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Effect of Plasma Treatment (He/CH_4) on the Glass Surface for the Reduction of Powder Flux Adhesion in the Spray Drying Process

(Kesan Rawatan Plasma (He/CH_4) terhadap Permukaan Kaca untuk Pengurangan Serbuk Lekatan Fluks di dalam Proses Penyemburan Pengeringan)

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ABSTRACT

A 50Hz glow discharge He/CH_4 plasma was generated and applied for the glass surface modification to reduce the powder adhesion on wall of spray dryer. The hydrophobicity of the samples determined by the water droplet contact angle and adhesion weight on glass, dependent on the CH_4 flow rate and plasma exposure time. The presence of CH_3 groups and higher surface roughness of the plasma treated glass were the factors for its hydrophobicity development. Response surface methodology (RSM) results using central composite rotatable design (CCRD) showed that optimal responses were obtained by the combination of parameters, CH_4 gas flow rate = 3 sccm and exposure time = 10 min. In optimum conditions, the contact angle increased by 47% and the weight of the adhesion reduced by 38% (w/w). The plasma treatment could enhance the value of the contact angle and thus reduced the adhesion on the spray dryer glass surface.

Keywords: Flux adhesion; hydrophobic; plasma treatment; powder; spray dryer; surface treatment

ABSTRAK

Pelepasan cahaya 50Hz plasma He/CH_4 dijana dan digunakan pada modifikasi permukaan kaca untuk mengurangkan lekatan serbuk pada dinding penyembur pengering. Hidrofobisiti sampel ditentukan oleh sudut sentuh titisan air dan pemberat lekatan pada kaca, bergantung kepada kadar pengaliran CH_4 dan tempoh dedahan plasma. Kehadiran kumpulan CH_3 dan kekasaran permukaan plasma yang lebih tinggi dengan rawatan kaca adalah faktor kepada pembentukan hidrofobisitinya. Keputusan kaedah gerak balas permukaan (RSM) menggunakan reka bentuk berputar komposit berpusat (CCRD) menunjukkan bahawa respons optimum diperoleh daripada kombinasi parameter, kadar pengaliran gas CH_4 = 3 sccm dan tempoh dedahan = 10 minit. Dalam keadaan optimum, sudut sentuh meningkat sebanyak 47% dan pemberat lekatan dikurangkan sebanyak 38% (w/w). Rawatan plasma boleh meningkatkan nilai sudut sentuh dan seterusnya mengurangkan lekatan pada permukaan kaca penyembur pengering.

Kata kunci: Hidrofobik; lekatan fluks; penyembur pengering; rawatan permukaan; rawatan plasma

Introduction

Spray drying is the most common and cheapest technique used to produce powder food products as compared to freeze dry. This process also reduces the cost of storage and transport costs and facilitate the operation of the product (Gharsallaoui et al. 2007). There are several advantages of using spray drying techniques such as reducing the problem of microbes in the product, limiting the oxidation of lipids (Keogh et al. 2001) and preserving the original structure of the emulsion (Millqvist-Fureby 2003).

One major problem in the spray drying process is the deposition of particles on the walls of the drying chamber that would indirectly affect the product quality through degradation of the deposited particles and contamination. Wall deposition level is influenced by several factors, including the operating parameters, the type and size of the spray dryer and the properties of the spray dryer wall (Keshani et al. 2015; Kota & Langrish 2006; Oakley 1994).

Various approaches have been used to tackle the problem of deposition on the surface of the wall, include the use of drying agents such as maltodextrin (Fang & Bhandari 2011). However, there are limitations in using this method in which the addition of drying agents will increase the cost of manufacturing, change the original taste of the product and will indirectly affect consumer acceptance of the product.

Besides, the previous research done to change the wall properties material of spray dryer focused on chemical apporach such as by using stainless steel (Bhandari & Howes 2005), Teflon (Keshani et al. 2013) and nylon (Kota & Langrish 2006). One of the novel method to change the surface characteristic of spray dryer is by using plasma technology. Plasma can cause changes in the topography (Coen et al. 2003), convert the chemical composition on the surface (Borcia et al. 2004) and can also be used for the purpose of cleaning and deposition. Previous study showed plasma was used in food packaging industry (Chaiwong et al. 2010) in order to increase the shelf-life of the products by making the packaging hydrophobic and waterproof. Type of gas used and plasma operating parameters affect the effectiveness of plasma treatment, for example gases such as fluorine gas and methane can be used to create hydrophobic surface (Yang et al. 2005).

Therefore, this study was focused on finding a new approach to address the problem of particles deposition on the walls of the spray dryer through modification of the surface characteristics using a helium/methane (He/CH_4) glow discharge plasma by using CCRD and optimized using RSM. CCRD type of design is selected in the case of two or three independent variables or factor. It is used to calculate the effects and analyze the response surface. This research study could provide information of spray drying efficiency particularly on the plasma treatment on drying chamber and cyclone of spray dryer. Furthermore, this study would also be a review on the recent technology applied to increase the efficiency of spray dryer.

Materials and Methods

MATERIALS

In this study, a microscope slide (borosilicate glass) was used to resemble the surface of the drying chamber wall, as it has similar characteristics. Microscope slides (Borosilicate, 76 × 26 × 1 mm) were obtained from Quasi-S Technology Sdn. Bhd. and were used to mimic the chamber wall of a spray dryer (BUCHI Mini Spray Dryer B-290), that was placed in pilot plant laboratory of Universiti Kebangsaan Malaysia (UKM).

GLOW DISCHARGE PLASMA TREATMENT IN HE/CH_4 (50Hz)

A 50Hz methane/helium plasma was generated in the stainless steel vacuum chamber (38 cm diameter × 34 cm high) as shown in Figure 1(a). The chamber has four rectangular windows used for plasma diagnostics. This chamber had two electrodes which were made of brass and has a thickness of 0.5 cm and a diameter of 9 cm. The gap between the two electrodes was 3 cm and the plasma was adjusted to occur in the space between the electrodes. The glass slide was placed on the lower electrode disc for the plasma treatment.

The microscope slides were placed on the bottom electrode of the vacuum chamber. In this study, the discharge voltage was kept constant at 7.8 kV (peak-to-peak value) at which the plasma was stable and no spikes occurred in the voltage waveforms. The I–V waveforms characteristics for the discharge are shown in Figure 1(b). The flow rate of helium gas was kept constant at 100 sccm. The glass slides were treated in different conditions in which the duration of treatment and proportion of CH_4 gas (by adjusting the flow rate) were varied and the effect on the surface methodology was evaluated.

SINGLE FACTOR EXPERIMENT

A preliminary study was carried out by the single factor experiment to determine the influencing factors involved in plasma treatment. The two factors that had been investigated were the flow rate of the seed gas, CH_4 and duration of treatment. These factors were selected based on previous studies (Yamamoto et al. 2004). Selection of the best levels for each factor was determined based on the two types of responses: contact angle and adhesion weight. The effect of CH_4 gas flow rate (1, 2, 3, 4 and 5 sccm) on the contact angle and weight of adhesion were studied while the plasma treatment was kept constant at 10 min and the best CH_4 gas flow rate was determined. After that, the effect of the duration of treatment in the range of 5-30 min was studied while fixing the CH_4 gas flow rate at 3 sccm to determine the best duration of plasma treatment.

CONTACT ANGLE MEASUREMENT

To test the wettability of the sample after treatment, the water contact angle (WCA) measurement test was done at room temperature. Static contact angle method (Drop Tensile Analyzer) was carried out at the Department of Nuclear, UKM. Approximately 0.5 mL of deionized water were dropped at 3 different points on the glass surface of treated and untreated samples. Contact angle measurements were recorded and analyzed for 3 replicates ($n = 3$) using an Automated Contact Angle Goniometer (Model 100) from Rame-Hart Inc. with Western Vision software.

DETERMINATION OF FLUX ADHESION WEIGHT

Oven drying method was used to determine the flux adhesion weight on the glass slides. Oven drying process was used to resemble the spray drying process. The glass surface that has been treated with plasma will be spray vertically with 3 mL of milk. After that, the slides were put in the oven (180°C) for 5 min. The temperature of 180°C was used to resemble the temperature of spray drying process. Drying time of 5 min was chosen to dry the 3 mL milk because in the spray drying process, it took about 30 min to spray dry 50 mL of milk. The weight of the slides before and after the drying process was measured ($n = 3$) using an analytical balance. After that, the flux adhesion weight between the treated and untreated slides were calculated using (1):

$$\text{Flux adhesion weight} = \text{weight of slide after drying} - \text{weight of slide before drying} \quad (1)$$

STRUCTURE AND MORPHOLOGY ANALYSIS: SCANNING ELECTRON MICROSCOPY (SEM)

The surface morphology was carried out in which the glass slide that has been treated with He/CH_4 plasma was analyzed by the SEM machine (JEOL JSM-5610LV, JEOL Ltd., Welwyn Garden City, United Kingdom). The slide was attached to the stub of the aluminium and was coated with gold in an argon environment. Then the sample was

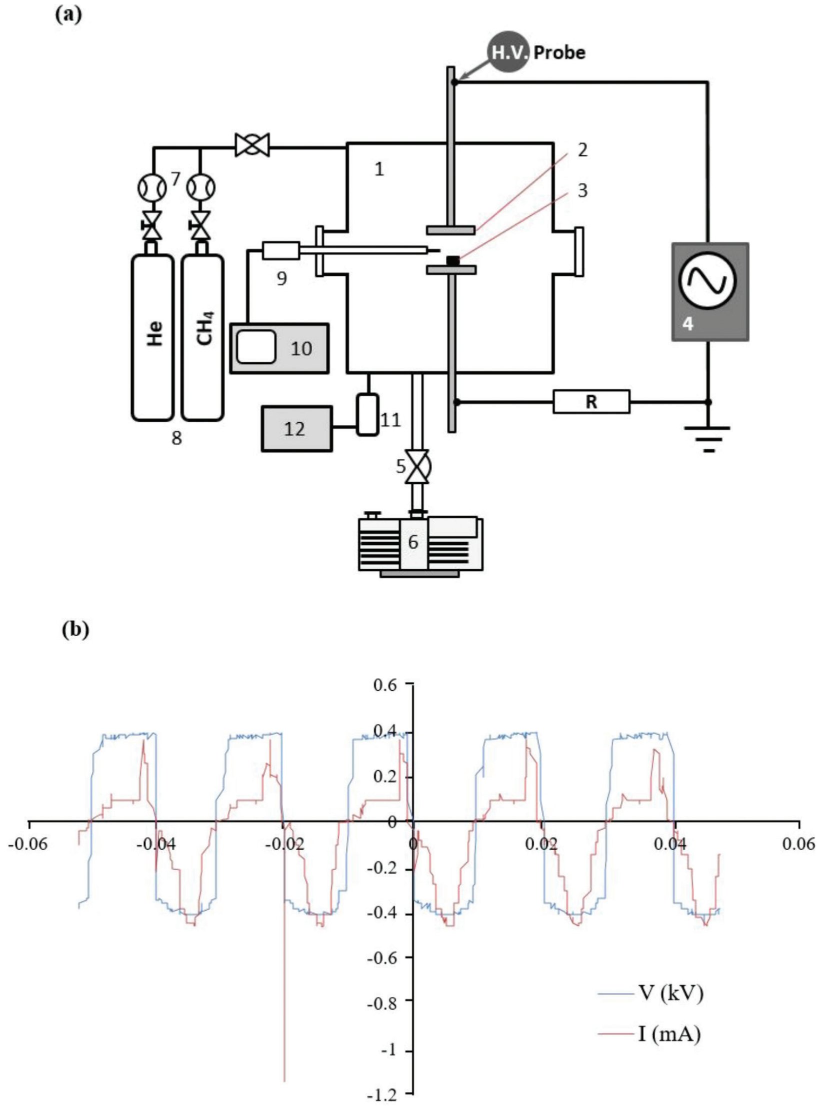


FIGURE 1. (a) Methane/helium glow discharge setup (1: Chamber, 2: Top electrode, 3: Sample on bottom electrode, 4: 50 Hz AC source, 5: Diaphragm valve, 6: Rotatory pump, 7: Mass flow controller, 8: Gas cylinder, 9: Langmuir probe, 10: Oscilloscope, 11: Pirani gauge, 12: Pressure meter, R: 1 kΩ current monitoring resistor); (b) The I–V waveform characteristics for the discharge

analyzed using the Scanning Electron Microscope (SEM) with the magnification of 10K to 30K times.

DETERMINING FUNCTIONAL GROUPS: FTIR-ATR

Analysis using the Fourier Transform Infrared (FTIR) Spectrometer, Perkin Elmer model 1600 coupled with Attenuated Total Reflectance (ATR) (PIKE Technologies, Madison, WI, USA) in the range of 4000-550 cm^{-1} was used to measure the change in intensity of the spectrum. The infrared rays will pass through the ATR crystal which is held in contact with the glass slide sample. Total internal reflection will occur at the interface and evanescent waves that are produced will penetrate the sample. The depth of penetration of these waves is usually between 0.5-2 μm. Alteration to the energy of the evanescent waves depends on the absorbtion of the sample. The attenuated energy will be transferred back and carried by the infrared rays that exit the crystal. The exiting rays will be gathered by sensors and the infrared spectrum will be produced by the FTIR spectrometer.

RESPONSE SURFACE METHODOLOGY: CENTRAL COMPOSITE ROTATABLE DESIGN (CCRD)

Central composite rotatable design (CCRD) was used to study the effects of two independent variables, namely the flow rate of methane gas (X_1) and the duration of treatment (X_2), on the dependent variables such as the contact angle (Y_1) and the weight of adhesion (Y_2). The range for the plasma treatment was set within 10 to 30 min and methane gas flow rate was set in the range of 1-3 sccm. This range was selected after preliminary studies were carried out to obtain the best results. The overall design consists of 13 run of experiments including 4 factorial arrangements and five central point.

STATISTICAL ANALYSIS

The experimental results in the single factor experiments were analyzed using SPSS version 23.0 (SPSS Inc., Chicago, IL, USA). The data were analysed by analysis of variance (ANOVA) method and the differences between means were determined, at 5% significance different (p<0.05). The mean values obtained for each analysis studied on the different samples were compared by One-Way ANOVA (Tukey's multiple comparison) and independent t-Test. The Design Expert (Version 6.0.10, Stat-Ease Inc., Minneapolis, USA) statistical software was employed to design the CCRD and to analyze the experimental data in RSM. Experimental data were fitted to the following second order polynomial model and regression coefficients were obtained. The significance of the model and the variable were determined at the 95% confidence level. Three dimensional response surface plots were generated based on the selected model to describe the relationship between independent variables (X_1 and X_2) and the dependent variable (Y_1 and Y_2).

MODEL VERIFICATION

Optimal conditions for the plasma treatment were obtained using the second-order polynomial model of RSM. The suitability of the model equation for predicting the response values was verified by conducting the treatment under the recommended optimal conditions. The experimental and predicted values of contact angle and weight of adhesion were compared in order to determine the validity of the model. To confirm the results, runs were carried out in replicate under the selected optimised conditions.

RESULTS AND DISCUSSION

SINGLE FACTOR EXPERIMENTS

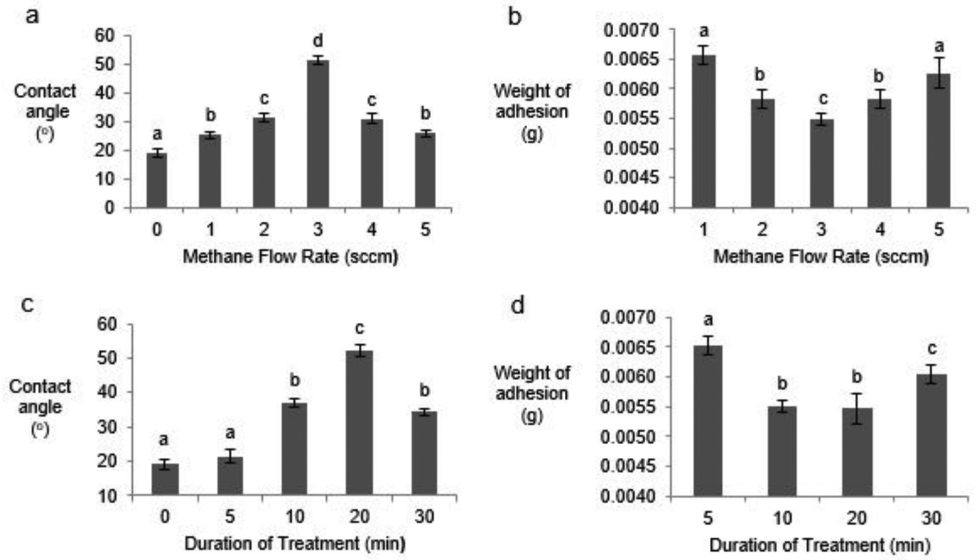
Effect of methane (CH_4) flow rate on contact angle and weight of adhesion Figure 2(a) shows the contact angle treated using different CH_4 gas flow rates. There were significant differences (p<0.05) in the contact angle of the untreated slide (CH_4 gas flow rate = 0) with the treated slides. The difference in the value of the contact angle during 10 min of plasma treatment proved that CH_4 gas flow rate plays an important role in producing the hydrophobic surface. The highest value of the contact angle (51°) was achieved at a flow rate of 3 sccm and began to decline at a rate of more than 3 sccm gas flow. This may be due to the use of low power sources in this study. Previous study (Wang & Xu 2002) proved that a high voltage was required to further increase the production of reactive species of CH_4. Similar results (Wen et al. 2006) found that low voltage will produce plasma with weak light intensity and not enough to reactivate the gas. Voltage used in this study was kept constant at 7.8 kV to obtain a stable plasma. Increasing the voltage more than 7.8 kV will produce flickering of the light from the plasma which indicated that the plasma was not stable. Plasma stability is important to ensure consistency during treatment.

The effects of methane flow rate on weight of adhesion are shown in Figure 2(b). The weight of adhesion decreased with the increament of methane flow rate up to 3 sccm. The value of contact angle reflects the total weight of adhesion where high contact angle value gave minimum adhesion weight. Previous studies also found an increase in the contact angle on the surface will reduce adhesion. This is due to the change in the surface roughness of the glass after the plasma treatment was applied. The increase in surface roughness will cause the contact angle increase, thereby reducing the adhesion to the surface (Avram et al. 2008; Van Der Wal & Steiner 2007).

Effect of duration of treatment on contact angle Previous studies proved that duration of plasma treatment play an important role in the production of desired surface (Avram et al. 2008; Van Der Wal & Steiner 2007; Yamamoto et al. 2004). In this study, the duration of treatment used was between 5 and 30 min. The range of treatment time used in this study was longer when compared with other studies (0-2 min) (Noh & Moon 2014). This is because the flow rate of the CH_4 gas used in this study was lower (1-5 sccm) when compared with other studies (0-50 sccm).

Figure 2(c) shows insignificant difference between the value of the contact angle of untreated slide (time = 0) with the slide treated for 5 min (p>0.05). This showed that 5 min treatment time was not enough to increase the contact angle. The results from previous studies have found the contact angle increased with increasing duration of plasma treatment. The results obtained from the previous study (Noh & Moon 2014) found that the contact angle of the glass surface increased as the duration of CH_4 plasma treatment increased. A rise in the contact angle value can also be seen in this study with increasing plasma treatment time (Figure 2(c)). The value of contact angle reached the highest on the 20 min treatment time and then started to decline on 30 min of treatment time. The decrease in the contact angle after 20 min may be caused by the erosion of materials that had previously been modified by the plasma in which previous studies have found that the longer the treated surface was exposed to the plasma, the surface will be modified by the formation of new functional group (Bismarck et al. 2008).

Correlation between contact angle and weight of adhesion The data of contact angle and weight of adhesion (shown in Figure 2) obtained from the single factor experiment were used to investigate the relationship between these two variables. There was a significant negative relationship between the contact angle and adhesion weight, (r = -0,924, p<0.01). The negative correlation means that by increasing the contact angle, the weight of adhesion will decrease or vice versa. The increment of the contact angle in this



[a-c] Different letters indicates significant difference (p<0.05)

FIGURE 2. (a) Contact angle variation with respect to methane flow rate (0-5 sccm) at the fixed conditions (Duration of treatment 10 min); (b) Weight of adhesion variation with respect to methane flow rate (1-5 sccm) at the fixed conditions (duration of treatment 10 min); (c) Contact angle variation with respect to the plasma exposure time (0-30 min) at the fixed conditions (CH_4 flow rate 3 sccm); (d) Weight of adhesion variation with respect to the plasma exposure time (0-30 min) at the fixed conditions (CH_4 flow rate 3 sccm)

study may be due to changes in surface roughness where it also affect the adhesion on glass surfaces. Similar result reported that a rough surface will reduce the adhesion of dirt or otherwise (Fuller 1975). The discovery of previous study (Bowden & Tabor 2001) also showed decreased adhesion by increasing surface roughness.

Structure characterization of surface glass Characterization of the structure of the glass surfaces before and after CH_4 plasma treatment were done using scanning electron microscopy (SEM) (Figure 3). Surface roughness or physical structure was an important factor in providing a hydrophobic surface characteristics (Bhushan & Jung 2011). This study found that there was an increase of the roughness on the treated glass surface (c and d) if compared with the untreated glass surface (a and b) where the increase in the roughness may be due to the presence of functional groups on the surface of the treated glass and thereby raised the value of the contact angle. The contact angle depends on surface roughness in which high contact angle showed liquid was rejected by the solid surface. The liquid can form a homogeneous layer interface with a solid or a composite layer interface with pockets of air trapped between the solid and liquid (Nosonovsky & Bhushan 2007). Other study (Cassie & Baxter 1944) showed that air pockets may be trapped in the cavity of a rough surface, resulting in a composite interface between the solid-liquid-air. The transition to a composite interface increases the contact angle and reduces the contact area between solid and liquid, which will indirectly reduce the adhesion of the liquid to solid.

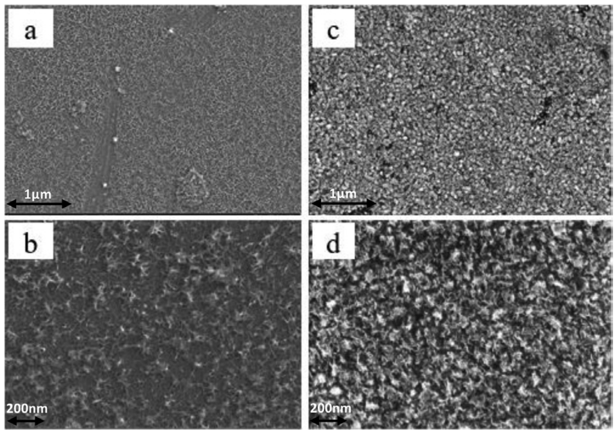


FIGURE 3. SEM images for untreated slide (a and b) and slide treated with plasma (c and d) with different magnification (a)(c) 10K x; (b)(d) 30K x

Determination of functional groups FTIR-ATR analysis was carried out to determine the presence of functional groups on the surface of the treated glass. Figure 4 shows the FTIR-ATR spectra on the treated and untreated glass surface. A small absorption peak appears after plasma treatment, which is not visible on the untreated slide. The peak which appeared at 1470 cm^{-1} is the CH_3 peak as reported in other studies (Fang et al. 2004; Noh & Moon 2014). The presence of CH_3 band can be considered as a cause of the changing structure of the surface through chemical reactions such as dissociation and excitation in the plasma. Other studies (Noh & Moon 2014) also found the presence

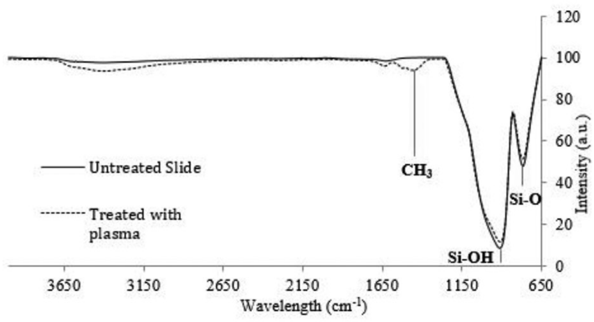


FIGURE 4. FTIR-ATR spectra on the surface of treated and untreated slides

of CH_3 path but the presence of other lines such as C-H were dominant. The presence of functional groups (non-polar) will prevent the entry of water molecules in the polar bonds in most of the surface of the glass, thus contributing to the improvement of the hydrophobic properties of the surface of the glass (Fang et al. 2004). The presence of a weak CH_3 peak reflects the little increment of contact angle in this study as compared with previous studies (Fang et al. 2004; Noh & Moon 2014).

RESPONSE SURFACE OPTIMIZATION

Single factor experiment was conducted as an initial step to get the levels for each of the plasma treatment parameters (gas flow rate and duration of treatment). The data obtained from these experiments were then used to determine the combination of the best parameters in the plasma treatment to optimize the gas flow rate and duration of treatment. So far, there is no relevant information on CH_4 plasma treatment optimization. Therefore, the objective of this study was to determine the optimum parameter combination treatment of plasma (gas flow rate and duration of treatment) to maximize the value of the contact angle and reducing the weight of the adhesion using RSM.

Fitting the model Based on the observations from single factor experiments, the ranges of each independent variable (gas flow rate and duration of treatment) that influence the contact angle and weight of adhesion were selected. Data for the contact angle (Y1) and the weight of adhesion (Y2) obtained from the experiments are listed in Table 1(a). Statistical results found quadratic model was the most appropriate model to match the contact angle data. However, the inverse transformation changes made to the contact angle data was to obtain the best results.

Table 1(c) summarized the results of the ANOVA and both models were significant at 95%. The value of the coefficient (R^2) for both models were 0.8584 for the contact angle and 0.8322 for the weight of adhesion. This suggested that the predicted models can define well the real behaviour of the system. Lack of fit (p>0.05) were insignificant for both models. This showed that the model was able to make good predictions for each responses.

It could be observed from Table 1(d) that both the linear and quadratic term for CH_4 gas flow rate had significant effect on contact angle (p<0.05). However, the duration of treatment did not affect both contact angle and weight of adhesion in this study. Previous research also showed that the duration of treatment did not give a significant effect on the contact angle (Wang & Xu 2002). Similar results found that long duration of treatment will erode the surface that has been modified previously by forming a new set of functional groups (Bismarck et al. 2008).

The quadratic and linear terms for the gas flow rate showed significant effects on contact angle (p<0.05). The study by other researchers (Wang & Xu 2002) proved that by increasing gas flow rate, the placement of the gas in the chamber will become longer and thus would improve the dissociation process of CH_4 gas. Based on Table 1(d), there were interactions that affect significantly on the adhesion weight in the form of x_1x_2. The interaction between gas flow rate and duration of treatment (x_1x_2) for weight of adhesion was positive which suggested it interaction resulted in high weight of adhesion. However, no significant interaction existed for contact angle.

Figure 5 shows that by increasing the gas flow rate and shorten the duration of treatment, the adhesion weight reached a minimum value. However, the weight of adhesion less reduced when the duration of treatment lengthen. This indicates that the minimum weight of adhesion could be achieved by conducting the plasma treatment in a short period of time. The increase of adhesion weight with increase in treatment time is due to the interaction of plasma species with substrate surface. Generally, a longer plasma treatment results in a smaller contact angle (Tan et al. 2010), which corresponding to the higher weight of adhesion. Previous research (Tan et al. 2010) shows that by increasing treatment time from 300 to 500 s the devices remain hydrophilic and never fully regain their hydrophobicity during the time period of the investigation.

DETERMINATION OF OPTIMUM PARAMETERS FOR PLASMA TREATMENT

Determination of the optimal parameter for CH_4 plasma treatment was based on the highest desirability. The main goal of this study was to achieve the highest value of the contact angle and minimum weight of adhesion. Table 1 shows the predicted value and the experimental value for each response in optimal condition. The optimal conditions for contact angle and weight of adhesion were achieved when the plasma treatment was carried out at 3.00 sccm CH_4 gas flow rate and a treatment time of 10 min, with the desirability of 0.866. The experimental values (n = 3) that were obtained for the contact angle and weight of adhesion in an optimal plasma treatment condition were 38.1 ± 0.75° and 0.0060 ± 0.0006 g. These values were then compared with the predicted value (41.5 ± 0.42°; 0.0052 ± 0.0001 g). The experimental result were very close to

TABLE 1. (a) The central composite design and experimental values obtained for the response variables; (b) Equation for the contact angle and weight of adhesion in determining the optimum parameters for plasma treatment; (c) Results summary of the ANOVA; (d) Estimated coefficient for experimental design

(a)

Run of experiments	X_1 (sccm)	X_2 (min)	Y_1 (°)	Y_2 (g)
1	3.00	10.00	33.6	0.0043
2*	2.00	20.00	35.2	0.0054
3	3.00	30.00	32.5	0.0056
4	3.41	20.00	41.1	0.0049
5	2.00	5.86	30	0.0059
6*	2.00	20.00	47.9	0.0055
7	0.59	20.00	19.9	0.0065
8*	2.00	20.00	38.2	0.0057
9	2.00	34.14	40.7	0.0059
10	1.00	30.00	34	0.0060
11*	2.00	20.00	44.8	0.0050
12	1.00	10.00	23.3	0.0064
13*	2.00	20.00	37.8	0.0055

* replication at center point
X_1: CH_4 flow rate; X_2: duration of treatment
Y_1: Contact angle; Y_2: Weight of adhesion

(b)

Response	Equation
Contact angle	<u>Actual equation</u> $1.0/(Y_1) = 0.090980 - 0.038294X_1 - 1.86697E\text{-}003X_2 + 6.24499E\text{-}003X_1^2 + 2.07529E\text{-}005X_2^2 + 3.62850E\text{-}004X_1X_2$ <u>Coded equation</u> $1.0/(y_1) = 0.025 - 6.057E\text{-}003x_1 - 3.112E\text{-}003x_2 + 6.245E\text{-}003x_1^2 + 2.075E\text{-}003x_2^2 + 3.629E\text{-}003\, x_1 x_2$
Weight of Adhesion	<u>Actual equation</u> $Y_2 = 8.25030E\text{-}003 - 1.44534E\text{-}003X_1 - 7.37500E\text{-}005X_2 + 4.25000E\text{-}005X_1X_2$ Coded equation $y_2 = 5.585E\text{-}003 - 5.953E\text{-}004x_1 + 1.125E\text{-}004x_2 + 4.250E\text{-}004x_1x_2$

X_1 (x_1): CH_4 Flow Rate; X_2 (x_2): Duration of treatment
Y_1 (y_1): Contact Angle; Y_2 (y_2): Weight of adhesion

(c)

Source	Sum of square	Degree of freedom	Mean square	F-value	p-value
Contact angle					
Model	7.062E-004	5	1.412E-004	8.49	0.0070
Residual	1.164E-004	7	1.663E-005		
Lack of fit	7.726E-005	3	2.575E-005	2.63	0.1868
Pure error	3.919E-005	4	9.797E-006		
Total	8.226E-004	12			
$R^2 = 0.8584$ *Adjusted* $R^2 = 0.7573$					
Weight of adhesion					
Model	3.659E-006	3	1.220E-006	14.88	0.0008
Residual	7.377E-007	9	8.197E-008		
Lack of fit	4.697E-007	5	9.394E-008	1.40	0.3827
Pure error	2.680E-007	4	6.700E-008		
Total	4.397E-006	12			
$R^2 = 0.8322$ Adjusted $R^2 = 0.7763$					

Continued

Continue TABLE 1.

(d)

Source	Coefficient	F-value	p-Value
Contact angle			
Linear			
x_1	-6.057E-003	17.64	0.0040
x_2	-3.112E-003	4.66	0.0678
Quadratic			
x_1^2	6.245E-003	16.31	0.0049
x_2^2	2.075E-003	1.80	0.2215
Interaction			
x_1x_2	3.629E-003	3.17	0.1184
Weight of adhesion			
Linear			
x_1	-5.953E-004	34.59	0.0002
x_2	1.125E-004	1.24	0.2952
Interaction			
x_1x_2	4.250E-004	8.81	0.0157*

x_1: CH_4 flow rate;
x_2: duration of treatment
*p<0.05

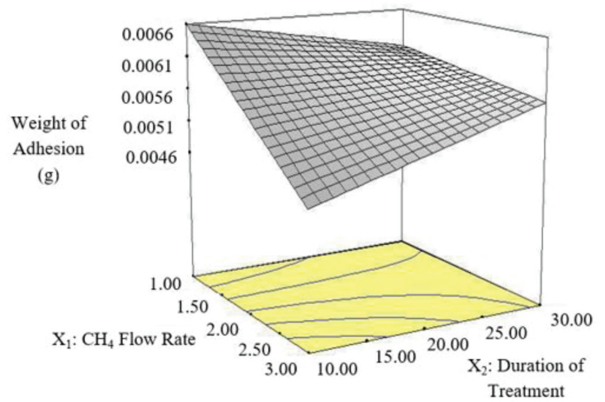


FIGURE 5. Response surface plot corresponding to weight of adhesion as a function of methane flow rate and duration of treatment

the predicted one. This implied that there was a high fit degree between the values observed in experiment and the value predicted from the regression model. Hence, the response surface modeling could be applied effectively to predict the contact angle and weight of adhesion in plasma treatment optimization.

CONCLUSION

In a preliminary study, the parameters studied, namely CH_4 gas flow rate and duration of treatment (min) showed significant effects (p<0.05) on the contact angle (°) and weight of adhesion (g). By conduction single factor experiments, the optimum level for each plasma treatment parameters were obtained and used to determine the combination of plasma treatment parameters for the contact angle and weight of adhesion using RSM. Experimental procedures in a single factor experiment considered parameters do not interact with each other, but the use of RSM will take into account the possibility of interaction between these parameters. The results from RSM showed a significant interaction effect between gas flow rate and duration of treatment for the weight of adhesion, while no interaction can be seen for the contact angle. In addition, the flow rate of gas was found to give a significant impact on the contact angle and weight of adhesion, while the duration of treatment had little effect on the contact angle and weight of adhesion. Optimal plasma treatment was achieved through RSM on CH_4 gas flow rate of 3 sccm and a treatment period of 10 min to produce the contact angle, 38.1 ± 0.75° and weight of adhesion, 0.0060 ± 0.0006 g. Compared with untreated surface, the contact angle increased by 47% and the weight of the adhesion reduced by 38% (w/w). This study showed there was an increase in the contact angle after the plasma treatment, however the value of the contact angle is still low and cannot be considered as hydrophobic. This was because there were some limitations and obstacles faced during conducting the plasma treatment such as the ability of the plasma system to provide the best results. Further work can be done using different plasma system which were more convenient to be handled such as atmospheric pressure plasma system that do not require the use of vacuum chamber.

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