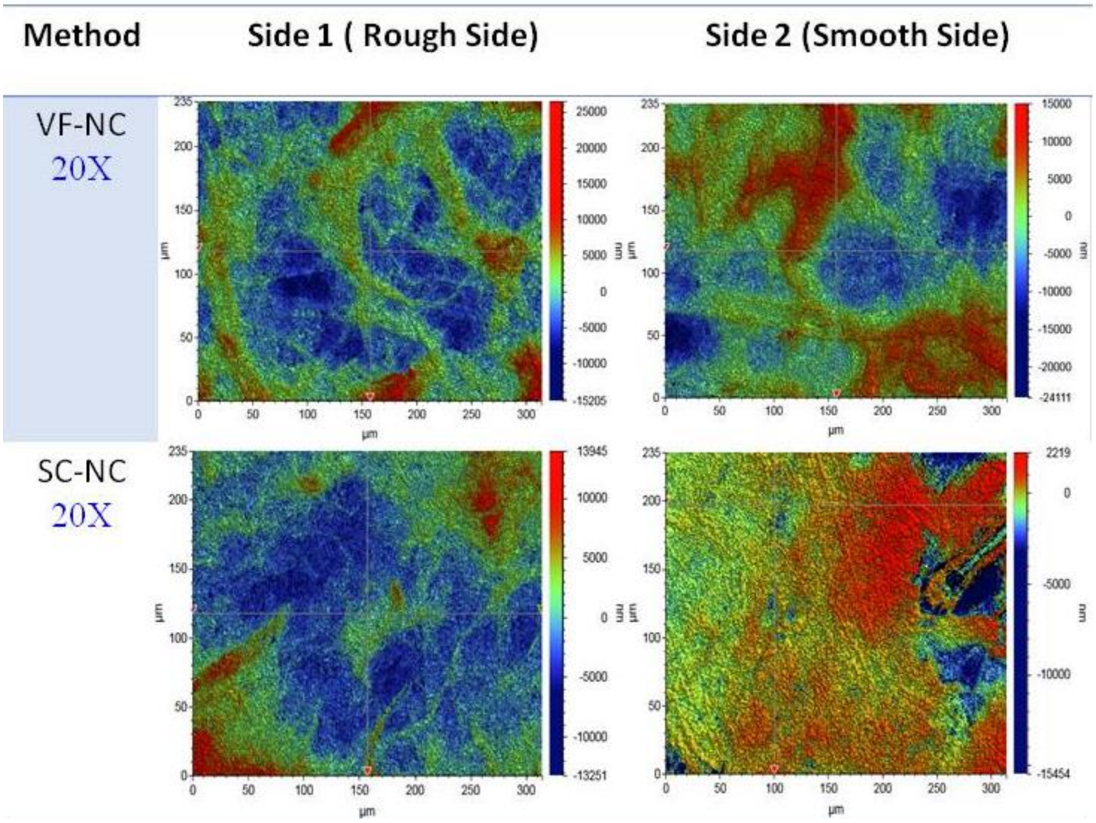

Figure 12. Optical profiler Images of CNF film (20X magnification)

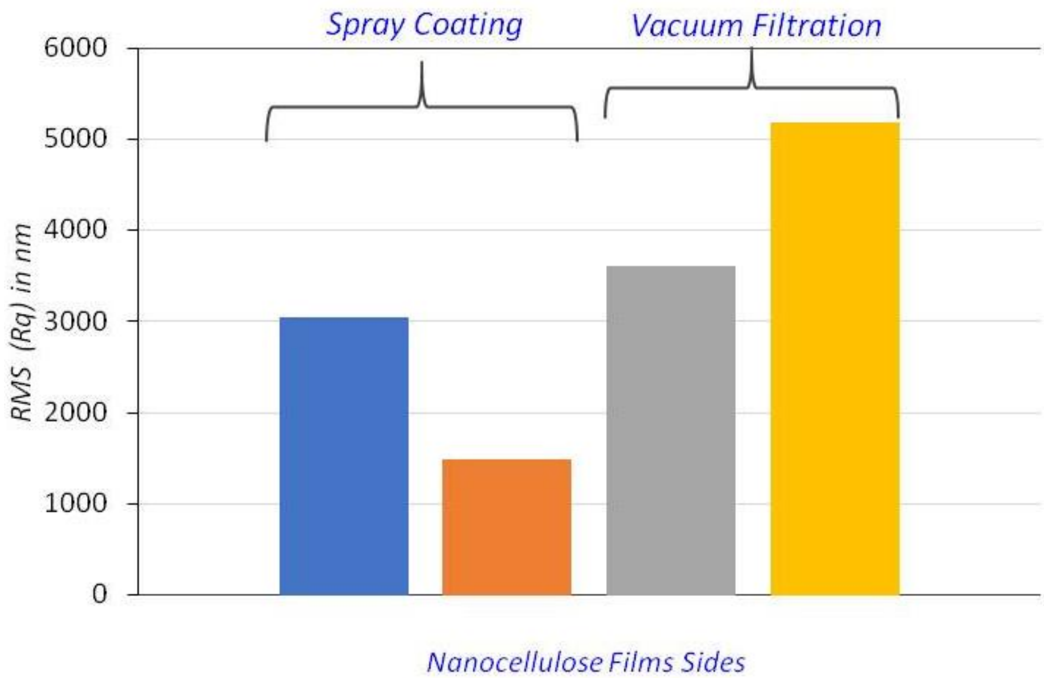

Figure 13. RMS values of CNF film

Figure 13 shows the roughness of the CNF film prepared from spray coating and vacuum filtration.

Figure 14 reveals the surface roughness of the CNF film prepared via spray coating and vacuum filtration. At lower magnification in optical profilometry, the surface roughness of the film was increased due to low magnification. The data was shown in Figure 15.

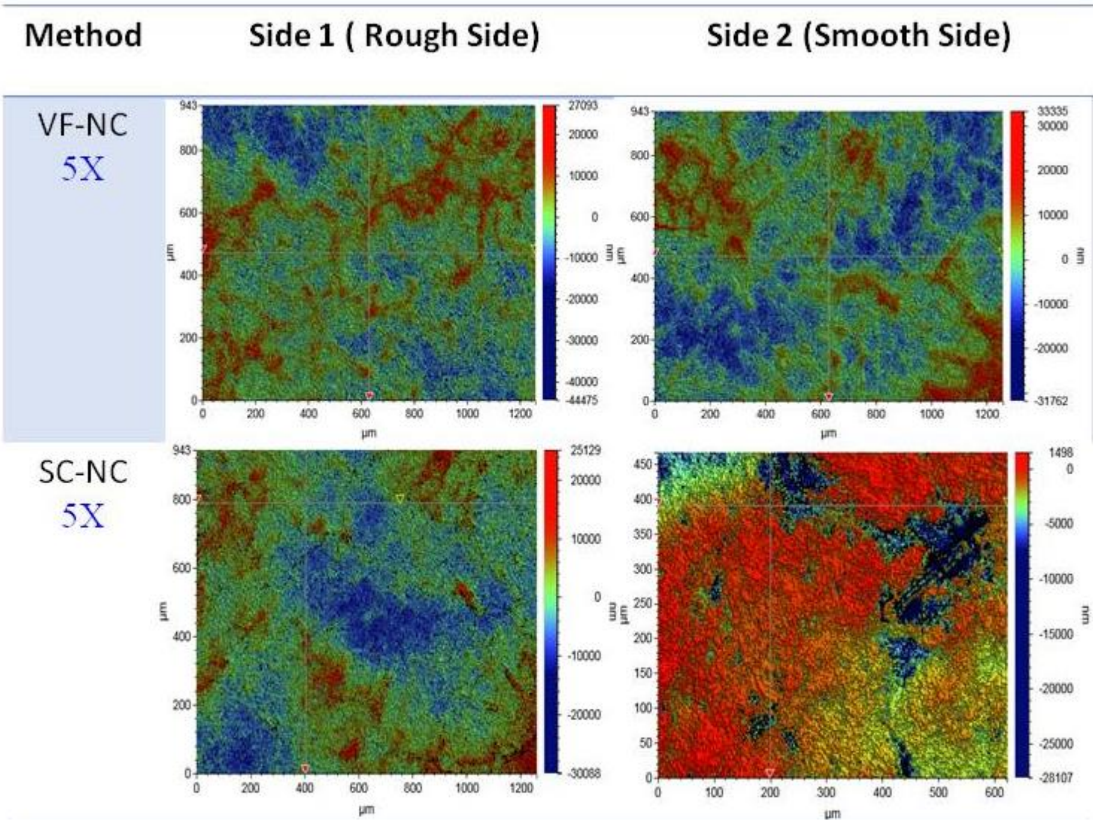

Figure 14. Optical profiler Images of CNF film (5X magnification)

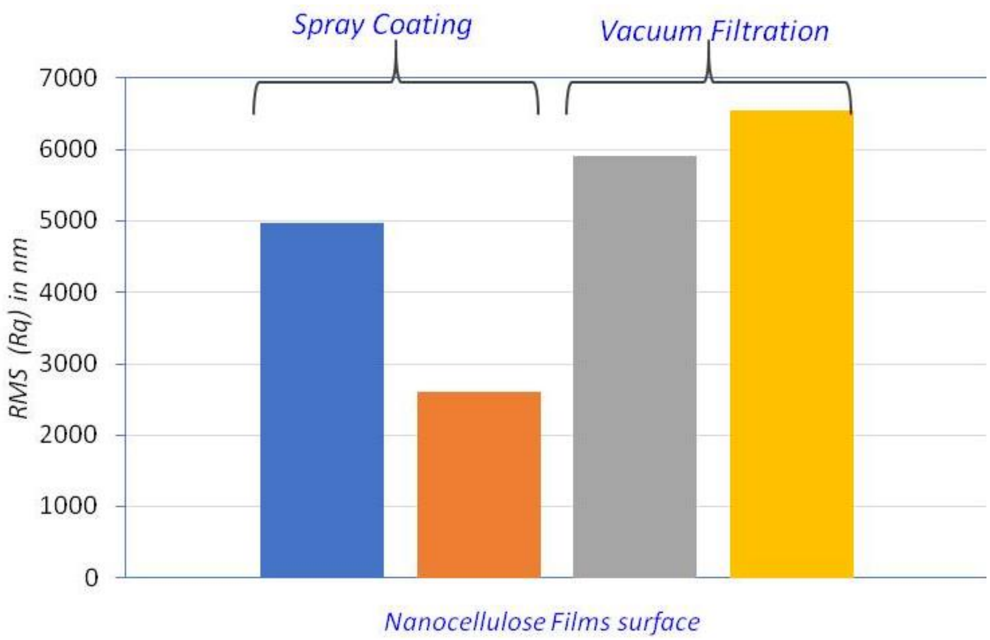

Figure 15. RMS values of CNF film

Figure 15 shows the roughness of the CNF film prepared from spray coating and vacuum filtration.

Table 1 summarized the surface roughness of CNF film prepared via spray coating and vacuum filtration. The roughness was measured various methods. These methods confirmed that CNF film produced via spray coating has lowest surface roughness on the smooth side than that of rough side. In comparison with the vacuum filtered CNF film, the spray coated film has low surface roughness on smooth side and can be a substrate for flexible and printed electronics [20].

Table 1. Summary of Surface Roughness of CNF film via various method

Films Preparation method	Technique used	Surface	RMS Roughness	
Spray Coating	Atomic Force Microscopy	Rough	414.0 nm (10μm x10μm)	51.4 nm (2μm x 2μm)
		Smooth	81.1 nm (10μm x10μm)	16.7 nm (2μm x 2μm)
	Optical Profiler 50x Image	Rough	2086.69 nm	
		Smooth	389 nm	
Vacuum Filtration	Atomic Force Microscopy	Free Side	417.7 nm (10μm x10μm)	102.3 nm (2μm x 2μm)
		Filter side	330.8 (10μm x10μm)	70.7 nm (2μm x 2μm)
	Optical Profiler 50x Image	Free Side	2673 nm	
		Filter Side	3751 nm	

3.4. Factors controlling the surface roughness of CNF film

Figure 16 reveals the factors controlling the roughness of the CNF film. The diameter and aspect ratio of cellulose nanofibrils decides the surface roughness of the film. The roughness can be decreased with decrease of diameter of fibers. From the spray coating experiment, spraying CNF suspension on the polished metal surface produce smooth CNF film which has considerate lower surface roughness. Base surface is another controlling parameter for surface roughness of the film.

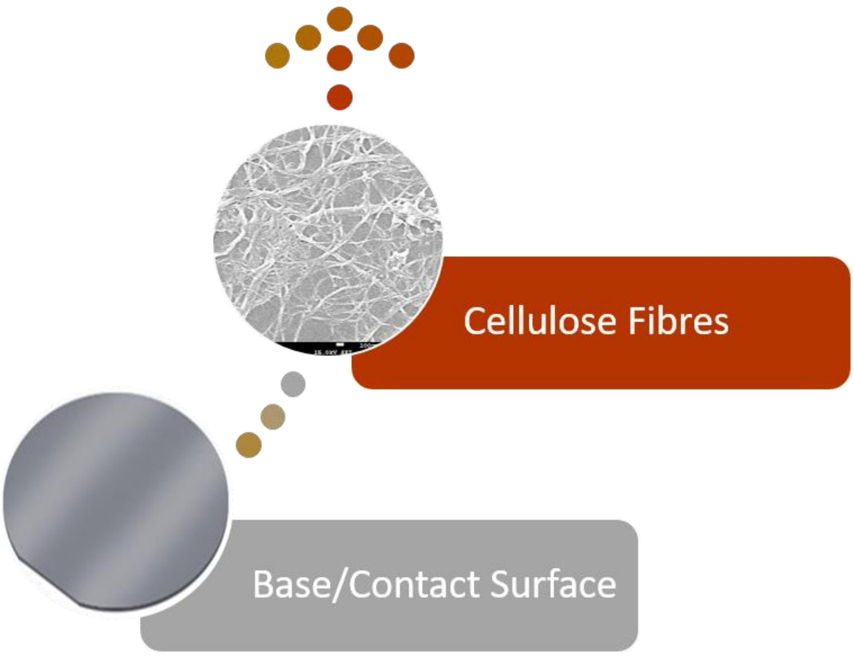

Figure 16. Factors controlling the surface roughness of the CNF film

Figure 17 shows the application of spray coated CNF film as a base substrate for developing printed electronics. The figure reveals various circuits printed on the smooth side of CNF film. As discussed earlier, the smooth side of the CNF film has lowest surface roughness and can be used as a base substrate for printing the ink in developing electronic circuits. The penetration of ink on the substrate is very important task in the developing printed electronics materials. The penetration of conductive ink on the substrates highly depends on the surface roughness and surface polarity of the base substrate either hydrophobic or hydrophilic [2, 20]. The smooth CNF film from spray coating can be a good substrate for electronics to replace synthetic plastics [15].

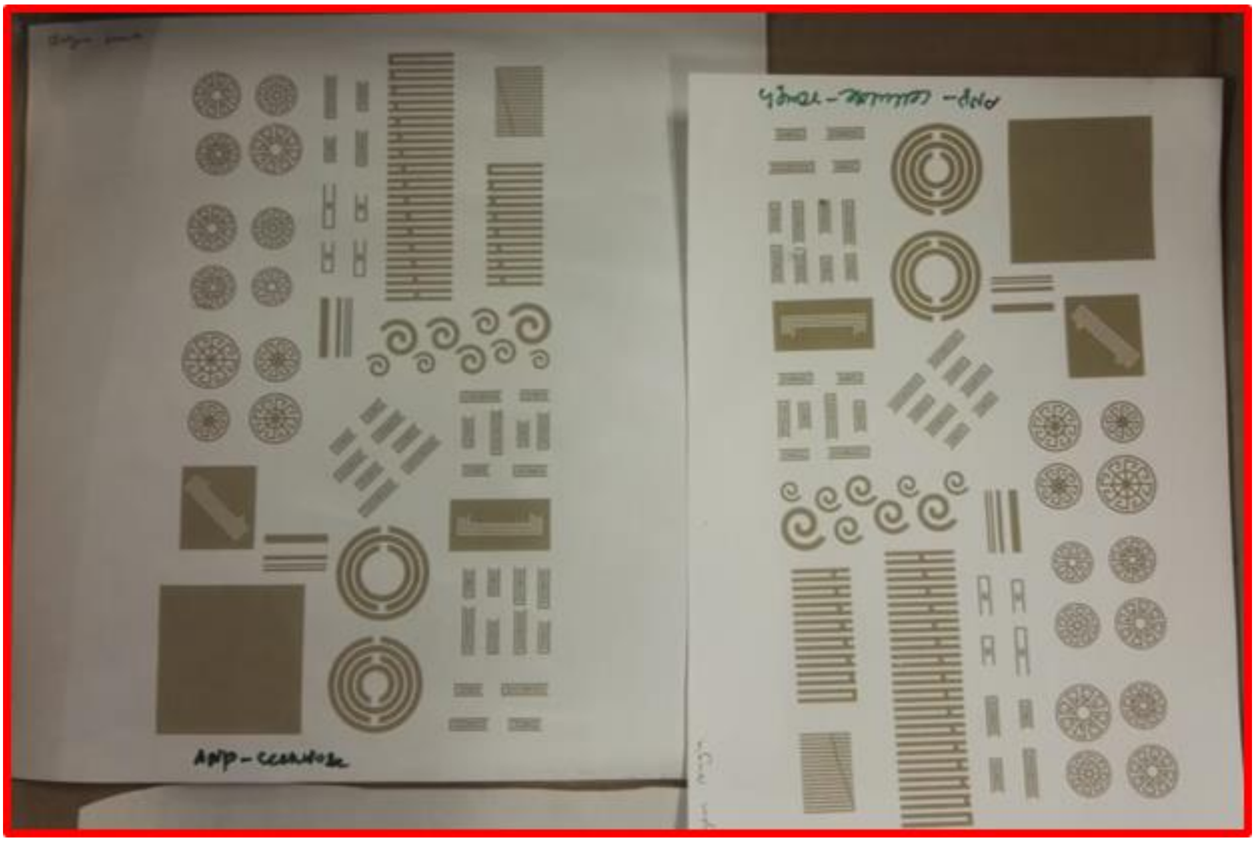

Figure 17. Various Electronic Circuits on Spray Coated Cellulose Nanofiber Film

4. Conclusion

Spraying CNF suspension on the polished stainless-steel plate is a novel approach for fabrication CNF film. This method produces the film with a good smoothness on the spray coated side of the film. This side has low RMS roughness value comparing with rough side of the film and filter side and free side of CNF film prepared via vacuum filtration. The lowest roughness of the CNF film is a base on developing substrate for printed electronics. CNF is an eco-friendly nanomaterial with biodegradability and a base biomaterial for developing substrate for flexible and printed electronics to replace the synthetic plastics.

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