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Effect of Plasma Treatment (He/CH₄) on Glass Surface for the Reduction of Powder Flux Adhesion in the Spray Drying Process

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Abstract. A 50Hz glow discharge He/CH₄ plasma was generated and applied for the modification of glass surface to reduce powder adhesion on the wall of spray dryer. The hydrophobicity of the glass samples determined by the water droplet contact angle and adhesion weight on glass, dependent on the CH₄ flow rate and plasma exposure time. There was a peak that appeared at 1470 cm⁻¹ on the surface of treated glass indicating the presence of CH₃ groups from ATR-FTIR data. Surface morphology analysis using scanning electron microscopy (SEM) showed changes of roughness in the surface-treated glass. The presence of alkyl group (CH₃) that deposited on the glass surface is one of the factors that contribute to the increase in the surface roughness. The surface roughness will reflect the value of contact angle where hydrophobic surface are rougher compared to hydrophilic surface. The plasma treatment could enhance the value of the contact angle and thus reduced the adhesion on the spray dryer glass surface.

INTRODUCTION

Spray drying is the most common and cheapest technique used to produce powder food products as compared to freeze dry. In addition, the equipment is easily available and the production cost is lower than other methods, for example, the cost of the spray drying process is 30-50 times cheaper than the freeze drying (1). It also reduces the cost of storage and transport and facilitate the operation of the product (2). Spray drying technique is commonly used in the food industry and more precisely in the dairy sector. There are several advantages of using spray drying techniques such as reducing the problem of microbes in the product, limiting the oxidation of lipids (3) and preserving the original structure of the emulsion (4).

Nowadays, the main challenges in the spray drying process are the controlling the characteristics of the powder produced and the cost. 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 (5). In order to reduce the particle deposition on the wall of the spray dryer, the size of the drying chamber must be large (6). Chamber walls made from nylon is better in reducing the particle deposition as compared to stainless steel surface (7). Furthermore, types of liquids/materials to be dried also influence the deposition on the walls of the drying chamber (8).
Various approaches have been used to tackle the problem of deposition on the surface of the wall including the use of drying agents such as maltodextrin (9). 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.

Therefore, this study is focused on 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/CH₄) glow discharge plasma. Plasma treatment can mechanically or chemically change the characteristics of the materials or surfaces. Plasma can cause changes in the topography (10), convert the chemical composition on the surface (11) and can also be used for the purpose of cleaning and deposition. Applications of plasma have high demand in the industry due to its low cost, free from heat damage and high processing power. Previous study showed plasma was used in food packaging industry (12) in order to increase the shelf-life of the products by making the packaging hydrophobic and waterproof.

The effectiveness of the plasma surface modification method had been demonstrated in previous studies using different types of non-thermal plasma operating at low, medium and atmospheric pressures (13); (14). Therefore, the plasma system was used in this study as a means to treat the surface of the drying chamber wall material and change its hydrophobicity property. The effectiveness of plasma treatment on the surface depends on the type of gas used and plasma operating parameters (15). To obtain a hydrophobic surface, gases such as fluorine gas and methane can be used (16). In addition, the operating parameters such as gas flow rate, temperature, treatment time, power and frequency also will affect the effectiveness of the plasma treatment (17). Previous research showed that the gas flow rate and treatment time played an important role in the production of hydrophobic surface (18) while increase in power did not have any effect. However, other studies (19); (20) found that the treatment time and power delivered were important in improving the wetness on the surface while the gas flow rate does not give any positive effect. The difference in the reported results above is attributed to differences in plasma systems used.

Plasma treatment using methane (CH₄) gas will reduce wetness on the surface of glass, thus reducing the adhesion to the surface. In this study, a microscope slide (borosilicate glass) was used to resemble the surface of the drying chamber wall, as it has similar characteristics. Spray drying process cause buildup of unspecified and unique pattern of wall deposits on the wall. For that reason, this work was attempted to see the potential of plasma treatment in addressing this problem by producing a hydrophobic glass surface.

**MATERIALS AND METHOD**

**Materials**

Microscope slides (Borosilicate, 76 mm x 26 mm x 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/CH₄ (50Hz)**

A 50Hz methane/helium plasma was generated in the stainless steel vacuum chamber (38 cm diameter x 34 cm high) as shown in Fig. 1. 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 is shown in Fig. 2. 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 CH₄ gas (by adjusting the flow rate) were varied and the effect on the surface methodology was evaluated.

Contact Angle Measurement

To test the wettability of the sample after treatment, the water contact angle (WCA) measurement test was done at room temperature (27°C). 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 three 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 sprayed vertically with 3 ml of milk. Then, the slides were put in the oven (180 °C) for 5 minutes. The temperature of 180 °C was used to resemble the temperature of spray drying process. Drying time of 5 minutes was chosen to dry the 3 ml milk because in the spray drying process, it took about 30 minutes 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 the following equation:

\[
\text{Flux adhesion weight} = \text{weight of slide after drying} - \text{weight of slide before drying}
\]

**Structure and Morphology Analysis: Scanning Electron Microscopy (SEM)**

In order to investigate surface morphology of plasma treatment, the glass slide treated with He/\(\text{CH}_4\) 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 analyzed using the Scanning Electron Microscope (SEM) at 10K to 30K times magnification.

**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 \(\mu m\). Alteration to the energy of the evanescent waves depends on the absorption 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.

**Statistical Analysis**

The experimental results in the single factor experiments were analyzed using Statistical Package for the Social Science SPSS version 23.0 (SPSS Inc., Chicago, IL, USA). The data was analysed by analysis of variance (ANOVA) method. 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. Significance differences between the means were determined by One-Way ANOVA (Tukey’s multiple comparison) and independent t-test \((p<0.05)\).

**RESULTS AND DISCUSSION**

**Effect of Methane (CH4) Flow Rate on Contact Angle and Weight of Adhesion**

Figure 3 (a) shows the contact angle of glass slide treated using different \(\text{CH}_4\) gas flow rates. There were significant differences \((p<0.05)\) in the contact angle of untreated slide \((\text{CH}_4\) gas flow rate = 0) and treated slides. The difference in the value of the contact angle during 10 minutes of plasma treatment proved that \(\text{CH}_4\) gas flow rate plays an important role in producing the hydrophobic surface. After the plasma treatment, a layer of hydrophobic coating is formed on the glass surface, and the contact angle increased, compared to those without plasma treatment \((17^\circ)\). It is suggested that the plasma treatment makes the surface hydrophobic due to the interaction of the plasma with the glass surface. The impact of active species (mainly ions) to the glass surface can remove the alkali ions and hydroxide, and generate radicals on the surface \((21)\).

The mechanism of interaction between the plasma and glass surface is discussed. Zhi et al suggested that \(\text{CH}_3\) and large molecule radicals can react with the radicals in the glass surface to replace OH, and the hydrophobicity of
the glass surface is improved accordingly (21). Since \(-\text{CH}_4\) molecule has 4 nonpolar covalent bonds carbon-hydrogen single bonds, this molecule is hydrophobic. Thus, this coating prevents the invasion of water molecules to the polar bonds in the bulk of glass.

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 (22) proved that a high voltage was required to further increase the production of reactive species of CH$_4$. Similar results (23) 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 CH$_4$ flow rate on weight of adhesion are shown in Figure 3 (b). The weight of adhesion decreased with the increment of methane flow rate up to 3 sccm (p<0.05). 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 (24); (25).

**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 (24); (25); (19). In this study, the duration of treatment used was between 5-30 minutes. The range of treatment time used in this study was longer when compared to other studies (0-2 minutes) (18). This is due to the flow rate of the CH$_4$ gas used in this study was lower (1-5 sccm) when compared to other studies (0-50 sccm).

Fig. 3 (c) showed insignificant difference between the value of the contact angle of untreated slide (time = 0) with the slide treated for 5 minute (p>0.05). This revealed that 5 minutes treatment time was not enough to increase the contact angle. Previous studies found that the contact angle increased with increasing duration of plasma treatment. Results obtained from the previous study (18) 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 also can be seen in this study with increasing plasma treatment time (Fig. 3 (c)). The value of contact angle reached the highest on the 20-minute treatment time and then started to decline on 30 minutes of treatment time. The decrease in the contact angle after 20 minutes might be due to the erosion of materials that had previously been modified by the plasma. This finding is similar to the previous studies mentioned that the longer the treated surface exposed to the plasma, the surface will be modified by the formation of new functional group (26).

![FIGURE 3](image)

**FIGURE 3.** (a) Contact angle variation with respect to methane flow rate (0-5 sccm) at the fixed conditions (Duration of treatment 10 minutes), (b) Weight of adhesion variation with respect to methane flow rate (1-5 sccm) at the fixed conditions
Correlation between Contact Angle and Weight of Adhesion

The data of contact angle and weight of adhesion (shown in Figure 3) obtained from the single factor experiment were used to investigate the relationship between these two variables. There was a significant negative correlation 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 study might be due to the changes in surface roughness where it also affects the adhesion on glass surfaces. The discovery of previous study (27) 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) (Fig. 4). Surface roughness or physical structure was an important factor in providing a hydrophobic surface characteristics (28). 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 (29). Other study (30) 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 4.](image)

Determination of Functional Groups

ATR-FTIR analysis was carried out to determine the presence of functional groups on the surface of the treated glass. Fig. 5 shows the ATR-FTIR 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 (31); (18). 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 (18) also found the presence of CH₃ 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 (31). The presence of a weak CH₃ peak reflects the little increment of contact angle in this study as compared to previous studies (31); (18).

![FTIR-ATR spectra on the surface of treated and untreated slides](image)

**CONCLUSION**

In this study, the parameters studied, namely CH₄ gas flow rate and duration of treatment (min) showed significant effects ($p<0.05$) on the contact angle (°) and weight of adhesion (g). Compared to untreated surface, the contact angle increased by 47% and the weight of the adhesion reduced by 38% (w/w) ($p<0.05$). 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 (90°C). 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.

These findings were supported by FESEM image and ATR-FTIR analysis on the treated glass where the surface roughness increased compared to the untreated sample due to the presence of CH₃ band which changeD the structure through some chemical reaction.

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