

The effect of molecular weight on the surface wettability of polystyrene treated with nitrogen plasma

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Abstract. The wettability of polystyrene thin film surface in the development of biosensor based on quartz crystal microbalance (QCM) is an important aspect in biomolecule immobilization. The polystyrene thin film was produced by a spin coating method. The wettability was achieved by modification of the polystyrene surface using a nitrogen plasma treatment. The aim of this work is to investigate the effect of polystyrene raw material molecular weight to the wettability of the polystyrene surface treated with the nitrogen plasma. A TMS-1200 micro profilometer was utilized to determine the surface roughness. The contact angle of the polystyrene surface was measured by a contact angle instruments to observe the surface wettability. The results showed a decrease in the surface roughness and the contact angle of polystyrene layer after the nitrogen plasma treatment, indicating the polystyrene surface changed to a higher wettability. Furthermore, the higher molecular weight of the polystyrene led to the decrease of the surface roughness and the increase of the wettability. The wettability depends on functional group in the polystyrene. The changes of polystyrene the functional group were determined by an FTIR spectrometry. The infrared spectroscopic measurement has confirmed the presence of polystyrene nitrile (C-N) group in the form of C≡N representing a polar group structure. Moreover, the intensity of the C≡N peak increased in the treated polystyrene with the higher molecular weight. The increase of the absorbance is related to the increase of the surface polarity and hence the wettability.

1. Introduction

On the application of a biosensor, the quartz crystal microbalance (QCM) is used as a biomolecule detector. The QCM is a chemical sensor device which is highly sensitive towards mass changes on its surface. A QCM consists of two electrodes sandwiching a disc of AT-cut quartz crystal. In the biosensor application of the QCM, a coating process is needed to protect the electrodes from oxidizing. Furthermore, the layer is also designed to immobilize biomolecules. A polystyrene layer is generally used as the coating layer as well as the immobilization matrix layer on the QCM [1, 2]. The polystyrene surface is generally hydrophobic and binds biomolecules through physical adsorption. The adsorption of the biomolecules is affected by wettability of the surfaces. The wettability of the polystyrene layer can be improved by modifying the surface morphologies [3-5]. In the previous research, the modification of the polystyrene layer with various molecular weight was carried out by means of UV radiation



treatments for 1 and 2 hours [5]. The longer period of the UV radiation on the polystyrene layer resulted in the lower contact angle indicating the surface is becoming more hydrophilic than the result of the short treatment.

It is desirable to establish a shorter treatment period. The surface modification can also be carried out by a plasma treatment. In particular, a plasma treatment of polymeric materials has become one of the most important methods to enhance the wettability and adhesion of biomolecules without affecting the bulk material features. The plasma treatment can change the microstructure and character of the polymer surface which results in the functionalization of materials. There were a significant number of publications related to the modified polymer surfaces using plasma treatment [6-11]. However, the modification of the polystyrene using a plasma treatment on the QCM sensor is still limited.

The surface of the polystyrene layer is modified using a nitrogen plasma to achieve better wettability of the surface. The molecular weight of the polystyrene raw material used in the film production is one of the factors which needs to be examined in the surface modification. In this paper, the effect of the molecular weight on the surface wettability of the polystyrene treated by nitrogen plasma was studied by means of a Fourier transform infrared (FTIR) spectrometry. The FTIR data was used to investigate the functional group of the polystyrene surface before and after plasma treatment.

2. Experimental method

The samples for this study were produced by depositing a layer of polystyrene thin film on the top of a commercial quartz crystal resonator. The resonator was purchased from PT Great Microtama, Surabaya, Indonesia. The polystyrene with various molecular weights (Mw) of 35,000 g/mol, 192,000 g/mol and 280,000 g/mol was purchased from Sigma-Aldrich. The polystyrene was dissolved in a chloroform solvent at a concentration of 3 %. Then, the solution was coated on the quartz substrate by using a spin coating technique. The spin coater was operated at 3000 rpm for 60 seconds. After the deposition, the sample was heated in the oven at a temperature of 150 °C for 60 minutes to evaporate the moisture on top of polystyrene layer. The modified polystyrene surface was produced by nitrogen plasma treatment generated in a mini-reactor using a low power (40 watts) plasma generator for 2 minutes. The process was maintained at a constant pressure by controlling gas flowrate at 20 ml/min. The nitrogen plasma system is shown in Figure 1. The surface roughness of the untreated and treated polystyrene surface was observed by a micro profilometer TMS-1200. The surface wettability of the polystyrene surface was measured by contact angle instruments. The procedure of the contact angle (CA) measurements was reported in the previous paper [5]. The functional group of polystyrene was studied by FTIR (8400S Shimadzu) spectroscopy.

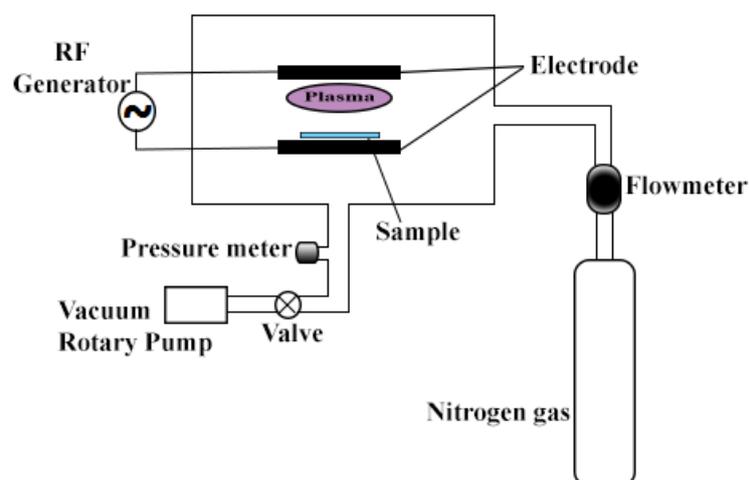


Figure 1. Design of nitrogen plasma system used in this experiments.

3. Results and discussion

Nitrogen plasma treatment has evidently modified the polystyrene surface. Figure 2 shows the surface roughness of the various molecular weight polystyrene before and after plasma treatment. The surface roughness increased with the increase of the molecular weight of the polystyrene. On the other hand, the nitrogen plasma treatment of the surface decreased the surface roughness. The higher of the molecular weights results in the reduction of the surface roughness. The reduction of the surface roughness can be a result of photochemical process, physical knocking by ion bombardment, and/or surface chemical reaction. The photochemical process breaks several polymer chains and opens opportunities to the surface chemical reactions. The process leads to the alteration of the surface architecture. Furthermore, the alteration was enhanced by the ion bombardment onto the surface.

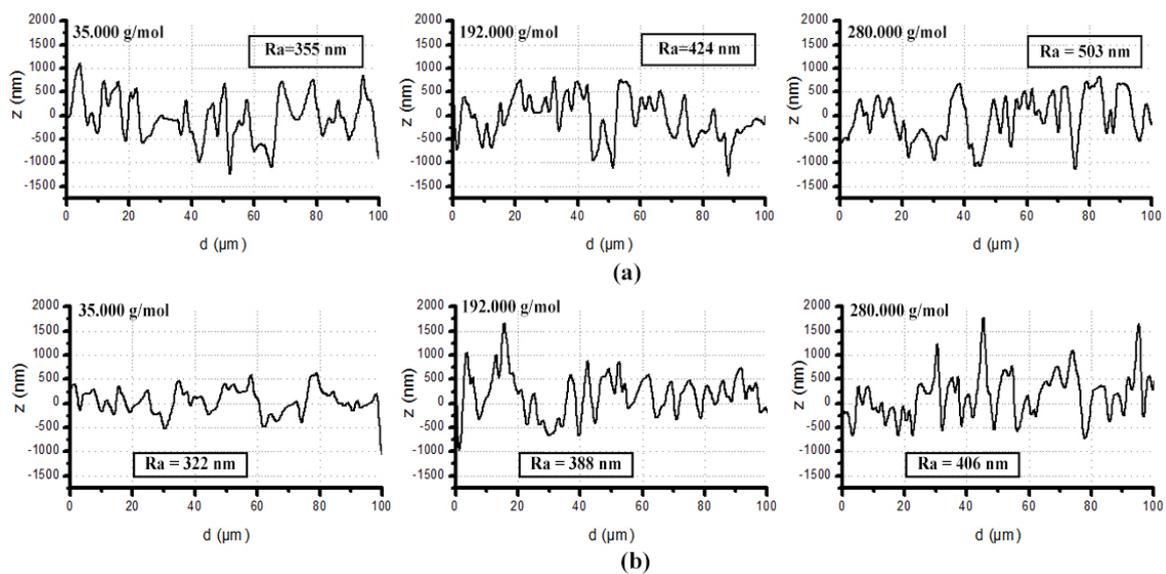


Figure 2. The surface roughness profile of polystyrene with various molecular weight of 35,000 g/mol, 192,000 g/mol and 280,000 g/mol: (a) untreated (b) plasma treated.

The surface roughness of the polystyrene has been known to relate with the wettability [12]. In this study, the wettability was examined using a contact angle measurements. The contact angle (CA) of the untreated polystyrene surface with the molecular weight of 35,000 g/mol was 82.639°. This result indicated that the surface exhibits weak hydrophilicity. After the plasma treatment, the contact angle was reduced dramatically to 42.808°. The reduction trend was also observed with the specimens having higher molecular weights as shown in Figure 3. The summary of the treatment results is shown in Table 1.

Table 1. Summary of the contact angle and roughness of the polystyrene with different molecular weight.

Molecular Weight (g/mol)	Untreated		Plasma Treated	
	Contact Angle (°)	Roughness (nm)	Contact Angle (°)	Roughness (nm)
35,000	82.690	355.42	42.808	329.28
192,000	84.122	427.68	46.966	388.61
280,000	85.836	519.69	52.535	456.56

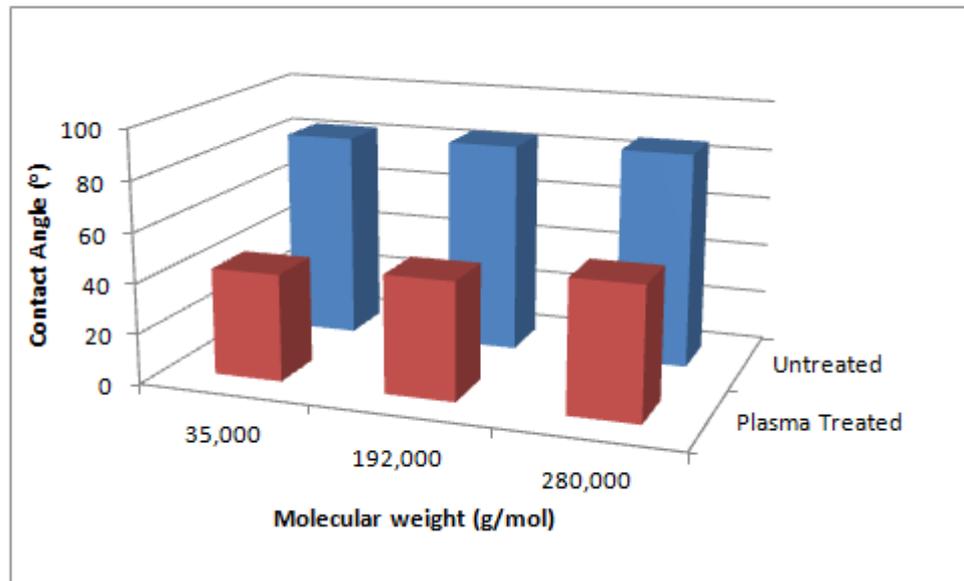


Figure 3. Contact angle vs molecular weight of Polystyrene layers: untreated (blue) and plasma treated (red).

Generally, the contact angle is the measure of the surface energy that controls the wettability of the surface [10]. A lower contact angle exhibits a higher wetting of the surface. The wettability is related to the polarity of molecules or polystyrene's functional group on the surface. The polarity of the functional group can be observed indirectly using an infrared measurement. The IR spectra of the untreated and the treated surface are shown in Figure 4.

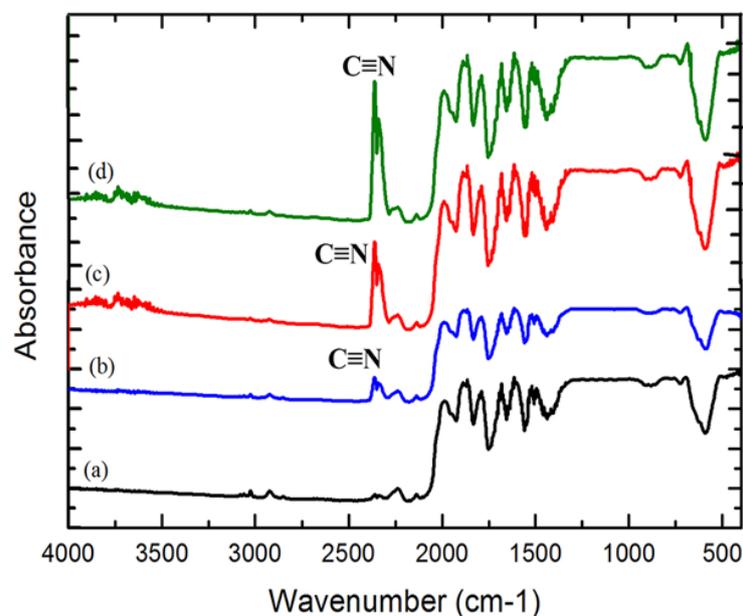


Figure 4. FTIR spectra of Polystyrene layers (a) untreated (b) plasma treated with the Mw of 35,000 g/mol (c) plasma treated with the Mw of 192,000 g/mol (d) plasma treated with the Mw of 280,000 g/mol.

The FTIR spectra show the appearance of a new vibration peak at 2300-2400 cm^{-1} , corresponding to $\text{C}\equiv\text{N}$ bond. The formation of $\text{C}\equiv\text{N}$ was initially triggered by the stoichiometry bond breaking of the polystyrene bonds due to the photochemical reaction enhanced by the ion bombardment. The breaking of the bonds was related to the molecular weight of the polystyrene. The broken bonds were passivated by the nitrogen atoms via the surface chemical reactions. The passivation was indicated by the incorporation of the nitrogen atom forming the $\text{C}\equiv\text{N}$ bonds. Furthermore, the IR absorption intensity of the $\text{C}\equiv\text{N}$ peak became stronger with the increase of the molecular weight. This indicates that the polymer with a larger molecular weight breaks more than the smaller molecular weight one. The more breaking has also been observed as the more reduction of the surface roughness.

The $\text{C}\equiv\text{N}$ functional group has been known as a polar group [13]. The IR spectra show a doublet indicating two vibrations of the polystyrene's functional group. Both of the two peaks simultaneously increased which confirm that the $\text{C}\equiv\text{N}$ has multiple bands of vibration with similar character or polarity. The polar $\text{C}\equiv\text{N}$ functional group interact strongly with the polar water molecules results in higher wettability.

4. Conclusion

The nitrogen plasma treatment on the polystyrene was evidently affected by the polystyrene molecular weight. The surface character of the polystyrene changed into hydrophilic after the treatment which is shown with the reduction of the surface contact angle. The contact angle was influenced by the decrease of the surface roughness. Furthermore, the presence of the $\text{C}\equiv\text{N}$ was also correlated with the decrease of the contact angle and hence the increase of the wettability. This is due to the $\text{C}\equiv\text{N}$ being a polar functional group which was produced by the bond breaking of the polystyrene and surface reaction incorporating N into the molecular structure.

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