Influence of the Nitrogen exposure time to the plasma treatment on the wettability of polystyrene surfaces

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Abstract. The wettability of material can change from hydrophobic to hydrophilic when treated using plasma nitrogen. The present work investigated the influence of the plasma treatment duration on the modification of polystyrene’s surface coating on a glass surface. The polystyrene layer was produced by means of spin coating method with the rotational speed of 3000 RPM for 1 minute. The plasma was established by a 2 MHz RF generator at the power of 40 watts, pressure of 0.3 Torr, flow rate 40 mL/min. The samples were treated at various exposure time which were 2 min, 5 min, 10 min, and 15 min. The wettability of the polystyrene was measured using a contact angle measurement before and after the nitrogen plasma treatment. Polar functional groups related to the wettability were observed by a Fourier Transform Infrared (FTIR). The longer the treatment duration, the smaller the contact angle was observed. A very low contact angle of 6.42° was achieved at a power of 40 watt at 0.3 torr for the exposure time of 15 min. This means that the surface of the polystyrene changed to super hydrophilic or super wetting. The FTIR results show the spectra of NH\textsubscript{2} and C-H functional group at the wavenumber of 3485 cm\textsuperscript{-1} and 2962 cm\textsuperscript{-1}, respectively. These functional groups indicate the existence of the polar groups, which contribute to the change of surface hydrophobicity into hydrophilicity.

1. Introduction
Plasma has wide applications in various fields, both industry, and research. The main applications of plasma are in the form of modifying the surface of various materials to improve their functionality. Plasma surface technology has the ability to change the surface of a material at a microscopic level, giving them different characteristics. Plasma treatment can be used on all types of materials. Plasma surface technology can be used for surface modification in polymers, semiconductors, glass, metals, and ceramics. Plasma can also be made using several different gases to create several effects on the surface. Some of the most often used gases for surface functionalization are plasma nitrogen and plasma oxygen\cite{1}–\cite{4}. The treatments in each of these plasmas have features related to the chemical activity of ions, the process of bombardment by electrons and other active species of plasma.

Polymers have been widely used for various purposes; one of them is by modifying the surface to change the surface wettability, affecting the hydrophilicity of the layer \cite{5}–\cite{6}. Polystyrene is a polymer that is non-polar with the chemical structure formula C\textsubscript{8}H\textsubscript{8} \cite{7}, \cite{8}. Several studies on plasma nitrogen treatment on changes in the hydrophobicity of the polystyrene layer have been carried out by researchers, among others: Idage and Badrinarayanan (1998) \cite{9} which studied the effect of plasma treatment of nitrogen on polystyrene making it more hydrophilic, Masruroh et al.\cite{10}, \cite{11} also examined the changes in the surface properties of polystyrene becoming hydrophilic due to the interaction of N atomic
species in plasma nitrogen and C atoms in polystyrene forming polar C≡N functional groups. The morphology and roughness of the layers also play a role in the level of wettability. There are many parameters in plasma, namely generator power, pressure, flow rate, and exposure time, which can affect the wettability of the polymer surface, beside the exposure time of plasma being very effective in the process of modifying surface properties [12]. This study will investigate how plasma nitrogen exposure duration, from 2 min to 15 min, affected in the hydrophobicity properties of polystyrene surfaces.

2. Materials and Method
The glass used in this study has a thickness of 1 mm. Before the nitrogen plasma treatment process, the glass was cut to 3 x 2.5 cm. The glass was then cleaned with distilled water using an ultrasonic cleaner for 3 minutes. Polystyrene with a molecular weight of 35,000 g/mol (Sigma Aldrich product) was dissolved with xylene solvent to produce 3% polystyrene solution. Polystyrene solution was deposited on the glass surface using a spin coater for 1 minute with a rotating speed of 3000 RPM. Glass with a polystyrene layer was then heated using an oven for 1 hour at 100°C to vaporize the remainder of the solvent. The plasma system used in this plasma treatment was the RF (radio frequency) plasma system - AC with a plasma frequency of 2 Mhz. The sample was placed in the plasma chamber. Measurement of contact angles for samples before and after plasma treatment was carried out using contact angle measurement (CAM). Samples before and after plasma treatment were carried out with an FTIR (Fourier Infrared Transfusion) test to determine the polar functional groups formed.

3. Results and Discussion
Wettability is generally characterized by measuring the contact angle between solid-liquid interfaces. In this study, to obtain the low contact angle (contact angle < 10°) nitrogen plasma treatment was carried out at the pressure 0.3 Torr, power 40 watts and gas nitrogen flow rate at 40 ml/min. Figure 2 shows the contact angle of samples for ordinary glass, and coated by polystyrene with untreated and treated by nitrogen plasma vs. duration of treatment. The contact angle of ordinary glass show the contact angle in the range of 45°. This contact angle refers to the hydrophilic when the contact angle < 90°. The contact angle tend to higher (θ = 82°) after coated by polystyrene is due to the hydrophobic nature of polystyrene.

Figure 1. Design of plasma system for modified polystyrene’s surface
Figure 2. Water contact angle results for (a) ordinary glass; (b) glass with a polystyrene layer; (c) glass with a polystyrene layer with plasma treatment

The longer duration of plasma treatment the contact angle become smaller. The contact angle exhibits the value of $6.42^\circ$ when the additional plasma treated duration for about 15 min as shown in Figure 3c. A very small contact angle below 10° indicates a nearly perfect wetting process; in other words, the surface of the coating becomes super hydrophilic. The surface of the sample exposed to plasma causes a change in the surface wettability as shown in Figure 3, which is the contact angle measurement in the sample after a specific time of plasma treatment. Before the plasma treatment, i.e., at 0 min of treatment time, the surface contact angle value was $82.02^\circ$. The value of the surface contact angle dropped when the sample was given plasma treatment of $45.01^\circ$ at 2 min treatment time, and the contact angle value decreased to $6.42^\circ$ at 15 min treatment time. The duration of the plasma treatment or plasma exposure on the surface causes an increase of possible interaction, in this case, the ion with the surface of the sample.
Figure 3. Contact angle measurement results for polystyrene surfaces after treated by plasma vs treatment times.

The surface wettability properties, which are related to hydrophilicity or the formation of the polar groups, can be affected by plasma treatment. From the optical emission spectroscopy (OES) measurement results as reported in the previous paper [10], the N₂⁺ ion species was found at the intensity of 423.753 nm. This indicates opportunities for the interaction of plasma species such as ions, which can interact with the surface and cause changes in the wettability of the layers, increase with the increased duration. This is also followed by the number of ion species per chamber volume, which is kept constant. The number of interactive ion species in the chamber is constant due to the supply of electrical energy input, which is not a time nor fixed function. In addition, the unchanged rate of Nitrogen gas input into the chamber and is held constant causes ion formation reactions to occur and was maintained, hindering any decrease in ion species density which then affects the possibility of species interaction with the surface at any time as determined by the relationship between power, energy and time below.

\[
\text{Power} = \frac{\text{Energy}}{\text{time}} = \text{steady/constant} \quad (1)
\]

Increasing the possibility of species interaction also allows the formation and increase of the number of specific functional groups that are polar on the layer surface. A functional group with polar properties causes stronger interaction of the surface with water, thereby increasing the surface wetness and decreasing the value of the contact angle. The sample with the longest treatment time for 15 minutes has the highest possibility of ion interactions with the surface. Thus the possibility of increasing the polar group on the surface also increases compared to the shorter treatment time. This is evidenced from the FTIR results in Figure 4, which indicate an NH₂ functional group at wave number of 3485 cm⁻¹ and the = C-H functional group appears at wave number of 2962 cm⁻¹ with asymmetric stretching vibration [13]-[15]. The FTIR results show a low transmittance of the N-H groups, which are polar groups at 15 min of treatment time compared to samples with a treatment time of 2 min. Additionally, there was a formation of = C-H polar groups at 15 min of treatment time. The low transmittance value is related to the high absorbance value of the polar group that has been identified at the associated wave number, which means that the number of polar groups has increased or, there were more polar groups at the 15 min treatment time than the 2 min treatment time. The FTIR results show the relationship between the value of the small contact angle of water at 15 min of treatment time.
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Figure 4. FTIR spectra of three samples for untreated and treated with plasma nitrogen at 2 minutes and 15 minutes.

4. Conclusion
The nature of polystyrene surface wettability changes after plasma nitrogen treatment. Polystyrene moisture was determined by measuring the contact angle and FTIR study. The longer duration of exposure to nitrogen resulted in a decreased contact angle. The lowest contact angle of 6.42° is obtained at a power of 40 Watt with a pressure of 0.3 torr with a treatment time of 15 min. This contact angle shows the surface of the polystyrene turning super hydrophilic. FTIR results showed the presence of functional groups NH$_2$ and C-H at wavenumbers 3485 cm$^{-1}$ and 2962 cm$^{-1}$. Both functional groups of NH$_2$ and C-H are polar. These results prove that increased wettability is indicated by a small contact angle value caused by the presence of functional groups NH$_2$ and C-H.

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