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Research Article

Central Composite Design of Spraying Process to Laminate the Paper Substrates with Cellulose Nanofibers (CNF) as Green Packaging Wrap

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Green packaging wrap is now required to replace the synthetic plastic coating on the paper substrates. The coating of natural biopolymers on the paper substrates would be a potential method to achieve an ecofriendly coating to replace the synthetic materials which give a threat to the environment. Recently, spraying cellulose nanofiber (CNF) on the paper substrates to boost the barrier and mechanical properties of the paper is a flexible process and potential for scalability. Sprayed cellulose nanofibrils fill the surface pores of the paper substrates and form a barrier film on the paper surface. The spray-coated CNF barrier film on the paper substrates reduced the air passage and increased the mechanical strength. To scale up the process of spraying, the optimization was performed via response surface methodology to investigate the interaction between input variables and their response in spraying process. The variables impacting on the barrier performance, CNF coat weight, and thickness of the coat during spraying are CNF suspension concentration (A), fiber diameter (B), and spray distance from tip to the surface (C). The linear models were developed for CNF coat weight and thickness of the CNF coat weight on the paper substrates. The quadratic model for air permeability was developed with input variables. It concludes that the CNF suspension concentration is a strong parameter for controlling the CNF coat weight and thickness of the CNF coat on the paper substrates. The developed linear and quadratic models were validated with the experimental data confirming that it was a good fit to the real experimental data. From the CCD investigation of spray coating of CNF on the paper substrates, >1 wt.% CNF coating on the paper surface produces good thickness and coat weight on the paper substrates and gives an impermeable CNF laminate on the paper substrates against air. In conclusion, these models could provide a platform for scaling up the spraying process for coating CNF-based nanomaterials on the paper substrates.

1. Introduction

Paper is being used as packaging materials and wrapper for various purposes [1]. It is made up mainly of cellulosic fibers which are an ecofriendly material and have considerable biodegradability in the environment [1]. However, it has poor barrier properties such as high air permeability and water vapour permeability [1]. Generally, cellulose fibers are hydrophilic in nature and absorb the water vapour from the environment. As a result, the fibers are swollen and have the widest pores in the paper substrates. As a consequence, the barrier performance becomes worst and allows air and water vapour across the paper and these results in consumption of paper in large quantities that leads to loss of forest resources. To resolve this issue, the paper is coated with either wax, synthetic plastics, or aluminum conventionally through coating, extrusion etc. However, these coats on the paper substrates are sometimes not recyclable and also a threat to the environment [2].

Recently, cellulose nanofibers (CNF) are a sustainable biomaterial and carbohydrate-based polymer at nanoscale [3]. CNF was produced mainly from woods through mechanical homogenization process, chemical method—acid hydrolysis, enzymatic methods [4]. The coating of CNF on the paper substrates promoted their barrier properties of the sheet via creation of tortuous pathway and forming lamination on the paper surface [5]. In addition to that, the surface pores were blocked by the cellulose nanofibrils from the process, which results in the enhancement of barrier performance and mechanical properties [6]. There are many methods of CNF coating on the paper substrates [2, 7]. Predominantly, spraying is a process of spray deposition of cellulose nanofibrils on the paper substrates via creation of spray jet by spray gun in the experimental setup. Unlike vacuum filtration, spraying is independent of CNF suspension consistency in the coating of CNF on the paper substrates [8]. This process has the lowest operation time normally less than a minute to coat the paper surface. So this process has received good attention for scale-up and industrial feasibility [9].

To scale up the spraying process for CNF lamination on the paper substrates, process optimization is required to investigate the effect of various input parameters on the CNF coating on the paper substrates. Response surface methodology (RSM) was advanced for the optimization of spray coating of CNF on the paper surface. This method could give the optimized condition for spraying process of nanofibrils on the paper substrates. The mechanics of RSM are based on design of experiments which works with a set of statistical and mathematical tools to get optimized responses for coating process. The most important advantages of the RSM approach are the reduction of number of experiments with trial and error and give the optimized responses for the coating process [10].

Recently, RSM approach was implemented on the spraying of cellulose nanofiber on the polished metal surface for fabrication of free-standing CNF film. The linear models with optimized parameters were developed for scaling up the spraying processing and were validated with experimental conditions. Central composite design (CCD) in RSM was implemented to optimize the process variable for spraying CNF on the paper substrates. This paper deals the CCD optimization via RSM to investigate the coating process for paper substrates and validate the model from the CCD-RSM via carrying out the experiments within the given optimal conditions [11, 12].

2. Materials and Methods

DAICEL Celish KY 100S micro fibrillated cellulose (DAICEL, Japan) was used as cellulose nanofiber for coating the paper substrates via spraying method. Distilled water was used for disintegration of cellulose nanofiber in a high-speed disintegrator. Brown paper is used as base cellulose substrate and normally used as wrapper and packaging material [1, 9].

2.1. Response Surface Method. In this investigation, CNF suspension concentration, fiber diameter, and the distance between the spray tips to paper were evaluated for the spraying cellulose nanofiber on the paper substrates. These input parameters are influencing on the CNF coat weight or basis weight of CNF layer and thickness of CNF layer on the paper substrates. The range of input variables was evaluated from the previous spraying CNF process on the paper substrates. The central composite design (CCD), one of the RSM methods, was implemented in this optimization work on the spraying CNF on the paper substrates to achieve high-performance barrier coating on the paper. The range of CNF suspension to be sprayed on the paper substrates varied from 0.25 wt.% to 2 wt.% CNF. DAICEL CNF (DAICEL Chemical Company, Japan) was used as nanomaterial for coating the paper substrates. This CNF has fiber diameter of approximately 73 nm and an average length of 8 microns. The fibrillation/reduction of cellulose nanofibrils was performed by high-pressure homogenization (HPH). This is a mechanical method on the extraction of nanofibrils from cellulose microfibrils from fiber cell walls [4]. Therefore, the fiber diameter in CNF suspension ranges from 70 nm to 20 nm for using to spray [13]. The spray distance ranges from 30 cm to 50 cm for adjusting in the experimental setup. In CCD, this method consists of eight factorial points, six axial points, and six points at the center. The total number of experiments was evaluated according to

$$N = 2^a + 2a + \mathrm{Kc},$$
$$N = 2^3 + 2 * 3 + 6 = 20, \tag{1}$$

where N denotes the total number of experiments, a is a number of variables, and Kc is a number of replicates.

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 \sum_{i=1}^{n=1} \sum_{j=i+1}^{n} b_{ij} X_i X_j, \tag{2}$$

where Y is the response (yield), n is the number of independent variables, b_0 is the constant coefficient, b_i is the linear coefficients, b_{ii} is the quadratic coefficients, b_{ij} is the

Table 1: Optimization of input variables.

Factor	Name	Units	Type	Subtype	Minimum	Maximum	Coded low	Coded high	Mean	Std. dev.
A	Suspension concentration	wt.%	Numeric	Continuous	0.25000	2.00	$-1 \leftrightarrow 0.85$	$+1 \leftrightarrow 1.90$	1.125	0.4409
B	Fiber diameter	nm	Numeric	Continuous	20	70	$-1 \leftrightarrow 0.32$	$+1 \leftrightarrow 0.53$	45	12.6
C	Spray distance	cm	Numeric	Continuous	30.00	50.00	$-1 \leftrightarrow 34.05$	$+1 \leftrightarrow 45.95$	40.00	5.043

second-order interaction coefficients, and X_i and X_j are the coded values of the independent variables [14]. For getting a good regression fit from response surface to actual surface, the range of input variables is carefully considered and listed in Table 1. Generally, the lowest and highest range of variable can be designated by −1 and +1, respectively. The CNF suspension concentration, fiber diameter of CNF, and spray distance were the important variables to impact on the basis weight and thickness of the CNF laminates on the paper substrates [1, 15, 16].

2.2. Method of Optimization. For optimizing the process conditions in CNF lamination via spraying, CCD is used as a RSM method. The Design-Expert 8.0.5 software (State-Ease Inc., Minneapolis MN, USA) was used for this investigation. The effect of three main variables on spraying was CNF suspension concentration, fiber diameter, and distance between the spray tip and the base. The variables are optimized and their interaction evaluated via this method. The level and ranges chosen for the factors are shown in Tables 1 and 2. The complete design consisted of 20 experimental points. The 20 samples were prepared in random order. In each experiment, the basis weight and thickness of CNF coat weight were measured and trail was performed in triplicates. The basis weight, thickness of the CNF coat weight, and air permeance of the CNF laminated paper substrates were taken mean values as responses. Table 2 shows the experimental design matrix and consists of corresponding outputs as responses.

3. Experimental Works

3.1. Spraying Cellulose Nanofiber Suspension on the Paper Substrates. Cellulose nanofiber supplied from DAICEL Chemical Industries Limited (Celish KY-100S evaluation) was used for spray coating purpose. The domestic spray gun is used for spraying cellulose nanofiber on the paper substrates. The spray gun produces elliptical spray pattern of spray jet of CNF on the paper substrates, and the distance between spray nozzle and paper substrate was maintained around 30 ± 2 cm. The coating was performed one pass to form a CNF layer on the surface of paper materials. The drying of spray-coated CNF on the paper was carried out in air drying under standard laboratory conditions. The experimental set is shown in Figure 1 [9].

3.2. Drying of Spray-Coated CNF Laminates on the Paper Substrates. The drying of spray-coated CNF barrier layers on the paper substrates was performed in the open air under standard engineering conditions. In brief, the wet spray-coated CNF barrier layers on the paper substrates were kept in the fume hood operating under constant velocity of air. The flowing air can dry wet spray-coated CNF barrier layers on the paper substrates. The dried CNF layers on the paper substrates were used for various characterizations such as surface topography, basis weight, thickness, and air permeability [9].

3.3. Basis Weight and Thickness 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 paper specimen, after 4 hours drying in the oven at a temperature of 105°C, by the area of paper specimen [9]. 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 measured at fifteen points on various locations of the spray-coated CNF paper specimen and averaged. The thickness was measured according to TAPPI T 411, 2015 [17].

3.4. Air Permeability. The air permeance of spray-coated CNF barrier layers on the paper specimen was measured with an L&W air permeance tester. This instrument has an operating range from 0.003 to 100 μm/Pa·S. The evaluated value less than 0.003 μm/Pa·S of the coated paper notifies that the product is an impermeable sheet against air and other gaseous substance. 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 films [9].

4. Results and Discussion

To overcome the global issue in synthetic plastic pollution, packaging materials from natural polymers have been utilized to replace the synthetic plastic packaging materials [2, 6, 7, 18]. Cellulose nanofiber (CNF) is a novel carbohydrate polymer fibrillated from cellulose fiber extracted from pulps [4]. It is reported that CNF has good mechanical and barrier properties with good biodegradability in the environment [19]. The CNF film required 40 days for complete disappearance of the film in the environment when the films with thickness of 3 to 100 microns were buried in humus soil for several days [20]. CNF has web-like structure containing crystalline part producing tortuous path in the fibrous matrix. As a result, CNF has good barrier properties against air and water vapour and oxygen [3, 19, 21]. CNF has good barrier properties and suitability for packaging application [22]. Because of CNF barrier performance, it can be used a coating material for paper and paperboard substrates to

Table 2: Design of experiments.

Std.	Run	Factor 1 A: suspension concentration wt.%	Factor 2 B: fiber diameter nm	Factor 3 C: distance between spray gun and surface cm	Response 1 Basis weight Gram per square meter	Response 2 Thickness of coat Microns	Response 3 Air permeability Microns/(Pascal·second)
19	1	1.125	45	40	14.691	74.48	0.003375
7	2	0.605	59.865	45.95	3.65	44.6	1.056
2	3	1.645	30.135	34.05	30.34	80.91	0.003
1	4	0.605	30.135	34.05	3.56	44.74	0.7809
8	5	1.645	59.87	45.95	30.92	93.33	0.006
15	6	1.125	45	40	14.691	74.48	0.003375
20	7	1.125	45	40	14.691	74.48	0.003375
10	8	2	45	40	30.67	85.97	0.003
12	9	1.125	70	40	29.37	87.33	0.003
14	10	1.125	45	50	20.63	65.68	0.0123
9	11	0.25	45	40	1.425	23.99	2.564
3	12	0.605	59.865	34.05	3.426	41.88	0.97
17	13	1.125	45	40	14.691	74.48	0.003375
18	14	1.125	45	40	14.691	74.48	0.003375
13	15	1.125	45	30	14.567	75.57	0.0567
11	16	1.125	20	40	12.456	25.78	0.003
5	17	0.605	30.135	45.95	3.322	43.8	0.987
4	18	1.645	59.865	34.05	35.37	88.91	0.003
16	19	1.125	45	40	14.691	74.48	0.003375
6	20	1.645	30.135	45.95	30.654	81.46	0.0115

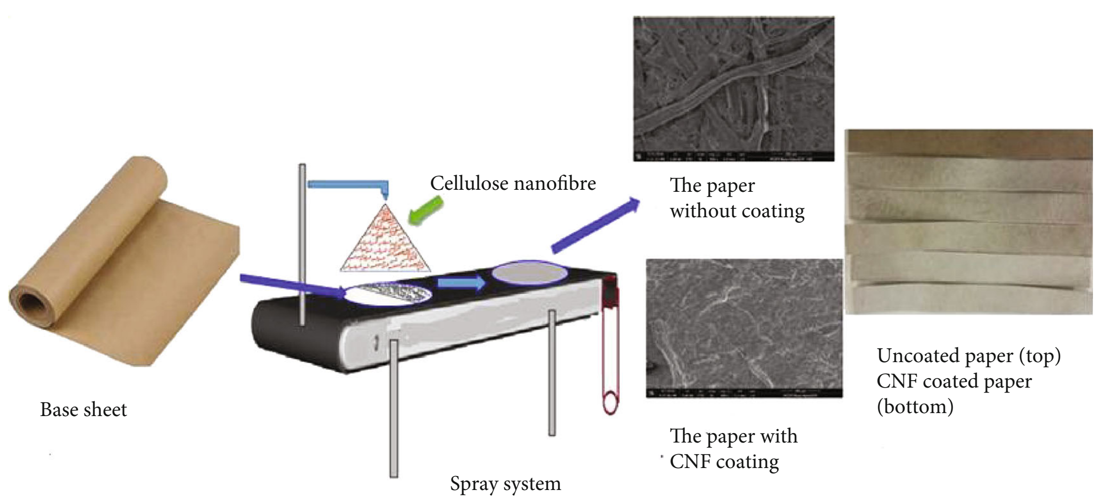

Figure 1: Spray coating experimental system for coating CNF on the paper substrates [9].

enhance their barrier performance and mechanical properties [1]. CNF coating is an alternative for wax coating, aluminum extrusion, and synthetic plastic coating on the paper substrates [23]. There are many methods for CNF coating on the paper substrates, namely, vacuum filtration, rod coating, bar coating, dip coating, and spray coating. Recently, spraying CNF on the paper substrates produces good barrier layers on the paper substrates and these layers act as good barrier against air, water vapour, and oxygen [8, 9].

Spray-coated CNF laminates on the paper substrates reduce the air permeability from 3.5 μm/Pa·S to < 0.003 μm/Pa·S [9]. Spraying is a flexible process for handling any type of CNF suspension concentration and an operation time of less than a minute in forming the barrier layers [8, 9, 15, 24]. This process has a potential for scale-up and requires the optimization for spraying to evaluate what variables influencing the properties of CNF barrier layers on the paper substrates. Response surface method (RSM) is a modeling

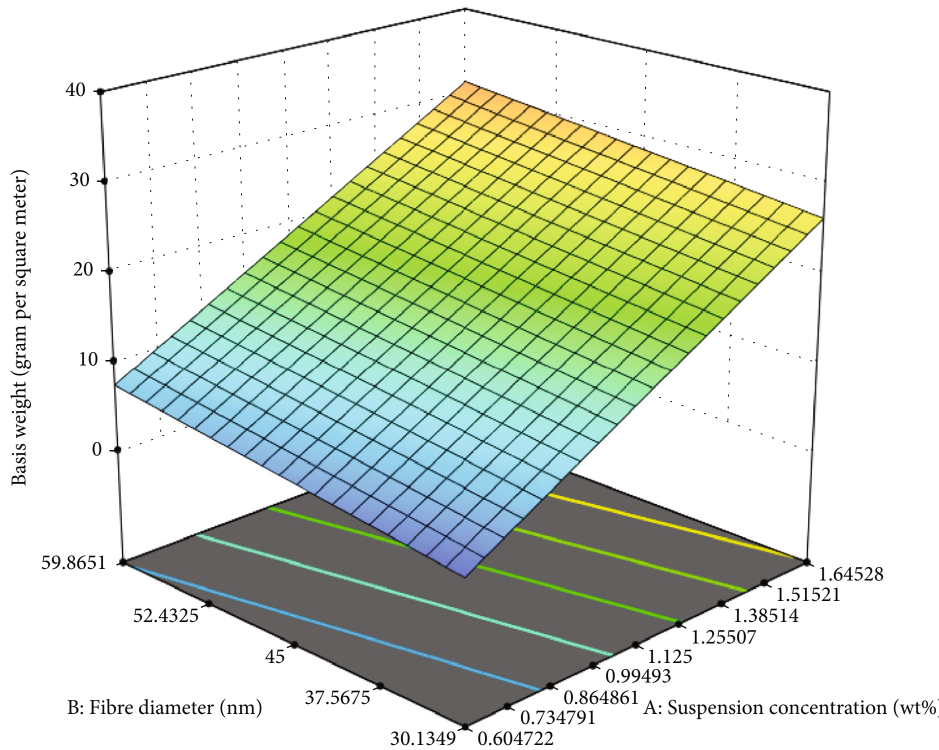

Figure 2: 3D surface plot of the interaction between fiber diameter of CNF and CNF suspension concentration and their effect on CNF basis weight/coat weight on the paper substrates.

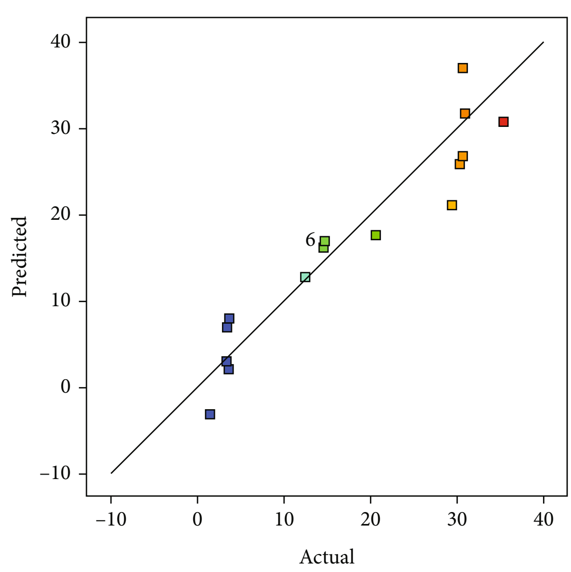

Figure 3: The predicted and actual plot for basis weight of the CNF laminated paper substrates.

Table 3: Fit statistics.

Std. dev.	4.02	R^2	0.8864
Mean	16.93	Adjusted R^2	0.8650
C.V. %	23.78	Predicted R^2	0.8009
		Adeq precision	22.2404

and optimization technique to evaluate and identify the correlation between. Additionally, this optimization approach explores the impact of various variables on their responses. RSM various variables and responses in the processes with the desired criteria in both design of experimental setup and processes are both mathematical and statistical methods for developing the modeling and analysis of the processes where the input variables stress on their responses and help to optimize the given processes.

CNF lamination on the surface of paper substrates gives promising results in the improvement of barrier performance against air and water vapour. CNF coating was carried out by many methods such as dip coating, rod coating, and bar coating. Recently, spraying of CNF on the paper substrates forms a good lamination on the surface of the paper substrates and formed a CNF film as laminates which acts as a barrier against air and water vapour. When comparing to other conventional coating method, spray coating is a feasible method and has advantages of operation time independent of CNF suspension concentration, counter coating on the base surface, and topography of the surface does not influence the coating surface. To scale up the spraying process for coating, the optimization of key variables and their interaction between them is necessary to analyse their response as outcomes such as CNF coat weight and thickness on the paper substrates.

4.1. CNF Coat Weight. The experimental study confirms that the CNF coat weight on the paper substrates strongly depends on the CNF suspension concentration. Spraying CNF with different concentrations on the paper substrates gives thin or thick CNF coat weight on the paper substrates.

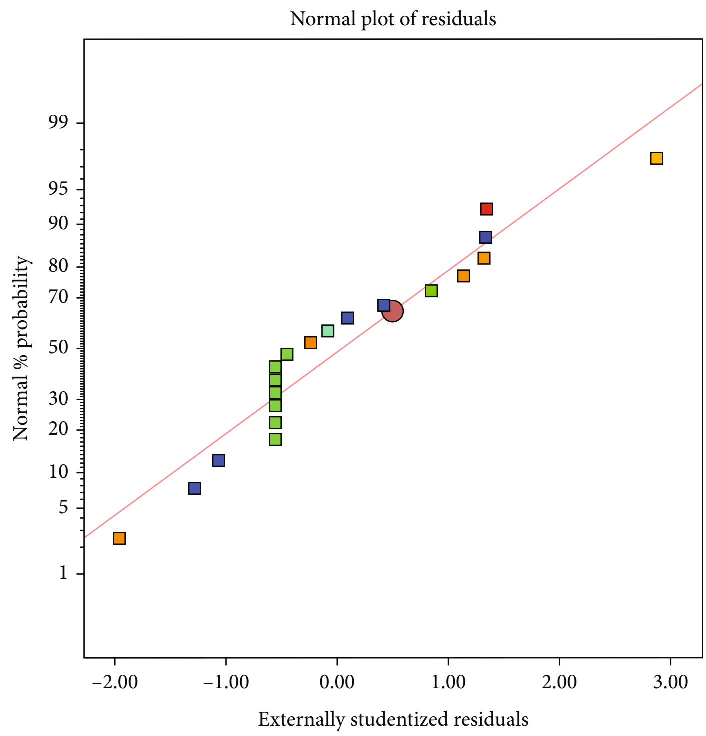

FIGURE 4: Normal plot for basis weight response.

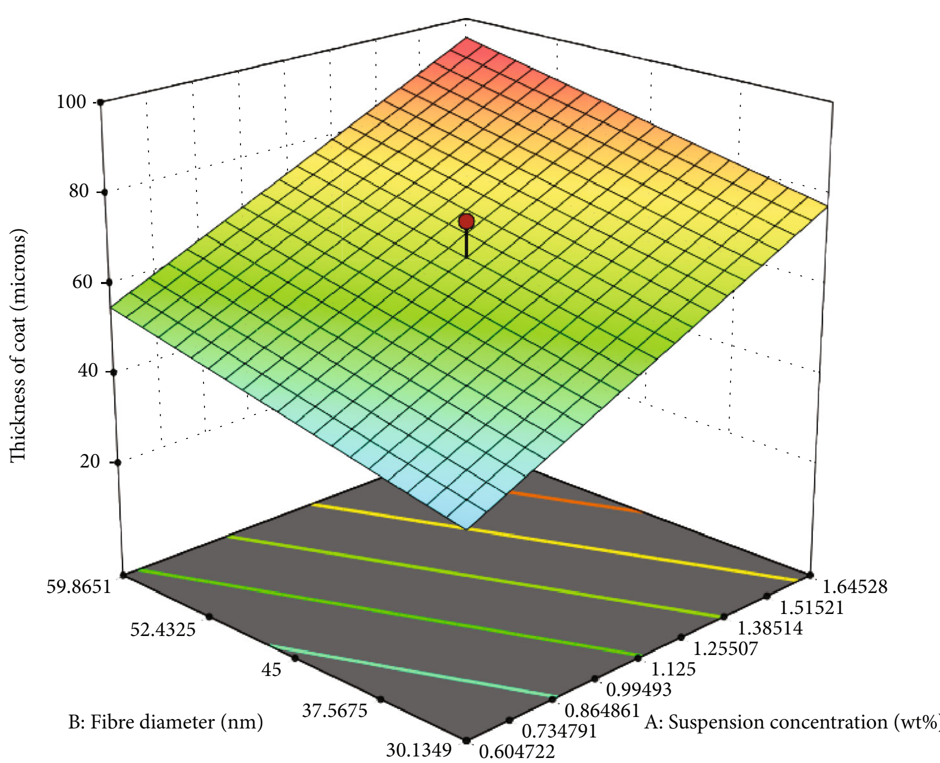

FIGURE 5: 3D surface plot of the interaction between fiber diameter of CNF and CNF suspension concentration and their effect on thickness of CNF coat weight on the paper substrates.

Figure 2 shows the effect of CNF suspension concentration on the CNF coat weight on the paper substrates. It is a direct relationship between the CNF suspension concentration and CNF coat weight. The diameter of CNF fibrils does not much influence on the CNF coat weight on the paper substrates. The cellulose nanofibrils can be reduced by

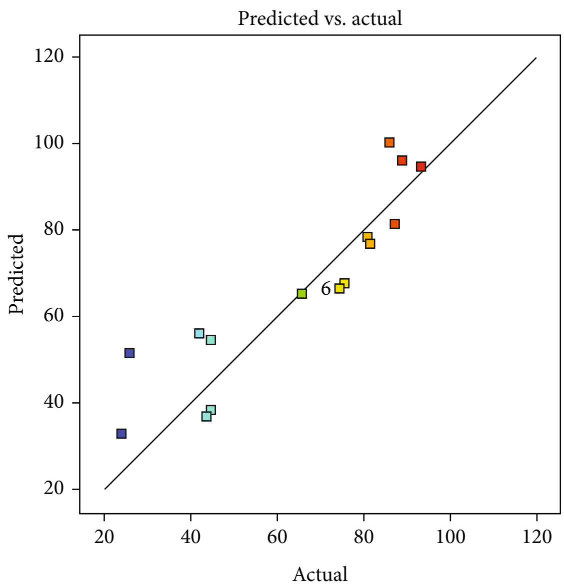

Figure 6: Plot between predicted and actual response for thickness of CNF coat as a response.

Table 4: Fit statistics.

Std. dev.	10.88	R^2	0.7762
Mean	66.54	Adjusted R^2	0.7343
C.V. %	16.36	Predicted R^2	0.6224
		Adeq precision	13.8549

high-pressure homogenization which is an energy consumption process [13]. Another issue is the increase of viscosity of CNF suspension while the fiber diameter reduced. As a consequence, CNF suspension behaves like thick gel-like fluid and very hard to spray the suspension for coating [1]. The linear model has been developed from this study as follows.

4.2. Final Equation in terms of Actual Factors.

$$\begin{aligned}\text{Basis weight} = &-19.30596 + 22.87146 \\ &* \text{suspension concentration} \\ &+ 0.167163 * \text{fiber diameter} \\ &+ 0.074463 * \text{distance between} \\ &\quad \text{spray gun and surface.}\end{aligned} \quad (3)$$

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The above correlation has been concluded that CNF suspension is a strong parameter for controlling the CNF coat weight on the paper substrates [9]. The advantages of reducing the diameter of cellulose nanofibrils can reduce the porosity of the CNF coated paper substrates and promote the tortuous pathway for air and water vapour. As a result, the barrier performance of the coated paper was increased.

Figure 3 shows the predicted and actual plot of CNF coat weight on the CNF laminated paper via spraying. The actual responses are the data from experimental works for various runs performed as per design of experiments. It was evaluated with the predicted values from the linear model. Table 3 summarizes the statistics containing the significant values of R^2.

The predicted R^2 of 0.8009 is in reasonable agreement with the adjusted R^2 of 0.8650; i.e., the difference is less than 0.2. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 22.240 indicates an adequate signal. This model can be used to navigate the design space.

Figure 4 shows the normal probability plot developed from RSM analysis for the CNF coat weight as one of the response. Figure 4 reveals the distribution of errors near the diagonal line and shows "S"-shaped curve on the diagonal line. It reveals that the transformed response required a better analysis.

4.3. Thickness of the CNF Coat. Figure 5 shows the effect of fiber diameter and CNF suspension consistency on thickness of CNF coat weight on the paper substrates. Thickness of CNF coated increases with CNF suspension concentration. It is confirmed that CNF suspension concentration is a predominant parameter for controlling thickness of the CNF coat on the paper substrates. It seems that thickness of the coat decreased with fiber diameter. It can be used as thin lamination of the paper substrates via spraying of highly homogenized CNF suspension on the paper substrates. During spraying of CNF suspension, the watery suspension could cause the reflection of spray jet from paper substrates and resulting poor lamination on the substrates. The spray of high viscous CNF suspension can easily coat the surface of the paper and adhere on the paper surface. The thickness and CNF coat weight are directly proportional to the CNF suspension concentration.

Figure 6 reveals the plot between predicted and actual values for the thickness of the CNF coat on the paper substrates. Table 4 summarizes the values from fit statistics, and the linear model has been developed and concluded that CNF suspension concentration is a strong parameter for controlling the thickness of CNF coat weight [9]. Table 4 reveals the lowest R^2 around 0.7742. This low value comes due to the processing of spray-coated wet CNF lamination on the paper substrates. Once the CNF was sprayed on the paper to form the wet lamination on the paper, CNF suspension moves here around on the paper when handling wet lamination of CNF paper for drying. This is why the variation in the thickness of CNF coat on the paper was observed during measurement, and as a result, low R^2 comes in the RSM software evaluation.

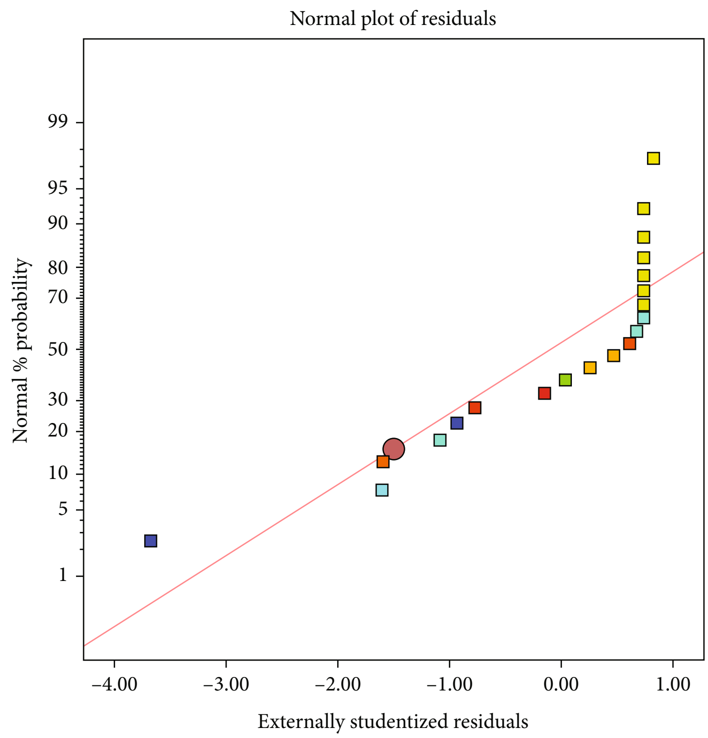

FIGURE 7: Normal plot of thickness of CNF coat.

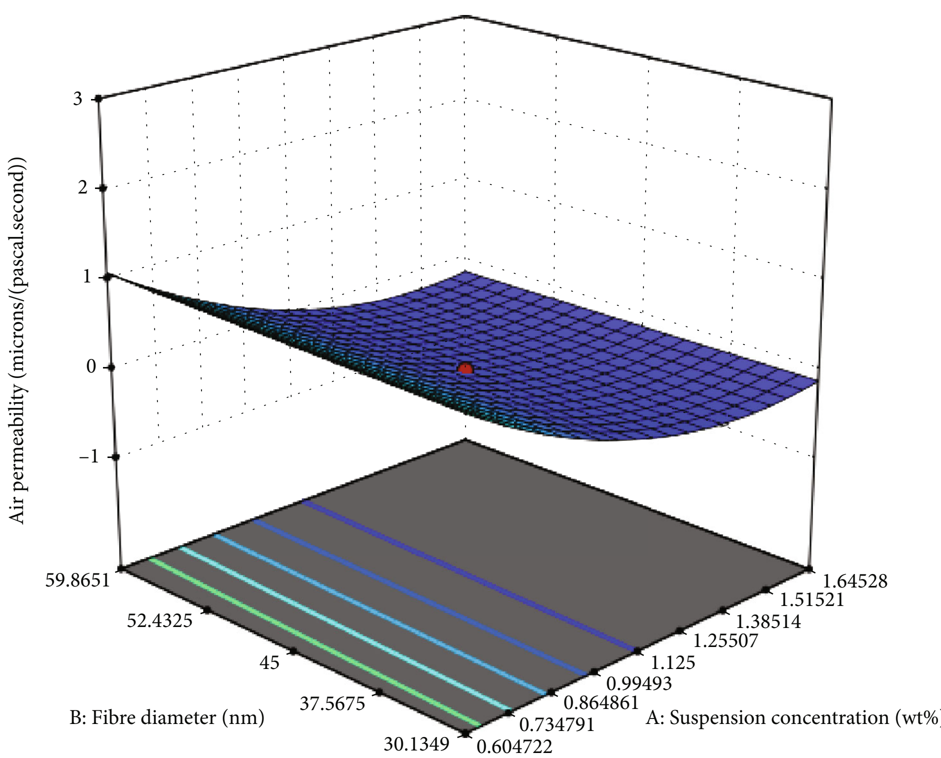

FIGURE 8: 3D surface plot of the interaction between fiber diameter of CNF and CNF suspension concentration and their effect on air permeability of the CNF laminated paper substrates.

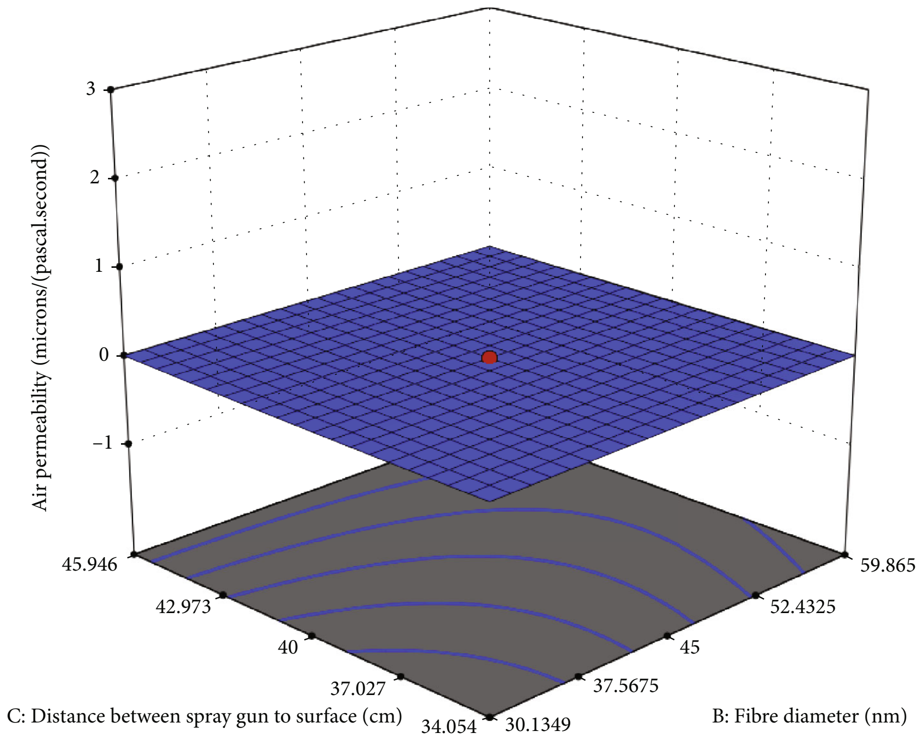

Figure 9: 3D surface plot of the interaction between fiber diameter of CNF and distance between spray gun and surface and their effect on air permeability of the CNF laminated paper substrates.

Table 5: Fit statistics.

Std. dev.	0.1711	R^2	0.9639
Mean	0.3240	Adjusted R^2	0.9315
C.V. %	52.82	Predicted R^2	0.7257
		Adeq precision	20.2558

4.4. Final Equation in terms of Actual Factors.

$$\begin{aligned}\text{Thickness of coat} = {} & 1.15967 + 38.53862 \\ & * \text{suspension concentration} \\ & + 0.597617 * \text{fiber diameter} \\ & - 0.121709 * \text{distance between} \\ & \quad \text{spray gun and surface.}\end{aligned} \quad (4)$$

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The predicted R^2 of 0.6224 is in reasonable agreement with the adjusted R^2 of 0.7343 (Table 4); i.e., the difference is less than 0.2. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 13.855 indicates an adequate signal. This model can be used to navigate the design space.

Figure 7 reveals the normal probability plot developed from RSM analysis for the thickness of CNF coat weight as one of the response. Figure 7 reveals the distribution of errors near the diagonal line and shows "S"-shaped curve on the diagonal line. It reveals that the transformed response required a better analysis.

4.5. Air Permeability. Air permeance of the CNF laminated paper substrates reveals the barrier performance of spray-coated CNF lamination on the paper substrates. The mechanism of barrier coating describes via the filling of surface pores on the paper substrates with cellulose nanofibrils. As a result, air passage across the coated paper is decreased and improved the barrier performance. At high CNF suspension coat weight, the barrier film formed on the surface of the paper and the coated paper becomes completely impermeable against air, oxygen, and water vapour.

Figure 8 reveals the effect of fiber diameter and CNF suspension concentration on the air permeability of the coated sheet as one of the most important response in the optimization studies. The air permeability of CNF coated sheet gradually reduced with increasing CNF concentration for coating on the paper surface. This quadratic model has been developed for this behaviour for reduction of air permeance of the CNF coated paper. CNF suspension concentration is the most important parameter for controlling air permeance of the paper substrates. During the spraying of watery CNF suspension, CNF nanofibrils fill the surface pores of the paper substrates and reduced the air permeance drastically from 3.54 μm/Pa·S. to 2.56 μm/Pa·S. At higher CNF coat, the CNF barrier film formed on the surface of paper

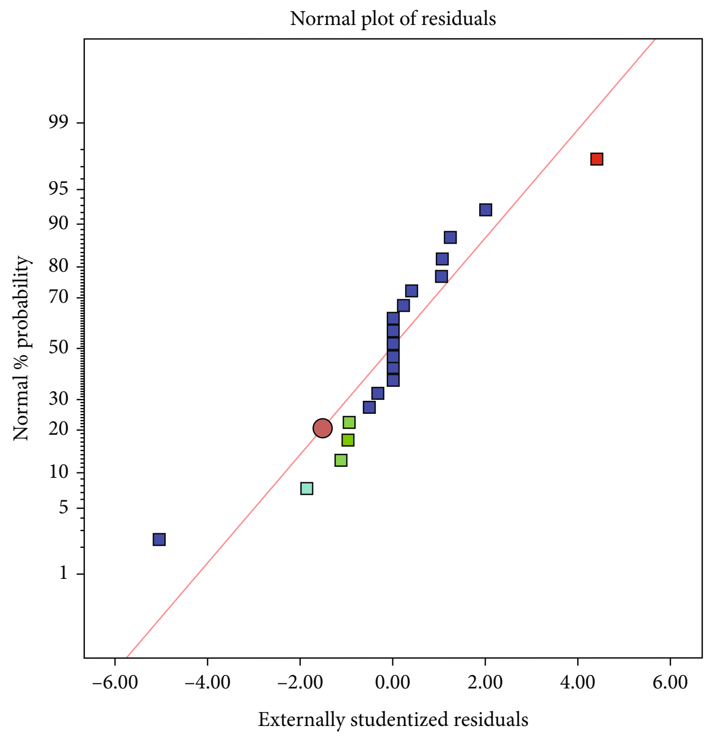

FIGURE 10: Normal plot for air permeability as one of the response for spray-coated CNF laminates on the paper sheet.

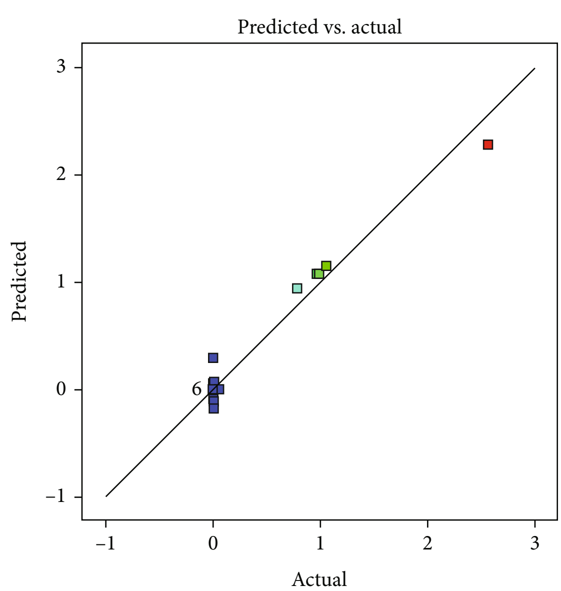

FIGURE 11: Normal plot for air permeability as one of the response for spray-coated CNF laminates on the paper sheet.

substrates resulting in the impermeable sheet against air and other gaseous substances.

Fiber diameter is a noted parameter for controlling air permeance of the paper sheet. The diameter of cellulose nanofibrils in raw CNF (DAICEL) is evaluated to be ~73 nm with an average length of 8 μm. The reduction of cellulose nanofibrils was performed via high-pressure homogenization. CNF are reduced to 40 nm and 20 nm and then sprayed on the paper substrates and evaluated air permeance. As a consequence, the air permeance was reduced and their mechanism for reduction based on the reduced pore size due to fiber diameter. However, it is small effect on air permeance of the coated sheet in this investigation.

Figure 9 reveals the effect of fiber diameter of CNF and the distance between the spray gun to the paper surface and their effect on air permeability of the CNF laminated paper substrates. 3D plots confirm that these parameters do not influence the air permeance of the CNF coated paper substrates.

4.6. Final Equation in terms of Actual Factors.

$$\begin{aligned}\text{Air permeability} = {} & +2.80938 - 4.27171 \\ & \text{suspension concentration} \\ & + 0.012308 \text{ fiber diameter} \\ & - 0.006268 \text{ distance between} \\ & \text{spray gun and surface} \\ & - 0.004260 \text{ suspension} \\ & \text{concentration} * \text{fiber diameter} \\ & - 0.011338 \text{ suspension concentration} \\ & * \text{distance between spray gun and} \\ & \text{surface} - 0.000178 \text{ fiber diameter} \\ & * \text{distance between spray gun and surface}\end{aligned} \tag{5}$$

The equation in terms of actual factors can be used to make predictions about the response for given levels of

Table 6: Response 1: basis weight.

Source	Sum of squares	df	Mean square	F value	P value	
Model	2020.80	3	673.60	41.60	≤0.0001	Significant
A: suspension concentration	1933.79	1	1933.79	119.42	≤0.0001	
B: fiber diameter	84.33	1	84.33	5.21	0.0365	
C: distance between spray gun and surface	2.68	1	2.68	0.1653	0.6897	
Residual	259.10	16	16.19			
Lack of fit	259.10	11	23.55			
Pure error	0.0000	5	0.0000			
Cor total	2279.90	19				

Factor coding is *coded*. Sum of squares is *type III-partial*.

Table 7: Response 2: thickness of coat.

Source	Sum of squares	df	Mean square	F value	P value	
Model	6575.47	3	2191.82	18.50	≤0.0001	Significant
A: suspension concentration	5490.53	1	5490.53	46.34	≤0.0001	
B: fiber diameter	1077.78	1	1077.78	9.10	0.0082	
C: distance between spray gun and surface	7.15	1	7.15	0.0604	0.8090	
Residual	1895.63	16	118.48			
Lack of fit	1895.63	11	172.33			
Pure error	0.0000	5	0.0000			
Cor total	8471.10	19				

Factor coding is *coded*. Sum of squares is *type III-partial*.

Table 8: Response 3: air permeability.

Source	Sum of squares	df	Mean square	F value	P value	
Model	7.83	9	0.8695	29.70	≤0.0001	Significant
A: suspension concentration	4.78	1	4.78	163.16	≤0.0001	
B: fiber diameter	0.0047	1	0.0047	0.1596	0.6980	
C: distance between spray gun and surface	0.0038	1	0.0038	0.1311	0.7249	
AB	0.0087	1	0.0087	0.2966	0.5979	
AC	0.0098	1	0.0098	0.3361	0.5749	
BC	0.0020	1	0.0020	0.0673	0.8005	
A^2	2.98	1	2.98	101.79	≤0.0001	
B^2	0.0001	1	0.0001	0.0021	0.9646	
C^2	0.0025	1	0.0025	0.0856	0.7759	
Residual	0.2928	10	0.0293			
Lack of fit	0.2928	5	0.0586			
Pure error	0.0000	5	0.0000			
Cor total	8.12	19				

Factor coding is *coded*. Sum of squares is *type III-partial*.

each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The predicted R^2 of 0.7257 is not as close to the adjusted R^2 of 0.9315 as one might normally expect (Table 5); i.e., the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. All empirical models should be tested by doing confirmation runs. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 20.256 indicates an adequate signal. This model can be used to navigate the design space.

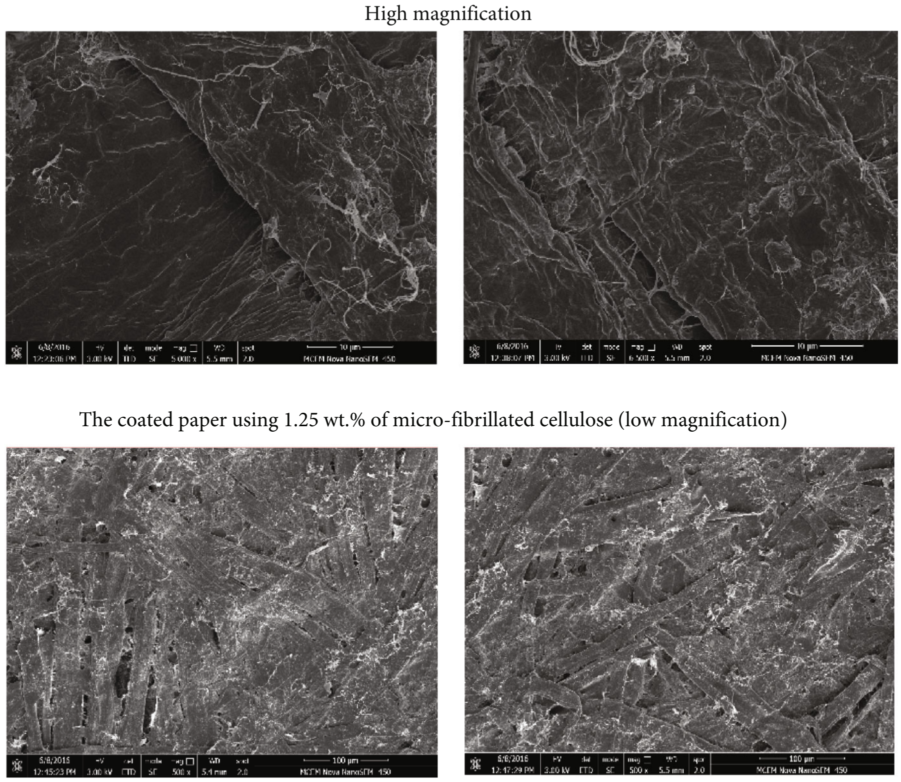

Figure 12: SEM micrographs of the spray-coated paper at hand low magnification. The high-magnification image shows the coating coverage of the surface of the base sheet. The surface of the coated base sheet shows different sizes of the cellulose fibers. SEM micrographs reveal the closure of surface pores on the paper by cellulose nanofibers.

Figure 13: 1.25 wt.% CNF spray-coated wet laminates of cellulose nanofiber on the paper.

Figure 14: Spray-coated CNF laminates on the paper.

Figure 10 reveals the normal probability plot developed from RSM analysis for the air permeability of CNF coated paper substrates as one of the response. Figure 10 reveals the distribution of errors near the diagonal line and shows "S"-shaped curve on the diagonal line. It reveals that the transformed response required a better analysis.

Figure 11 reveals the normal plot of the data on air permeability as one of the response in this design of experiments. Most of the data are laid on the diagonal line concluding that the data are significant.

4.7. ANOVA for Linear Model. The model F value of 41.60 implies the model is significant. There is only a 0.01% chance that an F value this large could occur due to noise. P values less than 0.0500 indicate model terms are significant. In this case, A, B are significant model terms. Values

Table 9: Comparison of ordinary experimental data with data from models.

Input variables	Responses	Experimental	Statistical models
CNF suspension concentration (1.25 wt.%)	CNC coat weight (g/m^2)	17.94 ± 3.25[a]	23.221[a]
Fiber diameter (~ 70 ± 3 nm)	Thickness of the CNF coat (μm)	82.35 ± 10.25[b]	87.51[b]
Spray distance (30 ± 2 cm)	Air permeability (μm/Pa·S)	`0.003375[c]	0.3[c]

[a]Due to handling of spray-coated wet CNF on the paper substrates, the fluctuations in coat weight were observed. [b]Due to the movement of spray-coated wet CNF on the paper substrates, the fluctuations in thickness were observed. [c]The mechanism of drop in air permeance was based on the number of pores in CNF coat on the paper substrates.

greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Tables 6–8 summarize ANOVA details of CNF coat weight, thickness of CNF coat weight, and air permeability. These tables reveal that F value is high for the CNF suspension concentration for all responses. It confirms that CNF suspension concentration is the predominant parameter for controlling the CNF coat weight and thickness of the coat and air permeance of CNF laminated paper substrates. CNF suspension concentration is a highly significant parameter for CNF coat weight, CNF coat thickness, and air permeability of the CNF laminated paper substrates. In all the above models, "P" value for CNF suspension concentration is less than 0.0001 and confirms that CNF suspension concentration has a predominant effect on the CNF coat weight, thickness of CNF coat weight, and air permeance of the CNF laminated paper substrates.

P values for fiber diameter and spray distance are 0.0365 and 0.6897 for the CNF coat weight response, 0.0082 and 0.8090 for the thickness of CNF coat weight, and 0.6980 and 0.7249 for the air permeability for CNF coated paper substrates.

4.8. ANOVA for Linear Model. The model F value of 18.50 implies the model is significant. There is only a 0.01% chance that an F value this large could occur due to noise. P values less than 0.0500 indicate model terms are significant. In this case, A, B are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

4.9. ANOVA for Quadratic Model. The model F value of 29.70 implies the model is significant. There is only a 0.01% chance that an F value this large could occur due to noise. P values less than 0.0500 indicate model terms are significant. In this case A, A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

4.10. Model Equation. The linear models have been developed by CCD in RSM for the response for CNF coat weight and thickness of CNF coat weight on the paper substrates. It optimized that CNF coat weight and thickness of the CNF coat rely strongly on the CNF suspension concentration rather than fiber diameter and spray distance. Equations (3) and (4) are linear models developed from the strong correlation between input factors and output responses which was affirmed by R^2 and its associated values. The above models are linear models confirming the relation between CNF coat weight and thickness which are responses and CNF suspension concentration as one of the most important input variables.

Equation (5) is a quadratic model for air permeance on the CNF laminated paper substrates. It confirmed the nonlinear relationship between air permeance and CNF coat weight and other parameters. P values for CNF suspension concentration and suspension concentration^2 are less than 0.0001 and are significant. This model confirms that air permeability of the paper substrates can be tailored via spraying of CNF on the paper substrates and is a strong function of CNF suspension concentration and fiber diameter. Experimentally, it was confirmed that increasing CNF concentration for coating on the paper substrates results in a considerable reduction of air permeance. At high CNF concentration coating on paper surface, CNF forms an impermeable barrier layer on the paper substrates and completely blocks the air passage across the coated paper. In the case of lower CNF coating, CNF fills the surface pores of the paper substrates and results in the reduction of air permeance. Fiber diameter is another key parameter for increasing the barrier performance of the paper substrates. Decreasing the cellulose nanofibrils for coating on the paper increases the tortuous pathway for gaseous substances. As a consequence, the barrier performance of the coated paper increased. Process parameters such as spray distance could play a little in the reduction of barrier performance of the coated sheet.

4.11. Experimental Confirmation. Spraying of cellulose nanofiber (CNF) on the paper substrates is a flexible process for coating CNF on the paper surface. Spraying CNF on paper substrates is independent of CNF suspension concentration in the process and has an operation time less than one minute. In order to verify the models from this optimization, 1.25 wt.% CNF was sprayed on the paper substrates to evaluate the models through the real values of the responses such as CNF coat weight, thickness of CNF coat, and air permeability of the CNF coated paper substrates [9].

4.12. SEM Micrographs. Figure 12 shows the 1.25 wt.% CNF coated paper substrates, and SEM micrographs reveal the blockage of surface pores in the paper surface with cellulose nanofibrils. In addition to that, the sprayed CNF forms barrier films on the surface of paper substrates and this film acts a barrier against air and water vapour.

4.13. CNF Laminates on the Paper (Visual Observance). Figures 13 and 14 show the visual observance of the CNF coated paper substrates. Spraying produced uniform coating on the paper surface. When increasing CNF suspension concentration on the paper substrates, the density of CNF coat on the paper increased and observed visually in Figure 14.

In comparison with experimental conditions, data are summarized in Table 9. It was observed that the experimental data are exactly matched with the data derived from the mathematical models. The responses obtained from mathematical model for an optimized input variable were compared with experimental results, and it is summarized in Table 9.

4.14. Application of Optimization. Apart from pure CNF coating on the paper substrates with optimized conditions, these models can be applied to the CNF suspension with bismuth compounds and any other antimicrobial agents sprayed on the paper substrates to increase the antimicrobial performance of the coating and barrier performance. In addition to that, the same optimized conditions were also implemented in the superhydrophobic CNF coating on the paper substrates to repel the biofilm formation on the paper substrates. Nanoclay+CNF composite suspension can be sprayed on the paper substrates to boost the barrier performance of the coated paper substrates. The incorporation of nanoclay into nanocellulose suspension for coating would increase the diffusion pathway for air, oxygen, and water vapour across the coated paper substrates. As a consequence, the barrier and mechanical performance of the spray-coated CNF-nanoclay paper substrate were elevated via the implementation of optimized conditions from the RSM method.

5. Conclusion

To scale up spraying process for coating CNF barrier layers on the paper substrates, various successful mathematical models were developed via central composite design (CCD) in response surface method (RSM). The main variables involved in the spraying process which impacts the bulk properties of the CNF coat on the paper substrates were CNF suspension consistency, fiber diameter, and spray distance in the experimental setup. The developed linear RSM models exhibit the relation between the input variables and the output responses such as CNF coat weight and thickness of CNF coat for spray coating process. In spraying process, the quadratic model was generated for the relation between the input variables and CNF coat weight and thickness of CNF coat and these effects on the air permeance of the spray coated CNF paper substrates. The developed models were authenticated via ANOVA. The model was experimentally fit with the optimized input variables, and the confirmation between both the results implies that the model is statistically significant. The relation between basis weight and thickness of the film was linear and verified both experimentally and mathematically. P value > F confirmed that the linear model for spraying process is significant. This RSM studies confirmed that CNF suspension concentration is a strong parameter for controlling the basis weight and thickness of the CNF film than that of fiber diameter and spray distance from the spray tip to the base in the experimental setup. Given this correspondence, RSM optimization of spraying process can be a good base for scaling up the process for industrial applications.

Data Availability

The underlying data supporting the results of this study have been included in the paper.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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