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The Optimization of Electrical Conductivity Using Central Composite Design for Polyvinyl Alcohol/Multiwalled Carbon Nanotube-Manganese Dioxide Nanofiber Composites Synthesised by Electrospinning

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Abstract: This research reports the characterization and statistical analysis of electrical conductivity optimization for polyvinyl alcohol (PVA)/multiwalled carbon nanotube (MWCNT)-manganese dioxide (MnO_2) nanofiber composite. The Central Composite Design (CCD), the most common design of Response Surface Methodology (RSM) had been used to optimise the synthesis process of PVA/MWCNT-MnO_2 nanofiber composite. The process parameters studied were; applied voltage (16 kV - 30 kV), solution flow rate (3- 5 mL h^{-1}) and surrounding temperature (17-30°C). Analysis of variance (ANOVA) was used to analyse the experimental results. The prediction of optimum value and the clarification of the interactions between the specified range factors were done by using the quadratic model. The results revealed that at the parameter condition of 23 kV for applied voltage, 4 mL h^{-1} solution flow rate and 18°C of surrounding temperature, the highest electrical conductivity of 2.66×10^{-5} S cm^{-1} was obtained. The predicted (2.81×10^{-5} S cm^{-1}) value after optimization process was in good agreement with the experimental data (3.06×10^{-5} S cm^{-1}). The model was able to accurately predict the response of electrical conductivity with less than 10% error. Referring to ANOVA results, it was statistically found that the surrounding temperature parameter given significant effect to electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite in both single parameter and interaction between parameter.

Key words: Nanofiber composite, central composite design, electrical conductivity, electrospinning

INTRODUCTION

The fabrication of nanofibers composite using electrospinning process has gained much attention due to the awareness of its potentials for many applications (Khajavi and Damerchely, 2007; Sambaer *et al*., 2009; Liao *et al*., 2011). The nanofiber characteristic with large surface area and high porosity compared to traditional fabrication technique, had made electrospinning as preferable method in producing fibers from polymer solution (Frenot and Chronakis, 2003). PVA is one of the polymers that had been given a great deal of attention in electrospinning process. The binding characteristics of PVA which facilitated fiber forming of those polymers or filler that are difficult to be processed by electrospinning has made PVA to be the most preferred polymer matrix for nanofiber composites (Huang *et al*., 2003; Koski *et al*., 2004). Furthermore PVA were relatively low in cost, high tensile strength and good polarity polymer (water soluble) compared to other polymers (Huang *et al*., 2003; Maatoug *et al*., 2007).

Since the discovery by Iijima (1991), carbon nanotubes (CNTs) had been given a great attention and focus. Many researchers had explored the idea of combining polymer/MWCNTs to functionalize and improved the physical properties of electrospun nanofibers (Shin *et al*., 2008; Kang *et al*., 2009; Chan *et al*., 2010; Mazinani *et al*., 2010; Rein *et al*., 2010). The unique characteristics of mechanical and electronic properties of MWCNTs have led it to be broadening for practical applications. Introducing MWCNTs into a polymer matrix improved the properties of the original polymer (Kiamahalleh *et al*., 2011). The uses of PVA together with MWCNTs to form nanofiber composite had been done by several researchers (Wong *et al*., 2009; Kim *et al*., 2010; Bartholome *et al*., 2008; Miaudet *et al*., 2007). Besides improving the tensile strength of the nanofiber composite, the existence of CNT provided

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electron conduction into the polymer structure (Nihei *et al*., 2007). However, it was believed that the electron conduction and stability of the MWCNT can still be further improved. One of the way is by introducing nanoparticles of metal and metal oxide with MWCNT (Ganchimeg *et al*., 2011).Thus, in the interest to improve electron interactions to obtain better electrical conductivity performance, manganese dioxide (MnO_2) had been introduced as filler with PVA/MWCNT nanofiber composite in this study.

Design of experiment (DOE) is a statistical method that allows researchers to optimize the planning of experimental work systematically by estimating the effect of several variables separately, simultaneously or as a combination (Sanchez *et al*., 1997; Amarandei *et al*., 2011). Response Surface Methodology (RSM) is one of the statistical methods which interpolate data in order to predict the correlation between variables (input data) and objectives (response data) (Barbuta and Lepadatu, 2008). The advantage of RSM is to minimize the number of experiment by giving accurate data and avoiding repetitions of experiment. Researchers are attracted to apply this statistical model for multiple factors experiment (Amiri *et al*., 2008).

In this study the optimization process was performed using Central Composite Design (CCD), one of the most frequently used design in RSM statistical models. The interactions between the input variables were clarified. The information collected was then used to design an optimum PVA/MWCNT-MnO_2 nanofiber composite. To the best of our knowledge, the use of DOE to determine the major factors and interactions that affect the electrical conductivity performance of PVA/MWCNT-MnO_2 nanofiber composite synthesised by electrospinning which has not yet been investigated. Thus, the aim of this study is to verify the factors that give significant effect on electrical conductivity performance of PVA/MWCNT-MnO_2 nanofiber composite by implementing CCD approach.

MATERIALS AND METHODS

Synthesis of PVA/MWCNT-MnO_2 nanofiber composites and their characterization: MWCNTs with average outer and inner diameters of the 40 and 20 nm were obtained from Chinese Academic of Science (China).The MWCNTs were immersed for four hour in a solution of manganese nitrate (Fisher Scientific). The mixture was stirred to enable better incorporation into the cavity of carbon nanotubes. After mixing, MWCNTs were separated from solution and dried. The ratio of MWCNTs with manganese nitrate used was 30:70. A complete description of the purification and filling of MWCNTs with manganese nitrate has been explained in detail elsewhere (Zein *et al*., 2007). The dried MWCNT- MnO_2 which dispersed using ultrasonic processor (USG-150) in distilled water was subsequently added to PVA solution. PVA 87% to 90 % hydrolysed with 30000 to 70000 g mol^{-1} of average molecular weight was bought from Sigma Aldrich.

The method for preparation PVA nanofiber was adapted from Koski *et al*. (2004). In each sample, 10 mL of PVA electrospun solution were prepared by using distilled water as a solvent. The ratio of PVA electrospun to MWCNT- MnO_2 used was 100:1. The MWCNT filled with MnO_2 were added into PVA electrospun solution and stirred at 80°C until a homogenous electrospun solution was obtained. The prepared electrospun solution was poured into a syringe pump to proceed with electrospinning process. Electrospinning process was carried out in a closed environment inside a transparent box with the tip to the collector distance (TCD) was 100 mm.

Field Emission Scanning Electron Microscopy (FESEM) observations were made using a LEO supra 50 VP microscope. The electrical conductivity of the nanofiber composite was measured based on direct current conductivity (σ^{dc}) by using Eq. 1 (Harun *et al*., 2008). Galvano Electrochemical Impedance Spectroscopy Technique (GEIS) obtained from Biologic Science Instrument Co. Ltd. was used to measure the resistance of the sample. Direct current conductivity was calculated by using the resistance value (R). The nanofiber composite was stripped from the aluminium foil and cut into 1×1 cm pieces to become the electrode. The electrodes were immersed in 6 M of potassium hydroxide (KOH) solution (electrolyte) and the measurements were performed in the frequency range from 100 kHz to 0.1 Hz at 1 V. The thickness (d) and surface area (A) of each sample was 0.01 cm and 1 cm^2, respectively:

$$\sigma^{dc} = \frac{d}{RA} \quad (1)$$

Statistical analysis using design of experiments: Design expert software, version 8.0.5 (Stat-Ease Inc., USA) was used in this study. CCD was chosen to run the statistical analysis. Table 1 shows the coded levels of the process parameters used in the DOE. The selected process parameters in this study were applied voltage (16- 30 kV), solution flow rate (3-5 mL h^{-1}) and the surrounding temperature (17-30°C). The selected range for applied voltage and solution flow rate were chosen based on the most frequent studied parameter for electrospinning

Table 1: Table for coded levels of variables for design of experiment

Factor	Parameter code	Coded levels of variables 1	- 0.5	0	0.5	1
Applied Voltage (kV)	A	16	19.5	23	26.5	30
Solution flow Rate (mL/h)	B	3	3.5	4	4.5	5
Surrounding Temperature (°C)	C	17	18.0	19	20.0	21

Table 2: Experimental matrix for CCD of electrospinning process of PVA/MWCNT/ MnO_2 nanofiber composite

Std.	Electrical Point type	A (kV)	B(mL h^{-1})	C (°C)	Conductivity (S cm^{-1})
1	Fact	16	3	17	0.0000162
2	Fact	30	3	21	0.0000170
3	Fact	16	5	21	0.0000118
4	Fact	30	5	17	0.0000190
5	Center	23	4	19	0.0000223
6	Center	23	4	19	0.0000223
7	Fact	16	3	21	0.0000161
8	Fact	30	3	17	0.0000176
9	Fact	16	5	17	0.0000188
10	Fact	30	5	21	0.0000132
11	Center	23	4	19	0.0000223
12	Center	23	4	19	0.0000223
13	Axial	19.5	4	19	0.0000146
14	Axial	26.5	4	19	0.0000200
15	Axial	23	3.5	19	0.0000230
16	Axial	23	4.5	19	0.0000169
17	Axial	23	4	18	0.0000266
18	Axial	23	4	20	0.0000203
19	Center	23	4	19	0.0000223
20	Center	23	4	19	0.0000223

process which had given significant effect to the material morphology (Thompson *et al*., 2007; Yordem *et al*., 2008; Heikkila and Harlin, 2008; Chen *et al*., 2009). Meanwhile, the selected studied range for parameter of surrounding temperature was chosen base on the capability of the air conditioner. The experiments were conducted based on the design matrix shown in Table 2. Table 2, shows the actual value of the experiments parameters with the respond data recorded for 20 different number of testing. The point type were divided into three different design point which were factorial, center and axial. The factorial part of the design consisted of all possible combinations of the +1 and -1 levels of the factors. The axial points had all of the factors set to 0, the midpoint, except one factor, which had the positive value (+) of alpha or negative value (-) of alpha (0.5). While the center points, as implied by the name, were points with all levels set to coded level 0, which was the midpoint of each factor range (0, 0). All data collected from the experimental works were recorded as shown in Table 2.

RESULTS AND DISCUSSION

Design of experiment

Model equation development and analysis: The mathematical model for desired response as a function of selected variables was developed by applying the multiple regression analysis method on the experimental data. Based on the input data given in Table 2, by using lambda equal to one ($\lambda = 1$), the summary output as shown in Table 3 (model summary statistic) concluded that the quadratic model was statistically significant to represent the results which simultaneously satisfied the 3 variables conditions. The model summary statistics focused on the model maximizing the value of adjusted R-squared and the predicted R-squared. R-squared was the correlation coefficient for the model while predicted R-squared was used to measure of how good the model predicted a response value.

The adjusted R-squared represented the amount of variation in the design model. The adjusted R-squared and predicted R-squared should be within approximately 0.20 of each other to be in reasonable agreement (Lachiver *et al*., 2006). If they are not within approximately 0.20 of each other, there might be a problem with either the data or the model. While PRESS was a measure of how a particular model fitted each design point. This model was used to predict the first point and then the new residual was calculated for this point. The coefficients for the model were calculated without the first design point. This was done for each data point and then the squared residuals were summed. To strengthen this conclusion, the ANOVA was a necessary test procedure where the experimental data was applied to verify the adequacy of the model used. The results of the ANOVA analysis obtained from design expert software are shown in Table 4. Table 4 gives the information on the feasibility of the model equation to present the results obtained from the experimental work.

The model equation consisted of quadratic parameter model terms (A^2, B^2 and C^2), single parameter effect term (A, B and C) and the interaction of parameter term (AB, BC and AC). From the ANOVA data (Table 4) the model F-value (Fischer's F distribution) of the model was 8.62.The F-value which was associated with the model was the ratio of the Model Sum of Square to Residual Sum of Square and showed the relative contribution of the model variance to the residual variance. A large number indicated more of the variance being explained by the model while a small number indicated the variance may be more due to noise. Further proof of the model adequacy in explaining the data is Lack of Fit F-value. The higher the number of lack of fit, it would be more likely that the model does not adequately fit the data. From the ANOVA data (Table 4) the Lack of Fit value of the model was 3.272×10^{-11} implying that the model adequately fit the data. The appropriateness of the model in explaining the model was depend by its R- squared value, the proportion

Table 3: Model summary statistics

Source	Std. Dev.	R^2	Adj. R^2	Pred. R^2	Press	Recommendation
Linear	0.0000039	0.1346	-0.0277	-0.5853	4.54×10^{-10}	
2FI	0.0000042	0.2002	-0.1689	-5.4617	1.85×10^{-9}	
Quadratic	0.0000018	0.8857	0.7829	0.3478	1.87×10^{-10}	Suggested
Cubic	0.0000008	0.9849	0.9523	-341.8332	9.82×10^{-8}	#Aliased

#Aliased: The aliased design resulted due to the insufficient unique design points to estimate all the coefficients for the chosen model. The model of this aliased design would not be able to be completely estimated

Table 4: Analysis of variance (ANOVA) with electrical conductivity value of PVA/MWCNT-MnO_2 nanofiber composite as the desired response

Source	Sum of square	Degree of freedom	Mean square	F-value	p-value Prob>F
Model	2.537×10^{-10}	9	2.819×10^{-11}	8.62	0.0012
A	5.101×10^{-12}	1	5.101×10^{-12}	1.56	0.2402
B	6.227×10^{-12}	1	6.227×10^{-12}	1.90	0.1978
C	2.722×10^{-11}	1	2.722×10^{-11}	8.32	0.0163
AB	6.845×10^{-14}	1	6.845×10^{-14}	0.021	0.8879
AC	5.445×10^{-14}	1	5.445×10^{-14}	0.017	0.8999
BC	1.867×10^{-11}	1	1.867×10^{-11}	5.71	0.0380
A^2	4.399×10^{-11}	1	4.399×10^{-11}	13.45	0.0043
B^2	4.287×10^{-12}	1	4.287×10^{-12}	1.31	0.2790
C^2	3.949×10^{-11}	1	3.949×10^{-11}	12.07	0.0060
Std. Dev.	1.809×10^{-6}		R-Squared		0.8858
Mean	1.940×10^{-5}		Adj R-Squared		0.7830
C.V.%	9.32		Pred R-Squared		0.3478
PRESS	1.868×10^{-10}		Adeq Precision		11.781
Lack of Fit	3.272×10^{-11}				

Table 5: Analysis of variance (ANOVA) for model reduction with electrical conductivity value of PVA/MWCNT-MnO_2 nanofiber composite as the desired response

Source	Sum of square	Degree of freedom	Mean square	F-value	p-value Prob>F
Model	2.493×10^{-10}	6	4.154×10^{-11}	14.55	<0.0001
A	5.101×10^{-12}	1	5.101×10^{-12}	1.79	0.2403
B	6.227×10^{-12}	1	6.227×10^{-12}	2.18	0.1636
C	2.722×10^{-11}	1	2.722×10^{-11}	9.53	0.0087
BC	1.867×10^{-11}	1	1.867×10^{-11}	6.54	0.0239
A^2	7.738×10^{-11}	1	7.738×10^{-11}	27.09	0.0002
C^2	3.660×10^{-11}	1	3.660×10^{-11}	12.82	0.0034
Std. Dev.	1.690×10^{-6}		R-Squared		0.8704
Mean	1.940×10^{-5}		Adj R-Squared		0.8105
C.V.%	8.71		Pred R-Squared		0.7502
PRESS	7.154×10^{-11}		Adeq Precision		14.423
Lack of Fit	3.713×10^{-11}				

of the variability in the data explained by the analysis of variance model.

In this study, the R-squared value obtained was 0.8858. This implied that 88.58% of the total variation in the data explained by the model equation, which signified that, the correlation between both experimental and predicted value from Table 3 can be accepted. Probability > F was probability of the observed F value to verify if the null hypothesis (H_0) was true (there were no factor effects) (Istadi and Amin, 2006). The small probabilities (less than 0.05) indicated that there was a model effect while large values (greater than 0.10) suggested no significant effect. Prob > F greater than 0.10 (model A, B, AB, AC and B^2) had allowed to consider reduction of the model. Furthermore, the predicted R-Squared of 0.3478 was not as close to the adjusted R-Squared of 0.7830. This might indicate a large block effect or a possible problem with the model. The reduction of model is shown in Table 5.

Referring to the results obtained from ANOVA after model reduction in Table 5, the F- value on the quadratic model shows the value of 14.55. The value of Prob > F (0.0001) which is less than 0.05 indicates the developed model is significant at the 95% Confidence Interval (CI). The R^2 value from ANOVA analysis of the reduced model after eliminating insignificant terms was decreased to 0.8704. The value of predicted R^2 of 0.7502 was reasonably in agreement with the adjustment R^2 of 0.8105. The adequate precision value (14.423) was used to measure the signal to noise ratio. Looking to the greater ratio of the adequate precision value, it was proven that this model could be used to navigate the design space.

Model terms of A^2 (quadratic applied voltage), BC (interaction of factor between solution flow rate with surrounding temperature), C (surrounding temperature) and C^2 (quadratic surrounding temperature) were the remaining parameter that were left after the elimination of all insignificant values. According to ANOVA results, the electrical conductivity of the nanofiber composite was affected by these following parameters; A^2, BC, C and C^2, which mean that any changes of these parameters, would cause a change in the electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite. Equations 2 represent the multiple regression analysis for the correlations of the process parameters to the electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite. This quadratic model equation was presented in coded factor. After the ANOVA had completed, the model analysis was followed by plot diagnostics using experimental values versus predicted values as shown in Fig. 1. Figure 1 shows the linear graft of the predicted and actual electrical conductivity for PVA/MWCNT-MnO_2 nanofiber composite by using Eq. 2. As observed, there was a high correlation to the linear regression fit with the R squared value of 0.8704 and the model obtained covered the experimental range studies adequately.

This demonstrated that the regression model equation provided an accurate description of the experimental data capturing the correlation between the formulation process parameters and the electrical

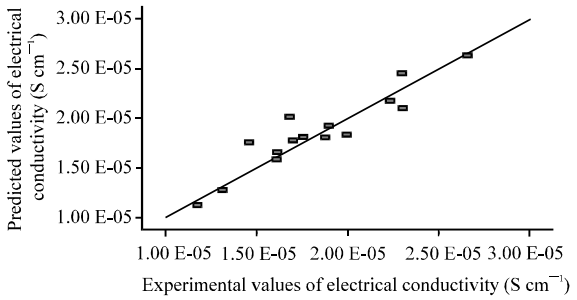

Fig. 1: The linear graft of actual experiment values and predicted values of electrical conductivity for PVA/MWCNT-MnO_2 nanofiber composite

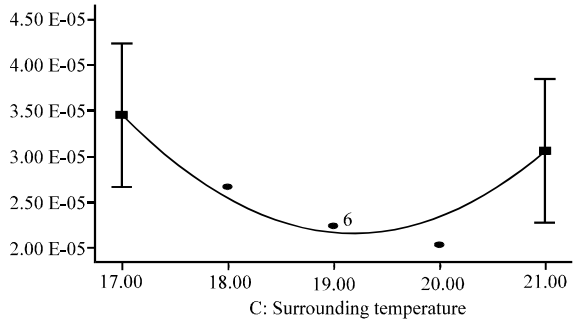

Fig. 2: The single parameter effect of surrounding temperature to the electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite

conductivity of the PVA/MWCNT- MnO_2 nanofiber composites:

$$\begin{aligned}\text{Electrical conductivity (S cm 1)} = {} & +2.175 \text{ x } 10\text{-}5 + 7.747 \times 10\text{-}7 \\ & * A - 8.559 \times 10\text{-}7 * B - 1.789 \times 10\text{-}6 \\ & * C - 1.527 \times 10\text{-}6 * B * C - 1.772 \times 10\text{-}5 \\ & * A2 + 1.218 \times 10\text{-}5 * C2\end{aligned} \quad (2)$$

Where:

A = Applied voltage (kV)
B = Solution flow rate (mL h^{-1})
C = Surrounding temperature (°C)

Single parameter effect

Surrounding temperature: Referring to the ANOVA data from the DOE in Table 5, only one single parameter was found to have statistically significant positive effect on the electrical conductivity of for PVA/MWCNT-MnO_2 nanofiber composite. The surrounding temperature was the only factor that had given significant effect to the for electrical conductivity PVA/MWCNT-MnO_2 nanofiber composite. The effect of surrounding temperature on the electrical conductivity of for PVA/MWCNT-MnO_2 nanofiber composite is shown in Fig. 2. The electrical conductivity of for PVA/MWCNT-MnO_2 nanofiber composite increased with the decreasing surrounding temperature. It was believed that this was due to the fact that low surrounding temperature promoting the stable fibers formed from changing to aggregate particle (Xiao *et al*., 2008). The changing of the condition of fiber to aggregate particle promoted the nanofiber to have low surface area. The low surface area of the nanofiber composite contributed to low charge carrier density. The conductivity was determined by the product of charge carrier density in the channel (Naber *et al*., 2006; Zhou *et al*., 2005), this low charge carrier density electrical conductivity of the nanofiber would contribute to low electrical conductivity of the nanofiber composite.

The interaction between parameters

Interaction between surrounding temperature and solution flow rate: In addition to the effect of the single parameter towards electrical conductivity value, the effects of interaction between the parameters towards electrical conductivity value were also evaluated. Figure 3a and b show the electrical conductivity value as a function of solution flow rate and surrounding temperature by response surface (3-dimentional) and interaction (2-dimensional) plots, respectively. As observed in Fig. 3a, the plotted points fall outside the range, thus the differences can be attributed to the factor effects. The electrical conductivity increased as the solution flow rate decreased. While in Fig. 3b, the electrical conductivity was highly pronounced as the solution flow rate increased at the lowest surrounding temperature. It was also observed that electrical conductivity increased as the surrounding temperature increased at the lowest solution flow rate. Solution flow rate determined the amount of solution available for electrospinning. This was apparent as there was a greater volume of solution drawn away from the needle tip. When the solution flow rate was increased, there will be more solution delivered to the tip of the needle. It was reported that the nanofiber diameter and beads would increase as the flow rate increased (Zhang *et al*., 2005; Haghi and Akbari, 2007). However there was a limit to increase the diameter of the fiber due to high flow rate (Rutledge *et al*., 2000). There was a corresponding increase in the stretching of the solution which counters the increase diameter due to the increase volume. Due to greater volume of solution drawn from the needle tip, the jet would take a longer time to dry. As a result, the solvents in the deposited nanofibers might not have enough time to evaporate given the same flight time. The residual solvents might cause the nanofibers to fuse together where they made contact forming web that

contributed to low electrical conductivity performance. It was believed that the interactions of solution flow rate between surrounding temperature occurred as surrounding temperature promoted stable phase which slow down the solidifying process of the electrospun solution during the electrospinning.

Process optimization of surrounding temperature parameter for electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite: In order to obtain the high electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite, the significant process parameters have to be optimized. The optimization process of PVA/MWCNT-MnO_2 nanofiber composite was performed by using numerical optimization. The regression models developed from ANOVA (Eq. 2) was used to predict the process parameters by giving the optimum electrical nanofiber conductivity of PVA/MWCNT-MnO_2 composite. The important data used for processing variables to have the optimum value of the electrical conductivity is shown in Table 6. While the results of validation experiments at optimum conditions is shown in Table 7.

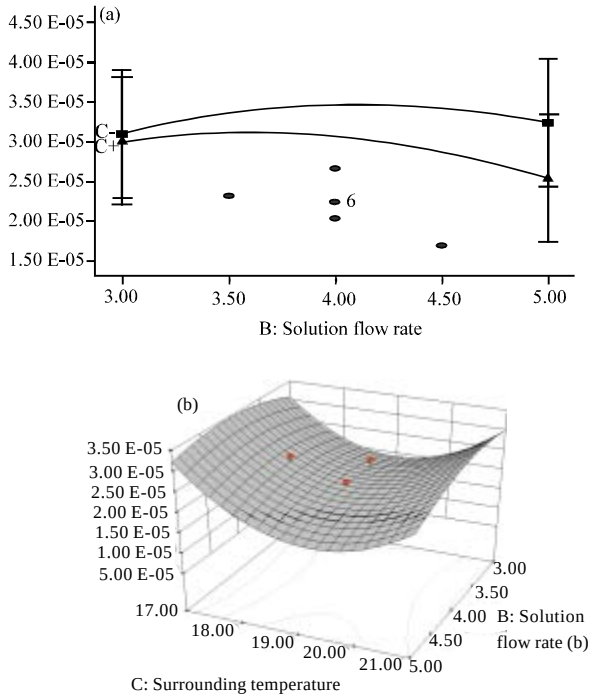

Fig. 3: The effect of parameter interaction between solution flow rate and surrounding temperature (BC) to electrical conductivity by (a) interaction plots and (b) response surface

The numerical optimization for electrical conductivity of PVA/MWCNT-MnO_2 was predicted by using Eq. 2. The electrical conductivity was predicted to obtain maximum value. The predicted optimum electrical conductivity were verified by carrying out suggested experimental run using the optimum conditions. The accuracy of Eq. 2 in predicting the optimum condition was evaluated by calculating the errors between the predicted value electrical conductivity with the value of experimental electrical conductivity. In order to determine the significance of the regression model in predicting the response, the obtained response from experimental work was then compared with the predicted response value from the model equation.

The optimization of electrical conductivity obtained in Table 7 shows the percentage differences between the predicted values and the experimental values were less than 10%. The results confirmed the expectedness of the model for the electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite in the experimental conditions. Thus, it can be concluded that the low surrounding temperature during the electrospinning process can lead to optimal high electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite.

Morphology analysis: Figure 4a and b show the SEM images of a PVA nanofiber and PVA/MWCNT-MnO_2 nanofiber composites with the same parameters (23 kV, 4 mL h^{-1} and 21°C). In Fig. 4a, it is observed that orientation of the nanofibers was randomly cross linking between each other and produced non uniform size fibers. Figure 4b shows the surface of the composite was smooth and averagely homogenous cross linking orientation which suggests a well distributed of composite film. Besides that, comparing the diameter of the PVA/MWCNT-MnO_2 nanofiber composite with

Table 6: The important data used for process variables to having the optimum value for electrical conductivity

Parameter	Goal	Lower limit	Upper limit
Applied voltage (kV)	is in range	16	30
Solution flow rate (mL h^{-1})	is in range	3	5
Surrounding temperature (°C)	in target	17	17

Table 7: The results of validation experiments at optimum conditions

Run	Applied voltage (kV)	Solution flow rate (mL h^{-1})	Surrounding temperature (°C)	Predicted electrical conductivity (S cm^{-1})	Experimental electrical conductivity (S cm^{-1})	Difference (%)
1	18.93	4.97	17.00	2.99×10^{-5}	3.06×10^{-5}	2
2	18.65	4.14	17.00	2.85×10^{-5}	3.06×10^{-5}	7
3	19.31	4.96	17.00	2.81×10^{-5}	3.06×10^{-5}	9

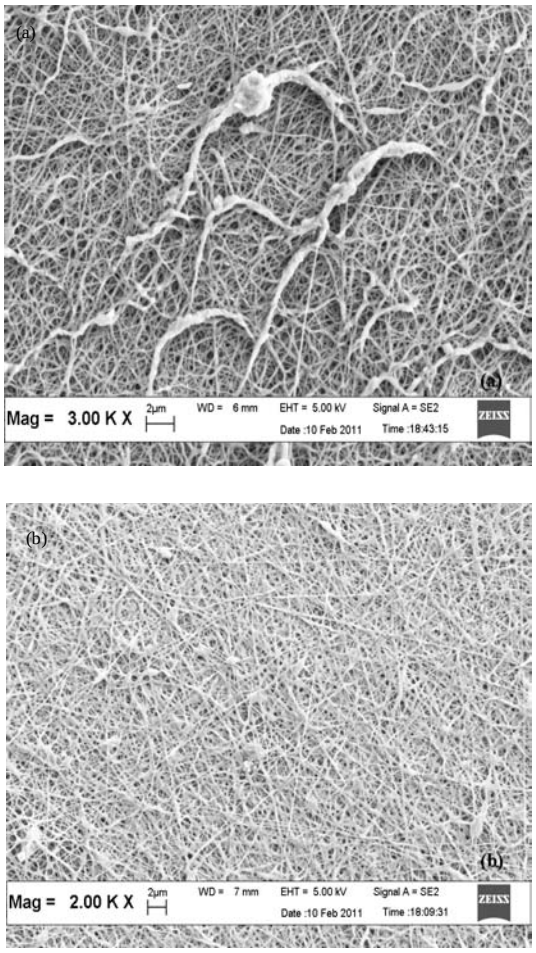

Fig. 4: SEM image of (a) PVA nanofiber and (b) PVA/MWCNT-MnO_2 (3%) nanofiber composite

PVA nanofiber in Fig. 4a, the nanofiber composite's diameter and the pores size had decreased. The diameter range decreased from the range of 200 nm down to 140 nm after MWCNT-MnO_2 was added to the neat PVA nanofiber.

The decrements of the diameter size of the composite might be contributed by the increment of the conductivity, as the conductivity of the electrospun solution increased, more charges would be carried out in electrospinning. The increase of charge would reduce the critical voltage of the solution and produced fiber in small diameter. Thus, the prediction on the morphology of high electrical conductivity PVA/MWCNT-MnO_2 nanofiber composite could be made by seeing the diameter size and alignment. It was reported by Dror *et al.* (2003) that good alignment of the nanofiber indicated the good form of interconnected linkages. These formed networks contributed to good electron mobilisation which had led to the high electrical conductivity in nanofiber composite.

CONCLUSIONS

This works demonstrated the statistical analysis of designed optimization for electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite. ANOVA was used to analyse the experimental results. In this optimization, the significant parameter had been chosen by using quadratic model regression. It was found that the model term of surrounding temperature (C) quadratic applied voltage (A^2), solution flow rate and surrounding temperature interaction (BC) and quadratic surrounding temperature (C^2) were the main significant factors that had contributed to high electrical conductivity of PVA/MWCNT-MnO_2 nanofiber composite. This result showed that there was an effect of interaction between parameters found in this investigation. Statistically, surrounding temperature had found to be the most significant parameter to the electrical conductivity behaviour of PVA/MWCNT-MnO_2 nanofiber composite. ANOVA analysis had revealed that the surrounding temperatures were significant in both single parameter (C) and interaction between parameter (BC). This result had proven that the low surrounding temperature was promoting the formation of stable nanofibers. The unstable condition of nanofiber would promote the nanofiber with low surface area which contributed to low charge carrier density that had low electrical conductivity. On numerical optimization response, the electrical conductivity was predicted to obtain maximum value of 2.99×10^{-5} (S cm^{-1}). Experimentally the models were able to accurately predict the response of electrical conductivity with less than 10% error. The experimental data (3.06×10^{-5} S cm^{-1}) were in good agreement with the predicted (2.99×10^{-5} S cm^{-1}) values after optimization process. Furthermore the SEM image had shown remarkable improvement of high electrical conductivity's morphology. It was believed that the small fiber networks had contributed to a good electron mobilisation which had led to a high electrical conductivity PVA/MWCNT-MnO_2 nanofiber composite. In the future, it is recommended that the response study of morphology should be included in studied parameter. We believed that producing small fiber network structure might improve the electron mobility and conductivity.

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