# The Effect of Substrate Temperature on Surface Modification of Polystyrene by using Nitrogen Plasma

**Novi A F, D J D H Santjojo and Masruroh**

Jurusan Fisika FMIPA Univ. Brawijaya, Jl. Veteran Malang 65145, Indonesia

Email: dsantjojo@ub.ac.id

**Abstract**. Studies on the effect of substrate temperature on the modification process of a thin layer of polystyrene samples deposited on glass by using spin coating technique have been conducted. The polystyrene thin film surface was modified by using nitrogen plasma generated in a vacuum reactor by a capacitive plasma generator with a frequency of 40 kHz. The substrate temperature was set by variation of 60, 70 and 80 °C during the modification process to determine the effect of substrate temperature on the level of roughness and hydrophobicity of the film. Observations were conducted by using optical microscopy, optical micro-profiler, and measuring the contact angle of liquid. The results showed a decrease in roughness due to modification at a temperature of 60 °C and 70 °C. On the other hand, the treatment at a temperature of 80 °C resulted in an increase of roughness. By measuring the contact angle, it was proven that hydrophobicity is not only influenced by the surface roughness of thin layers.

**Keywords**: polystyrene, nitrogen plasma, roughness, hydrophobicity.

## 1. Introduction

Quartz Crystal Microbalance (QCM) is a piezoelectric sensor that has been widely used because it can record real-time response and high sensitivity to a change in mass [1]. In the field of medical instrumentations, the QCM is equipped with a layer of a particular material so that it can function as a bio-immunosensor for a specific protein [2]. Enhancement of the performance of QCM biosensor can be done by coating the surface of the sensor with a thin layer of binding biomolecules such as polystyrene [3]. The QCM sensor surface that is generally hydrophobic as it can bind more protein through physical adsorption processes. The hydrophobicity of the surface of solids can be improved by modifying the surface morphology. According to previous studies, UV-irradiation of polystyrene resulted in the more hydrophilic surface which can be observed by a contact angle measurement [4]. Other studies observed the effect of different solvent on the polystyrene surface roughness. All of the studies implied that a rougher surface of the polystyrene thin film enhanced the immobilization of biomolecules [5].

Another technique to modify a polymer surface is by means of nitrogen plasma treatment. The plasma treatment can change microstructure and character of the polymer surface resulting in surface functionalization of materials. The process is carried out in a vacuum vessel filled with nitrogen gas. The gas is then subjected to a high electric field between two electrodes. A nitrogen plasma is produced in the form of glowing species of high energy nitrogen. Interactions between the nitrogen and the surface can result in reaction and diffusion of the nitrogen on the surface of objects [6]. Controlling the reactions on the surface of the thin film is critical to produce certain surface roughness.

One important parameter affecting the reactions is the substrate temperature. This study is intended to investigate the effect of the substrate temperature on the roughness and hydrophobicity of the polystyrene film.

## 2. Experimental Method

Samples in this study were a thin film of polystyrene on the surface of a glass substrate. The film was deposited by using a spin coating technique. First, raw polystyrene material was dissolved in a chloroform solution at a concentration of 3%. Then, the solution was dripped onto the glass surface rotating at high speed (2000 rpm). After the deposition, the sample was annealed for 1 hour at a temperature of 100 $^o$C to remove moisture and the remaining solvent. The polystyrene surfaces were then modified by using nitrogen plasma generated by a plasma generator with a frequency of 40 kHz in a vacuum chamber. The following figure shows a schematic representation of the nitrogen plasma system used in this study.

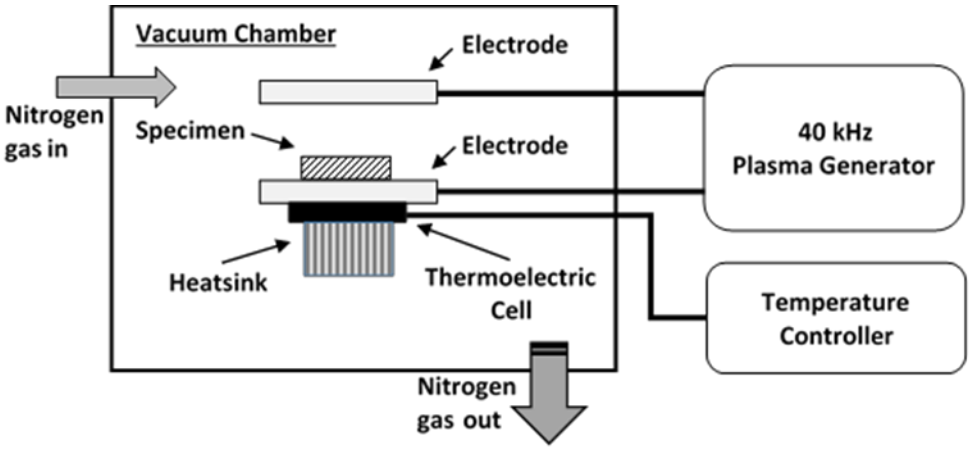


**Figure 1**. Nitrogen plasma system

A capacitive plasma was produced by a set of two parallel plate electrodes. The distance between the electrodes was 0.8 cm. A cooling system was attached at the bottom of the lower electrode consisting of thermoelectric and thermal radiators.The samples were loaded into the reactor and placed on the top of the lower electrode.

In this study, the reactor was vacuum pumped until the pressure reached 0.0188 torrs. Then, the nitrogen gas was introduced into the chamber. The flow of the nitrogen gas was set to 20 mL/min. The plasma was then ignited, and the power was kept to 40 watts. When the plasma was formed, the pressure in the reactor increased to 0.3198 torrs. The temperature of the lower electrode was controlled by adjusting the thermoelectric voltage. During the modification process, the substrate temperature was set to 60, 70 and 80 $^o$C respectively.

Observations of the samples were carried out before and after the modification of the polystyrene. Surface morphology was first observed by using an optical microscope. An optical micro-profiler was then used to measure surface roughness of the samples. Hydrophobicity of the samples was observed by a contact angle of liquid measurement.

## 3. Results and Discussion

The spin coating technique employed in this study produced homogeneous polystyrene thin film. The homogeneity of the polystyrene thin film was examined before the plasma treatment process by using an optical microscope. This examination ensured similar conditions of the samples before the treatment. Typical microstructure of the polystyrene film deposited on a glass substrate is shown in Figure 2. From Figure 2, it can be seen that the polystyrene thin film formed a grainy pattern. The size of the grains is relatively uniform.

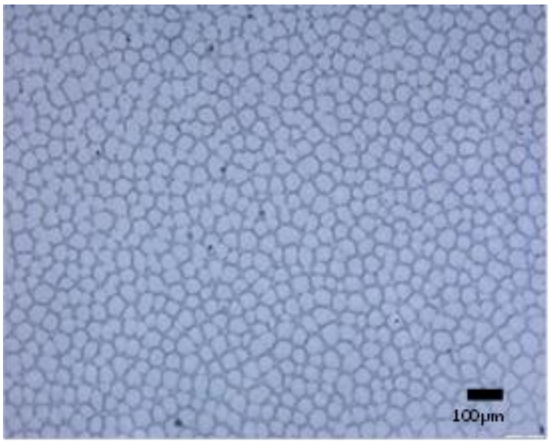


**Figure 2**. Optical microscope surface image of polystyrene thin film.

Topological structure and roughness of the samples which was measured by the optical micro-profiler are shown in Figure 3**.** Determination of the roughness is carried out by two methods, each of which produces a value Sz and Sa. Sz is the value obtained from roughness measurement technique which is calculated from the value of the highest peak and the deepest valley. Sa represents the average roughness value per area.

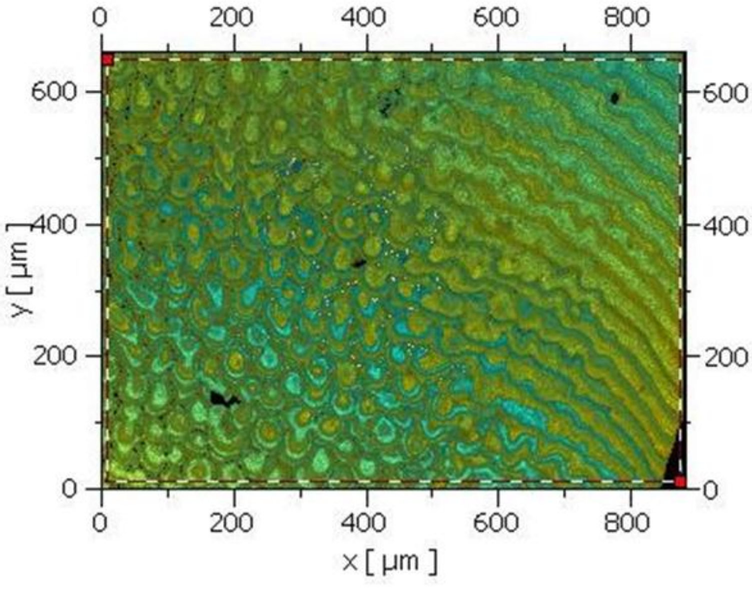


**Figure 3**. Micro profile image obtained by using TMS 2000

Roughness measurements on samples before the plasma modification show that the roughness of the polystyrene surface was 7.0 nm (Sz) and 274 nm (Sa)**.** Surface roughness measurements performed on the plasma treated samples are shown in Figure 4. The roughness of the surfaces increased significantly at a low substrate temperature of 60 °C i.e. 7.37 nm (Sz) and 307 nm (Sa). However, the average roughness (Sa) decreased after 60 °C.

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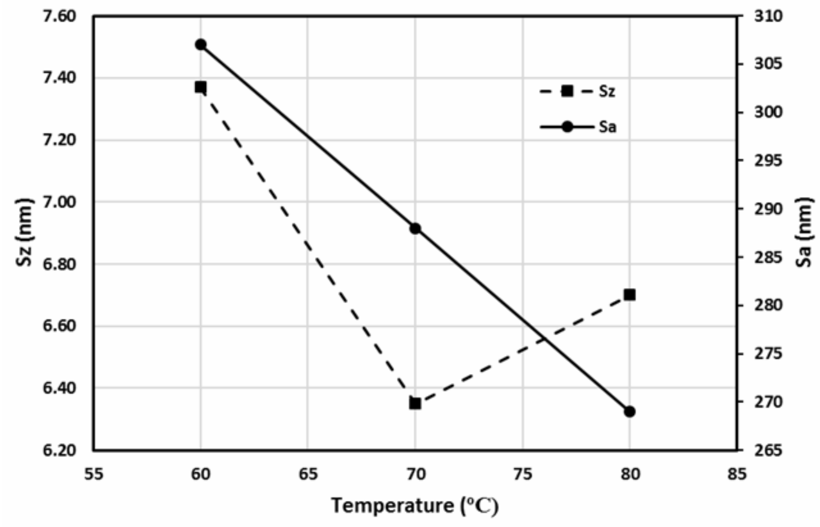


**Figure 4**. Roughness measured with Sa and Sz due to variation of substrate temperature

Sz, on the other hand, decreased from 60 °C to 70 °C then started to increase after 70 °C. The increase was due to the very active surface of the polystyrene approaching its melting point (90 °C). In general, plasma consists of high-energy and charged particles. These particles can produce collisions between ions and the substrate causing the increase of substrate temperature. This situation can affect the polystyrene surface. Besides the physical bombardment, some chemical reactions are possible during the treatment [7].

In this study, we also conducted a study on the effect of surface roughness and hence the substrate temperature on the hydrophobicity of the film. A contact angle measurements performed before and after treatment of liquid nitrogen plasma to determine the level of hydrophobicity. Nitrogen plasma treatment affects the contact angle of the polystyrene layer as shown in Figure 5.

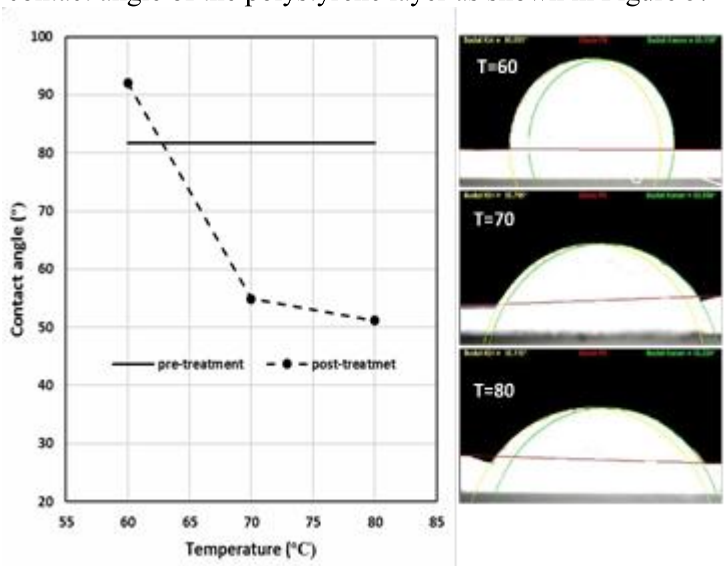


**Figure 5**. The effect of substrate temperature on contact angle

Figure 5 shows that the plasma treatment increased the hydrophobicity of the polystyrene surface significantly. The increase is strongly related to the roughness of the surface. Higher contact angle i.e.

higher hydrophobicity was obtained on the rougher surface. The results obtained in this study indicate that after plasma treatment process at the substrate temperature of 60 $^{O}$C, the roughness of the polystyrene increased by 0,37 nm (Sz) or 33 nm (Sa). The increase produced a high contact angle of about 92 degrees which is more hydrophobic than untreated sample. A similar study showed that the increase of roughness decreases the surface energy resulted in higher hydrophobicity [8].

The higher the substrate temperature, the contact angle of polystyrene-water tends to decrease. As the temperature of the substrate increased, the polystyrene microstructure becomes more dynamic. The smoother surface is a result of the reaction between the nitrogen and the more dynamic microstructures. Some damages were noticed on specimens treated at 80 $^{O}$C.

The decrease of the contact angle at higher substrate temperature is linear with the average roughness (Sa) but is not linear with the change of roughness (Sz). The surface energy becomes smaller at the smoother surface. However, the surface energy does not depend on the roughness, but also the microstructure of the materials. Some evidence of this phenomenon was also observed by another researcher [8].

## 4. Conclusion

Based on this research, it was found that the influence of the substrate temperature on the surface modification process of polystyrene thin film was significant. The highest roughness of the polystyrene after treatment was achieved at 60 ºC. The roughness becomes lower after treatment at higher than 60 ºC. The very active surface at the temperature close to the melting temperature could be the reason of the smoothing. However, the smoothing phenomena from 70-80 ºC showed a small decrease of the hydrophobicity. From these results, it can be concluded that the surface roughness does not entirely influence the hydrophobicity. New microstructures on the surface induced by the plasma treatment may cause a lower surface energy.

## 5. References

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