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# Surface Modification of Polystyrene by Nitrogen Plasma Treatment

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Additional information is available at the end of the chapter

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## Abstract

Polystyrene has been utilized in biomedical purposes, interacting with various biological molecules. The interactions can be physical adsorption or a long-lasting chemical bonding, depending on the surface characteristic and behaviors. The characteristic can be designed related to the targeted interactions with the molecules by creating certain roughness, morphology, and patterns of the surface. Original characteristics of the material were usually enhanced by its surface modifications. Plasma treatments have been used to modify the polymer surfaces, resulting in a specifically targeted behavior such as hydrophobicity and molecule selectivity through the physical adsorption. A nitrogen plasma treatment is one of the effective and economical surface modification processes. The nitrogen gas is abundant in the atmosphere and generates nontoxic active plasma species for the polymer surface modification. The plasma treatment effectively changes the hydrophobicity and adsorption of the surface.

**Keywords:** nitrogen plasma, surface modification, adsorption, polystyrene

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## 1. Introduction

Polystyrene (PS) has long been recognized and widespread in the world. It is a thermoplastic aromatic polymer. The polystyrene is conventionally utilized in a wide range of application such as packaging, laboratory ware, house items, building materials, and so on [1]. However, it is also known that PS has been developed as functional materials in the form of a thin film and a microsphere [2]. In the field of biomedical, PS is extensively utilized in vitro as cells or bacteria storage [3] or in vivo as a drug-delivery system [4]. In fact, the polystyrene has also been used in biosensors [5–7]. Most of the applications require a hydrophilic surface to

improve the interaction of the surface with proteins. Physical adsorption of protein on the surface is the key to how the PS will be utilized. In a biosensor, for example, selective adsorption is needed to immobilize a specific kind of biomolecule or protein [6]. The adsorption phenomenon is controlled by surface forces such as the weak van der Waals force and surface ionic force, hydrogen bonding, or surface wettability. In some cases, a long-lasting bonding is needed to immobilize the biomolecules involving stronger chemical covalent bonds. A cross-linker, which is incorporated in the functional layer, provides a covalent bonding between the surface and the molecules. The cross-linker can also be produced by the chemical modification of the functional surface [8]. The adsorption of the polystyrene depends on its surface properties that can be designed widely to immobilize macromolecules such as proteins and enzymes.

However, PS originally has a low-surface energy and poor polarizability, resulting in a hydrophobic surface. On the polystyrene surface, the adsorption is caused by mainly the intermolecular attraction forces. The forces often referred to the van der Waals forces originated from intramolecular electric polarities in the polymer chains. Two types of polarities exist, that is, alternating polarities and stationary polarities. The latter is often called the dipoles. The alternating polarities emerge when molecules come close to each other causing disruptions in the electron clouds. The alternating polarities are the solution of the disruptions, resulting in a kind of a molecular bond. Unlike the dipoles, the attraction forces due to the alternating polarities that drastically decrease with the increase of intermolecular distance. The hydrophobicity and protein adsorption are also affected by the combination of two polarities. The more alternating polarities result in the more hydrophobic surface and vice versa. Chemical functional groups such as  $-\text{OH}$ ,  $=\text{O}$ ,  $-\text{NH}_2$ ,  $=\text{NH}$ , and  $\equiv\text{N}$  produce stationary polarities, resulting in hydrophilic property [9].

One way of designing the appropriate adsorption is controlling the surface topography and morphology of the polymer. The performance of a biosensor can be enhanced by optimizing the surface roughness of its functional polymer [6]. Surface roughness is the topographical material's characteristic related to micro-profile of its surface. A higher surface roughness usually resulted in the wider contact area with other materials such as biomolecules on the surface. If the surface is adhesive to the biomolecules, the rougher the surface will attract more biomolecules. However, the physical adsorption is relatively weak, limiting the net attracted biomolecules by resorption (re-desorption) process [10]. The other way of controlling the adsorption was by surface activation [11].

In recent years, plasma treatment has been a common method to modify, activate, and functionalize the surface of polymers [12]. The plasma is the fourth state of a material, consisting of energetic atoms, ions, molecules, and radicals. Free electrons in the plasma maintain its quasi-neutral and equilibrium conditions. However, internally, the plasma has unique properties which can be designed and controlled for many purposes. Plasma surface treatment for polymers generally utilizes low-temperature plasma which is non-destructive to the bulk of the polymers. The low-temperature plasma is generated at low vacuum or better in the atmospheric environment. Another technique of lowering the temperature is by utilizing a low-frequency plasma, for example, a 40-kHz plasma [13]. A number of gases are usually

used in the polymer plasma treatment including Ar, N<sub>2</sub>, O<sub>2</sub>, and NH<sub>3</sub>. The processing gas is selected related to its plasma-state characteristics required for the intended process. Foerch and Hunter, for example, showed that nitrogen plasma treatment resulted in additional nitrogen atoms in the hydrocarbon network of the treated polymer [14]. Another researcher used oxygen plasma to modify a hydrophobic polymer into a hydrophilic polymer [13].

Plasma treatment for the modification and functionalization of polymer surface is very effective since the plasma interacts physically and chemically with the surface. The short time shot for every treatment makes the technique more efficient than other surface treatment processes. Depending on the property and character of the plasma, the treatment is able to produce group functionalization, graft polymerization, or molecules cross-linking which can affect the polymer's surface roughness [4].

This chapter discusses surface modification of polystyrene. Nitrogen plasma is utilized to control the wettability of the polystyrene surface. The wettability is related to the hydrophilic or hydrophobic character of the surface. Research has shown that hydrophilic surface can adsorb protein molecules twice as much as hydrophobic surface [15]. The wettability of the surface can be evaluated or determined by surface-water contact measurement or surface contact measurement in short. In general, the wettability of the surface depends on the surface roughness, morphology, and microstructure.

The polystyrene layer is a thin film produced by means of a spin-coating technique. A number of aspects of the procedure affect the properties of the thin film. Two aspects, which are solvent and raw polystyrene molecular weight, were considered importantly related to the nitrogen plasma treatment process and results. The plasma character was diagnosed using optical emission spectroscopy (OES). Specimen characterizations were intended to determine the surface roughness, surface wettability, and surface microstructure.

## 2. Experimental

### 2.1. Synthesis and deposition of polystyrene thin film

The polystyrene thin film was synthesized and deposited by a spin-coating method. Polystyrene raw material was dissolved into a polystyrene solution. Three raw materials, which were obtained from Sigma Aldrich with different molecular weights ( $M_w$ ), were utilized in this work, that is, 35, 129, and 280 kDa. This work utilized four different solvents to investigate the relation between the solvent and the effect of the plasma treatments. The solvents, that is, chloroform, toluene, xylene, and tetrahydrofuran, were also obtained from Sigma Aldrich. Each of the solutions was then deposited on a substrate by the spin-coating method. The specific quantity of the solution drop and rotation per minute was optimized and set for all the specimens. The polystyrene films were then heated in an oven after the deposition. The treatment was carried out to dry the excess solvent and to enhance interfacial bonding between the film and the substrate.

## 2.2. Plasma treatments

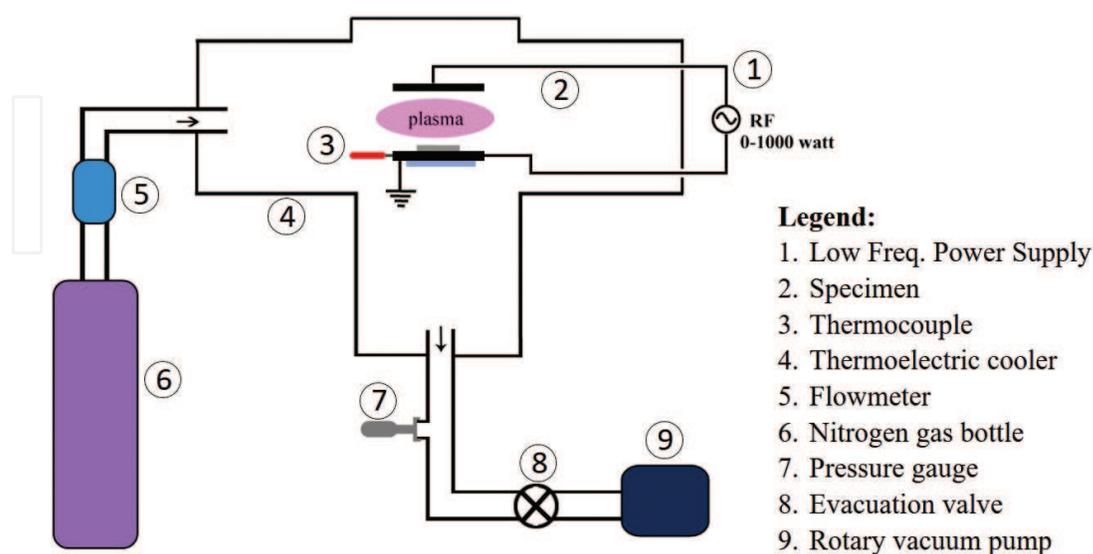
A mini plasma reactor was utilized to treat the surface of the deposited film. Nitrogen gas was introduced into the reactor after evacuation procedure. A flow meter controlled the quantity of the gas during the plasma treatment. The plasma was generated by a 40-kHz AC power source. Only a small power of 40 watts was set for this 2-min' process. The schematic design of the plasma system is shown in **Figure 1**.

The character of the plasma was diagnosed with a spectrometer which has a range of 200–900 nm. Optical emission from the plasma was detected through a quartz window of the chamber. A fiber optic picks up and delivers the light to the spectrometer. The spectrometer was connected to a computer for data acquisition and processing.

## 2.3. Characterizations

Observations and characterizations of the specimens were conducted before and after the plasma treatment. First, the specimen was characterized by means of a Fourier transform infrared (FTIR) spectrometer (*Aurora 4000*). The characterization identified functional groups of bondings, which specify the polystyrene microstructures.

The second measurement was the topographical measurement which was performed by an interferometric surface micro-profiler (*TMS 1200 Polytech TopMap- $\mu$ Lab*). The topographical measurement system provides non-destructive observation and measurement. The interferometric system employed a Mirau objective. The Mirau objective is basically a combination of a microscope objective lenses and a special interferometer called Mirau interferometer. The interferometer is a modification of the Michelson interferometer for the practical function in the objectives of the microscope. The key difference between the two interferometers is that the Mirau exploits parallel arrangement of beam splitting rather than perpendicular beam



**Figure 1.** A schematic design of plasma reactor for nitrogen plasma treatment.

splitting in the Michelson interferometer [16]. Unlike the conventional profiler relying on a stylus which results in edging errors and damages, the interferometric system scans the surface vertically and records the data without mechanical contact. The interference patterns are produced when the differences in the path lengths between the measurement beam and the reference beam are nearly zero. During the vertical scanning, then a correlogram is recorded at each pixel in the camera. The correlogram or the interference signal is then processed into the three-dimensional surface profile. Based on the profile metrology, surface roughness, irregularity, and other topographic features can be determined.

Finally, the wettability of the specimens was observed and characterized by contact angle measurement. The specimen was placed on the observation stage of the system. The stage can be adjusted so that the surface of the specimen is perfectly aligned horizontally. A small droplet (30  $\mu$ L) of pure water is usually used in the measurement procedure. A camera captures the image of the droplet and sends it to a computer.

### 3. Results and discussions

Wettability is a critical property in the development of biosensors, especially during immobilization of biomolecules. The immobilization of the molecules by physical adsorption can be realized by a thin film of polystyrene. However, optimization should be performed since the thin film serves the immobilization as well as mechanical interfacing. Both the functions strongly affect the overall performance of the biosensor. Modification of the thin film's surface is one of the methods to enhance the immobilization. Controlling the wettability means designing the surface roughness, morphology, and microstructure. It is obvious that hydrophobicity of surfaces is directly related to the roughness.

This chapter discusses a technique of the plasma treatment on polystyrene thin film. It is desirable that the modification process does not affect the bulk of the thin film. Nitrogen plasma was utilized to modify the polystyrene surface. The characteristics and states of the plasma strongly control the reactions on the surface. Furthermore, the final result of the treatment depends also on the compositions, microstructures, and characteristics of the original material. The effects of the nitrogen plasma treatment on the polystyrene surface will be examined related to the original material produced with different raw materials' molecular weight and with the different solvents used during the deposition.

#### 3.1. The effect of solvent during deposition process on the polystyrene surface and microstructure

The polystyrene film was deposited by means of the spin-coating method. Polystyrene raw material was in the form of chips or granules. The raw material was dissolved into a polymer solution before spin-coated on the substrates. The solvents used to make the solution were chosen by considering the Hansen solubility parameters (HSPs) for the polymer and the solvents. The HSP considers three interactions, that is, non-polar or dispersive interaction, polar

or dipole-dipole interaction, and hydrogen bonding interaction. The three parameters for the solvent and the solute are used to calculate the polymer solubility sphere, Ra

$$Ra = \sqrt{4(\delta_{D,s} - \delta_{D,p})^2 + (\delta_{P,s} - \delta_{P,p})^2 + (\delta_{H,s} - \delta_{H,p})^2} \quad (1)$$

where  $\delta_{D,s}$  is the HSP for dispersive interaction of the solvent,  $\delta_{D,p}$  is the HSP for dispersive interaction of the polymer,  $\delta_{P,s}$  is the HSP for polar interaction of the solvent,  $\delta_{P,p}$  is the HSP for polar interaction of the polymer,  $\delta_{H,s}$  is the HSP for hydrogen bonding interaction of the solvent, and  $\delta_{H,p}$  is the HSP for hydrogen bonding interaction of the polymer.

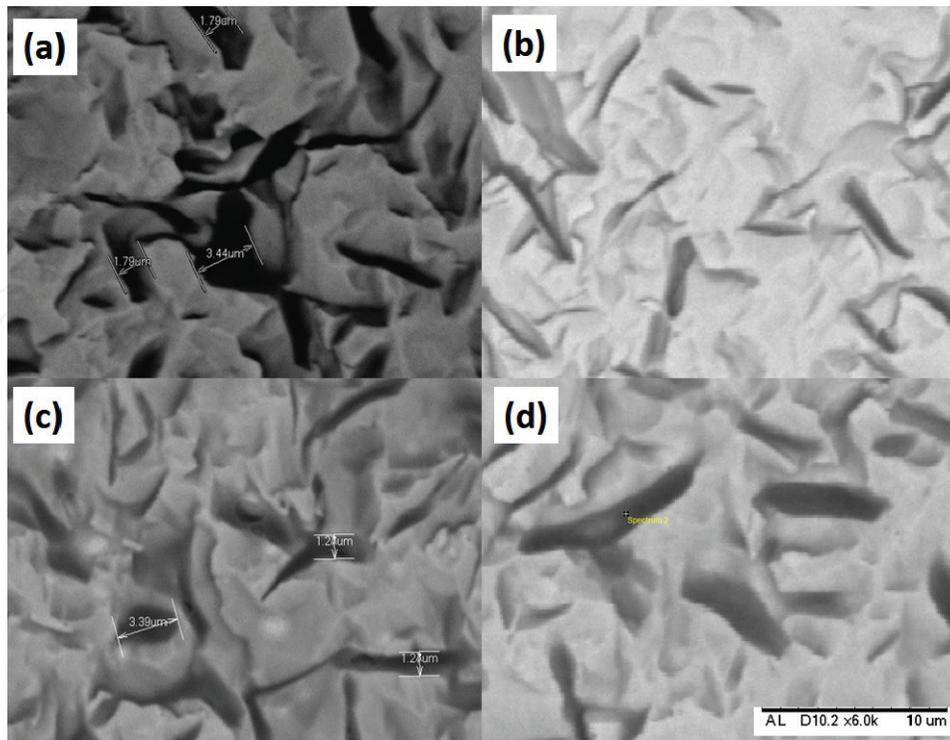
The possibility of the polymer to be dissolved in the solvent is predicted by comparing the Ra with the radius of the interaction of the polymer, Ro. The ratio (Ra/Ro), which is often called RED affinity number, should be less than 1. Smaller RED means that the polymer is easier to be dissolved in the solvent [17]. **Table 1** shows the HSP for the polystyrene and the four solvents [18]. The two last columns show the result of Ra and RED calculations based on the parameters and Ro = 12.7 for the polymer.

As previously described, this work examined four solvents. The results of spin-coating deposition of the polystyrene on a glass substrate with the variation of solvent were observed using SEM imaging as shown in **Figure 2**. The SEM micrograph of the deposited films noticeably shows that the different solvent resulted in the different morphology of the film. The difference is caused by variation in the solvent evaporation during the spin-coating process. The mechanism of the solvent evaporation is controlled by the solubility parameters and vapor pressure [19]. Koenhen and Smolders found that the solubility parameter was proportional to the vapor pressure [20]. Since the solubility parameter represents the cohesive energy, the higher the cohesive energy results in higher vapor pressure or vice versa. The solubility parameters of the solvents, that is, chloroform, tetrahydrofuran, toluene, and xylene, are 18.7, 18.5, 18.3, and 18.2 MPa<sup>1/2</sup>, respectively [21], while the pressure vapor of the above solvents is 669, 637, 577, and 562 mmHg, respectively. Measurements of the surface roughness of the polystyrene thin film produced using different solvents are shown in **Figure 3**. The axis represents different solvents sorted from its lowest pressure vapor to the highest one.

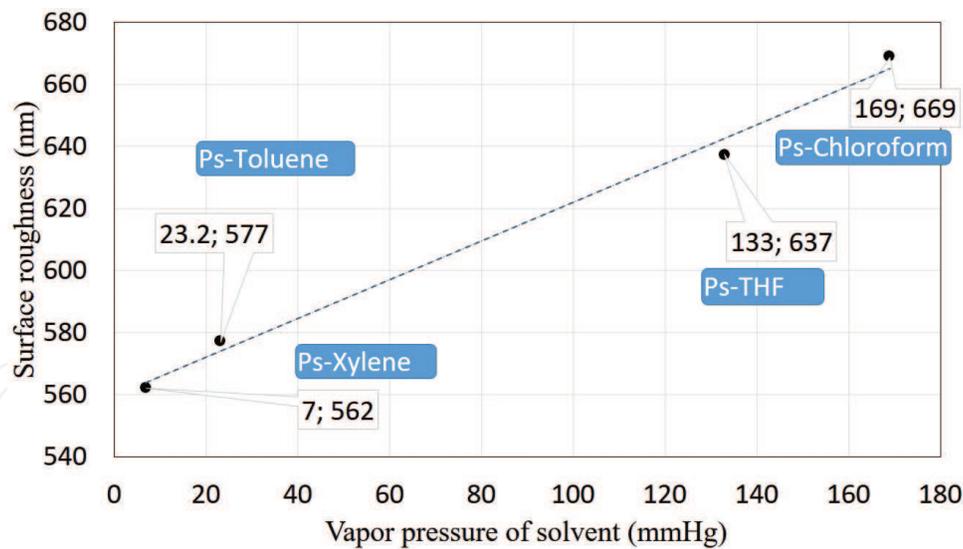
The effect of the solvent on the wettability of the surface of the deposited polystyrene was observed by contact angle measurement. The results are shown in **Figure 4**.

Material	$\delta_d$ (MPa) <sup>1/2</sup>	$\delta_p$ (MPa) <sup>1/2</sup>	$\delta_h$ (MPa) <sup>1/2</sup>	Ra	RED
Polystyrene	21.3	5.8	4.3	—	
Xylene	17.8	1.0	3.1	8.57	0.67
Toluene	18.0	1.4	2.0	8.26	0.65
THF	16.8	5.7	8.0	9.73	0.77
Chloroform	17.8	3.1	5.7	7.63	0.60

**Table 1.** Relation of HSP and the RED number of solvents.

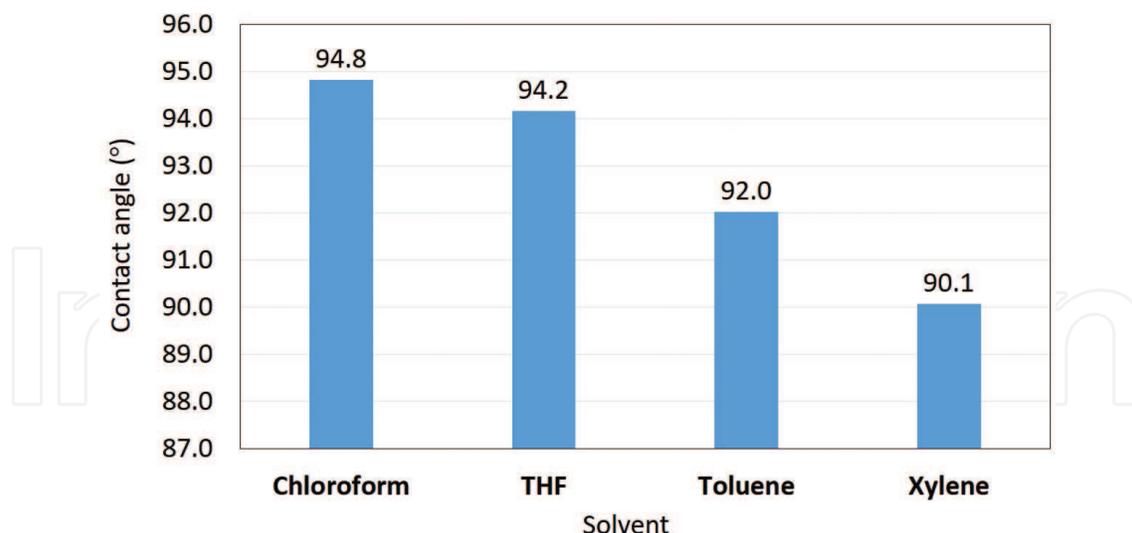


**Figure 2.** SEM micrograph of polystyrene film produced with different solvents: (a) chloroform, (b) tetrahydrofuran, (c) toluene, and (d) xylene.



**Figure 3.** Graphical relationship between the solvent vapor pressure and surface roughness of the resulted polystyrene film.

The result shows that all of the polystyrene specimens were hydrophobic since their contact angles are above  $90^\circ$ . Polystyrene has a  $\text{CH}=\text{CH}_2$  bond interconnected to a benzene ring ( $\text{C}_6\text{H}_5$ ). The molecule is non-polar which has a small electronegativity. This makes sense since the C and H atoms have similar electronegativity, that is, C = 2.25 and H = 2.20. On the other hand,



**Figure 4.** The effect of solvent on wettability represented by contact angle.

the polar water ( $H_2O$ ) molecule results in strong cohesive forces. The adhesive interaction between the polystyrene surface and water then is weaker than the cohesive water interaction.

Although the specimens were hydrophobic, the contact angle measurements showed differences related to the variation of solvent utilized during the deposition process. Considering the phenomena described in **Figure 3** where the variation of the solvent significantly controlled the surface roughness, it can be seen that the difference of the wettability of the polystyrene depends on the surface roughness. Polystyrene thin film which produced using chloroform showed the highest surface roughness and surface contact angle, while the one produced using xylene showed the lowest.

### 3.2. The effect of nitrogen plasma treatment on the surface roughness and wettability of polystyrene produced with different solvents

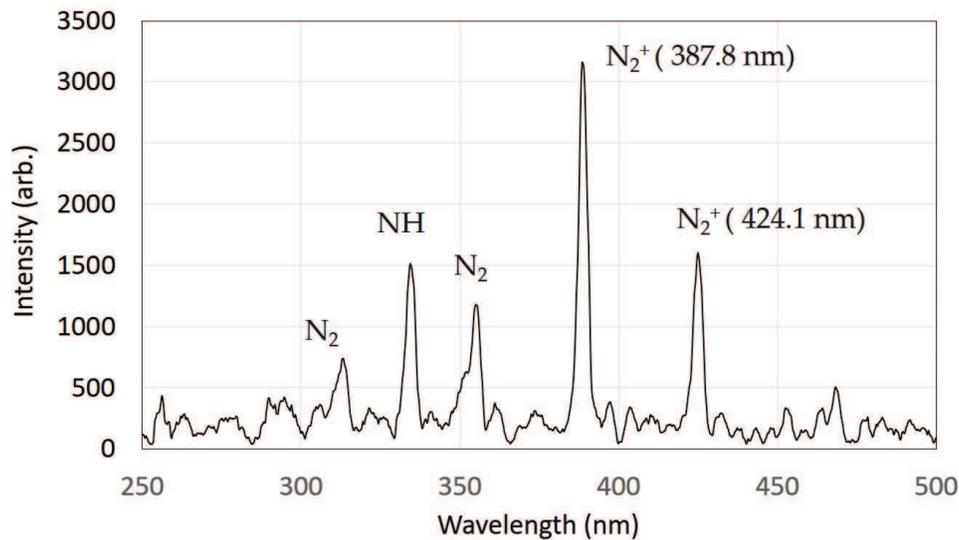
The original hydrophobic property of the polystyrene film can be modified by a plasma treatment. This section discusses the effect of the treatment on the surface roughness and wettability of the polystyrene specimens produced with various solvents. As discussed earlier, plasma treatment is one of the effective methods to modify polymer surfaces. The plasma used in this work is the nitrogen plasma. The generated plasma was monitored using optical emission spectroscopy (OES) technique. **Figure 5** shows a nitrogen plasma spectrum generated by our system as discussed in the previous section.

Typically, the plasma consists of some species such as an  $N_2^+$  ion, energetic  $N_2$  and NH radical as identified in the spectrum [22]. The existence of the NH was due to the small percentage of hydrogen gas left during the evacuation procedure. The surface modification can be controlled by physical and/or chemical processes. The physical process is effected by ion and atomic bombardment without any formation of new compounds. The ions and atoms will bounce back accompanied by some ejected ions and atoms from the thin film. On the other hand, the chemical processes are initiated by ions or radicals which significantly change the microstructure of the polystyrene.

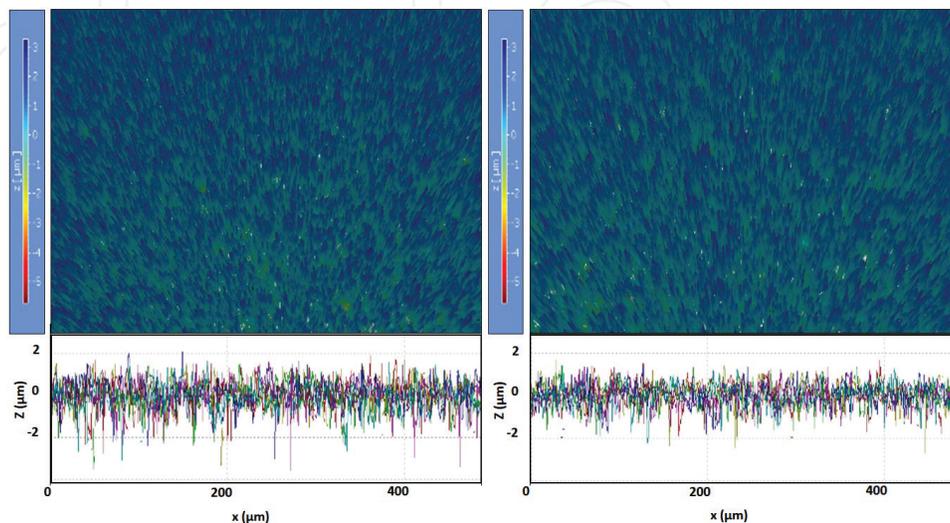
Both of the two processes can result in modification of the surface roughness. The changes of the surface roughness depend on the initial state of the specimen which was controlled by the solvent used in the deposition process. **Figure 6** shows the topographical measurement of the polystyrene specimen produced with THF solvent before and after the plasma treatment.

The surface roughness of the polystyrene specimen before and after treatment was 637 and 535 nm. Evidently, the plasma treatment decreases the surface roughness of all the specimens produced with different solvents as shown in **Figure 7**.

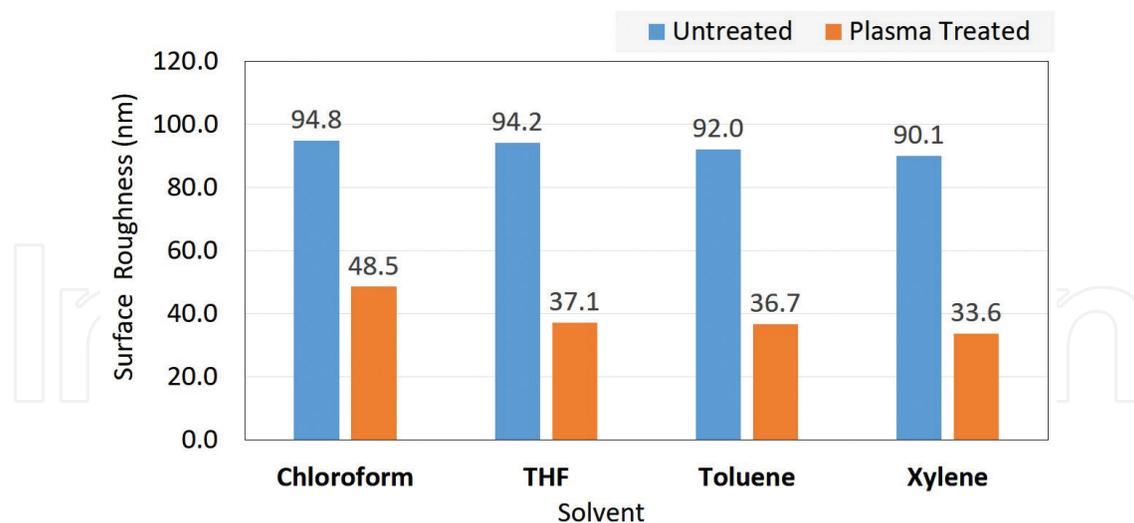
It can be seen from **Figure 7** that the effect of the treatment greatly reduces the surface roughness by 107 nm in average except for the polystyrene produced with xylene solvent. The changes of the surface were firstly caused by the physical process, where ion and atom bombardments eroded the polystyrene surface. The threshed particles were then redeposited on the surface filling pits. Illustratively, the mechanism is described in **Figure 8**.



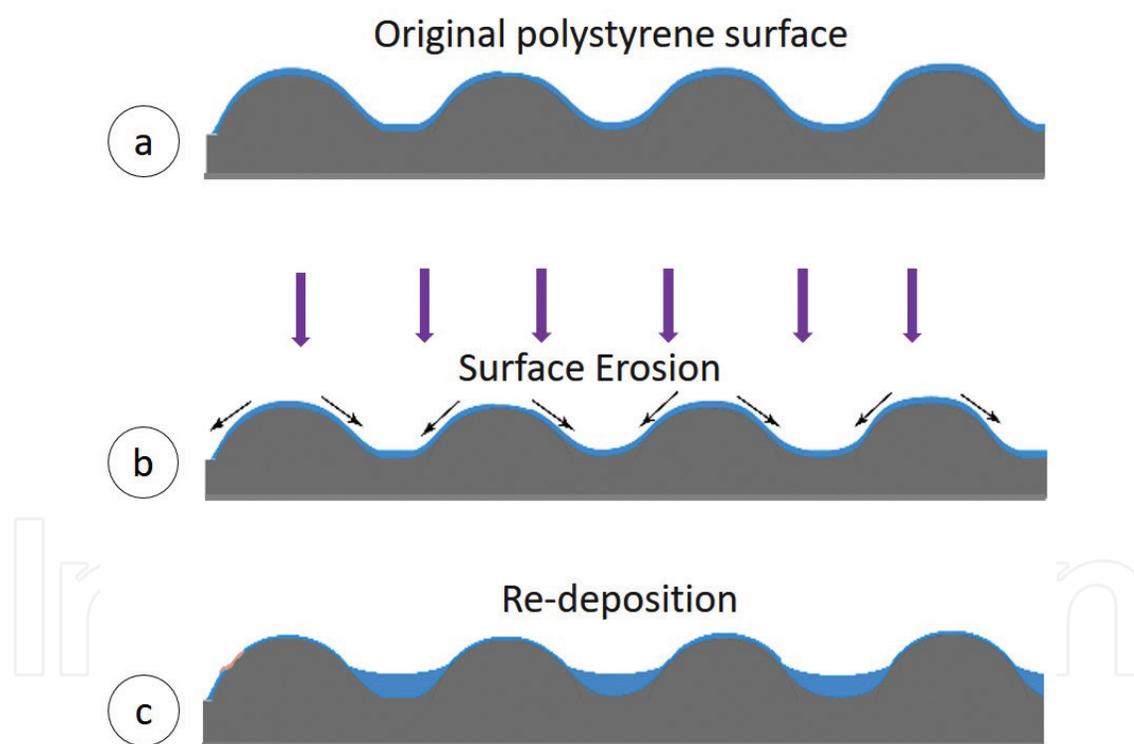
**Figure 5.** Nitrogen plasma spectrum.



**Figure 6.** Surface profile of polystyrene thin film produced with THF solvent before and after the plasma treatment.



**Figure 7.** Comparison of the decrease in surface roughness of the polystyrene produced with different solvents before and after the plasma treatment.



**Figure 8.** Illustration of the surface process during the plasma treatment of the polystyrene thin film.

The effects of surface roughness on the wettability have been studied for long. Wenzel's law, for example, concludes that the surface roughness amplifies the surface wetting property where the hydrophobic surface becomes more hydrophobic and hydrophilic surface becomes more hydrophilic [23]. The law was constructed by relating the macroscopic Young's and the effective contact angles. Furthermore, it should be assumed that the liquid has full contact with the rough surface. The expression of Wenzel's law is written with the equation:

$$\cos \theta_m = r \cos \theta_y \quad (2)$$

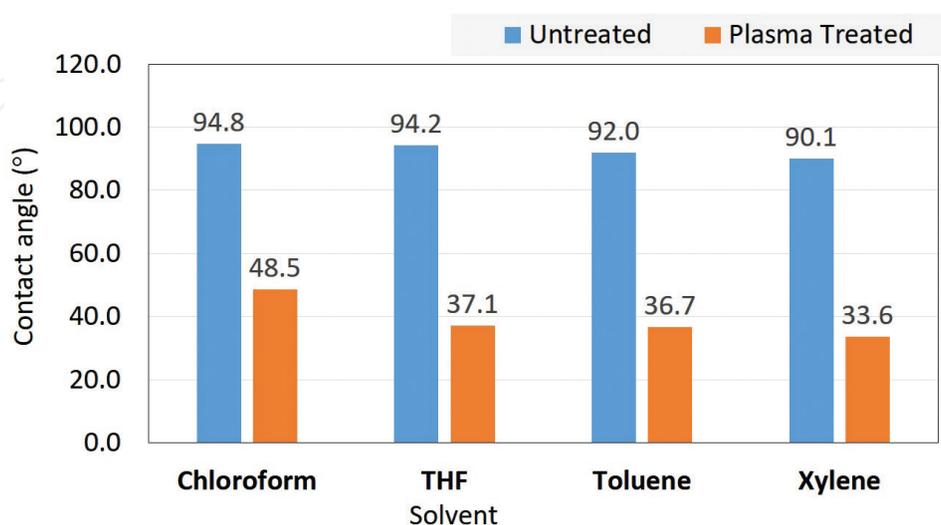
where  $\theta_m$  is the effective contact angle and  $\theta_y$  is the contact angle calculated from the Young equation. The roughness parameter  $r$ , which is larger than 1, can be calculated by taking the ratio of the actual area of the polymer surface to the normally projected area.

Results of the contact angle measurements of the polystyrene film specimens show that all of them became hydrophilic after the plasma treatment. The relation between the contact angle and the variation of solvent is shown in **Figure 9**. It can be seen from **Figures 7** and **9** that the decrease in surface roughness decreases the contact angle. The variation of solvent during the thin film production clearly affects the change of the wettability. The observation indicates that the effect of the solvent on the treatment and the resulted surface wettability were also influenced by the chemical process. Nitrogen radicals in the plasma induce reactions on the surface of polymers. The reactions break some hydrogen bonds of the polystyrene molecules, resulting in the reactive surface. The neighboring reactive sites may produce new functional groups. Indeed, the functional group was observed and identified by means of FTIR spectroscopy (**Figure 10**).

The infrared spectra in **Figure 10** show the effect of the plasma treatment noticeably at wave number between 2300 and 2400  $\text{cm}^{-1}$ . Two strong peaks appear after the plasma treatment. The two peaks were related to a complex  $\text{C} \equiv \text{N}$  bond [24]. The existence of the two stretch vibrations reflects the effect of the carbon or hydrogen environment to the carbon-nitrogen bonding. The carbon-nitrogen bonding is polar, which contributes to the wettability of the polystyrene surface by polar-to-polar interaction.

### 3.3. The effect of nitrogen plasma treatment on the surface roughness and wettability of polystyrene produced with different raw materials' molecular weight

Further study, related to the contributions of the surface roughness and the functional group to the wettability due to plasma treatment, was carried out by observing the phenomena on



**Figure 9.** Changes of the contact angle of specimens before and after plasma treatment.

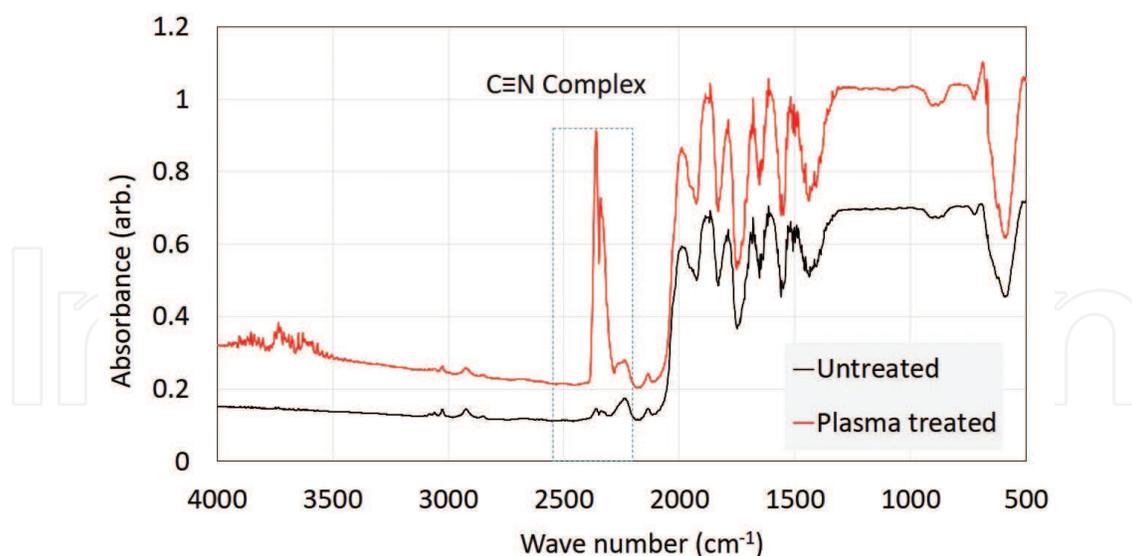


Figure 10. Infrared spectra of untreated (red) and plasma-treated (blue) polystyrene thin film.

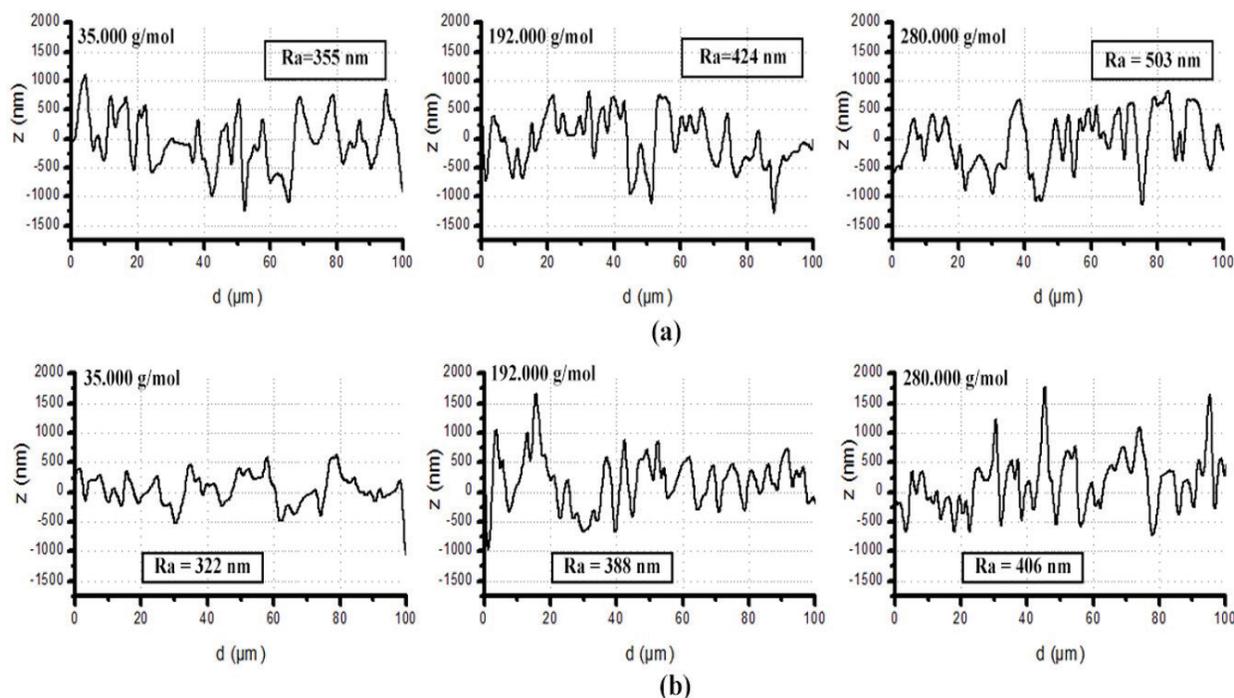
polystyrene thin film deposited with different raw materials' molecular weight. Polystyrene has various molecular weights ( $M_w$ ) and its related polymerization degree [25]. The variation of the polystyrene's molecule weight used in the thin-film production produces various surface properties as well. The surface roughness and the wettability will also be affected. During this study, three kinds of raw materials, which have different molecular weights, that is, 35, 129, and 208 kDa, were used to produce the polystyrene thin-film specimen. Surface profiles of the specimens, which were characterized using the topographical measurement, are shown in **Figure 11**.

Observations during the film production showed that larger molecular weight polystyrene made the polymer precursor solution more viscous. **Figure 11a** shows that larger  $M_w$  resulted in a higher surface roughness. The thicker film was also apparently related to the higher roughness. The molecular weight affects the kinetic stabilization rate of the polystyrene during the deposition [26]. Together with the vaporization rate, the deposition mechanism results in various morphologies and microstructures.

As described in the previous section, the plasma treatment induced the physical and chemical reactions on the surface of the polystyrene. The physical ablation of the surface has a different effect on different weight molecules. The effect of the plasma treatment on the surface roughness is shown in **Figure 11b**. A greater effect was observed on the specimen with a larger molecular weight, that is, 97 nm.

The wettability represented by the contact angle of the untreated and plasma-treated specimens with different  $M_w$  is shown in **Figure 12**.

The contact angle measurement on untreated specimens shows that the increase in surface roughness due to the molecular weight is followed by only a small change in the contact angle. This indicates that the variation of surface roughness in the range of 300 to around 500 nm has a small effect on the wettability.



**Figure 11.** Surface profile of polystyrene with different molecular weights before (a) and after (b) plasma treatment.

After the plasma treatment, the surface roughness and the contact angle were greatly decreased. The decrease of the surface roughness was larger for the larger Mw, but the decrease of the contact angle was smaller for the larger Mw. The plasma treatment has less effect on changing the wettability of the larger Mw. While the physical ablation greatly changes the surface roughness, the chemical surface reactions seem to control the change of morphology and microstructure of the surface.

FTIR characterization of the plasma-treated specimens, which are shown in **Figure 13**, revealed the change of the two peaks between  $2300$  and  $2400\text{ cm}^{-1}$ . The peaks correspond to the polar  $\text{C}\equiv\text{N}$  complex group. The absorbance and the integrated area of the peaks increase with the increase of the Mw. The integrated area shows that the surface concentration of the complex or nitrile complex of the polystyrene thin film increases related to the higher  $M_w$ . The breaking of polymer chains and of the hydrogen bonds attracts the nitrogen ions to the structure and creates new microstructures.

Beside the FTIR spectra, the OES data can also be used to confirm the surface reactions by observing the change of the plasma state and species [27]. The plasma generator used in this work is a low-frequency 40-kHz AC. There have been a number of researchers who studied the application of the low-frequency plasma, especially in polymer treatment [13]. Lower-frequency plasma produces a higher ion density and a lower temperature [28]. This condition is beneficial for polymers having a low melting point. **Figure 14** shows the optical emission of the nitrogen plasma at the range where the  $\text{N}_2^+$  intensities change with the variation of  $M_w$ .

It can be seen from **Figure 15** that the intensities of the peaks at 387.8 and 424.1 nm decrease with the increase of the polystyrene Mw. The peaks are associated to the existence of the  $\text{N}_2^+$

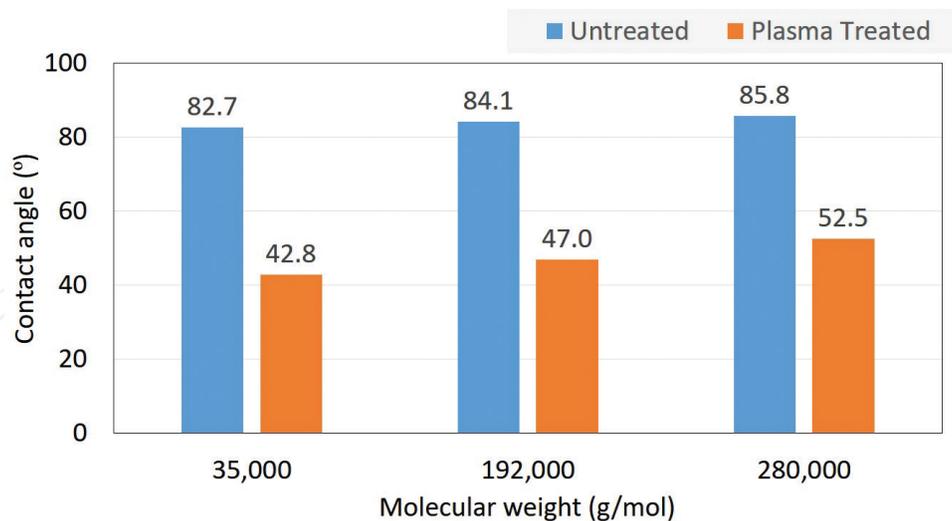


Figure 12. Contact angle of untreated and plasma treated polystyrene surface with different molecular weights.

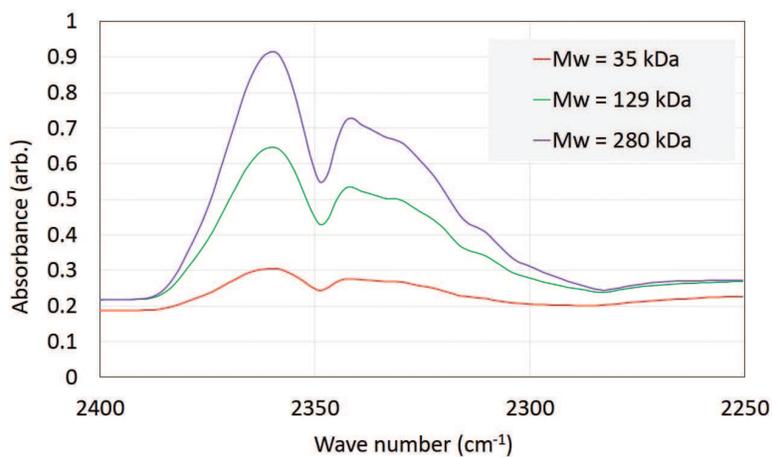


Figure 13. Stretching band of C≡N complex appearing after the plasma treatment.

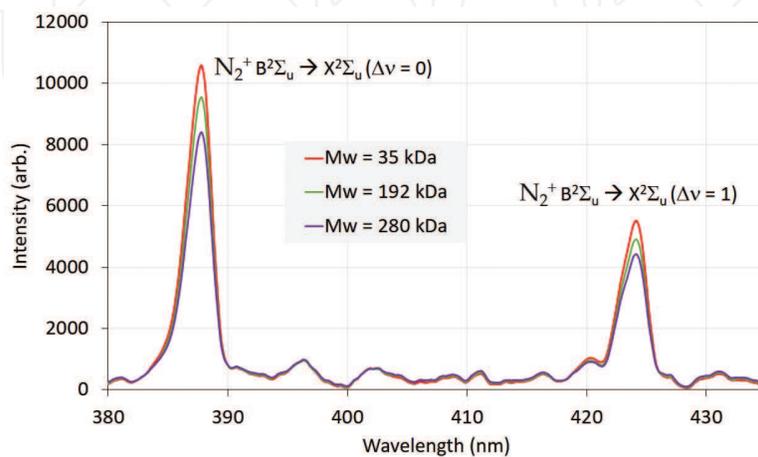


Figure 14. The effect of polystyrene Mw on the plasma optical emission spectrum during the treatment.

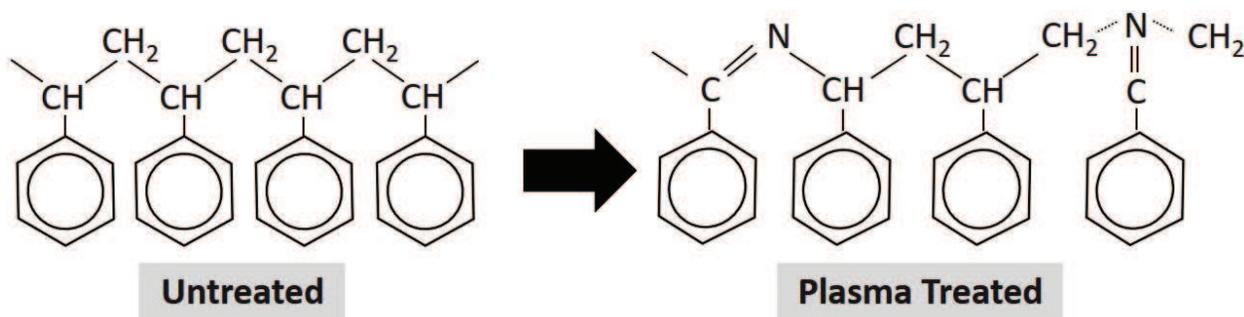
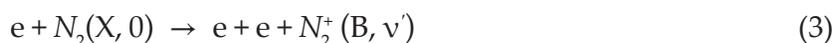


Figure 15. A hypothetical model of the molecular restructuring of polystyrene by nitrogen incorporation.

ions which undergo  $B^2\Sigma_u \rightarrow X^2\Sigma_u$  transitions ( $\Delta v = 0$  at 387.8 nm and  $\Delta v = 1$  at 424.1 nm). In the plasma, the ions are firstly produced by a complex ionization and excitation, resulting in the first negative band transitions. The simplified reaction can be seen as follows:



The decrease of the peak indicates the reduction of the concentration of the  $N_2^+$  ions in the plasma which is related to the surface reaction. The reaction controlled by the  $N_2^+$  ions leads to the incorporation of the nitrogen into the polystyrene network. The larger molecular weight of the polystyrene, the more nitrogen atoms are needed in the network. The nitrogen atoms, which originally come from the  $N_2^+$  ions, have to be withdrawn from the plasma. This makes the concentration of the  $N_2^+$  ions to decrease with the increase of the polystyrene Mw.

Based on the FTIR and the OES spectra, a hypothetical model to predict the bond breaking and the restructuring of the polystyrene surface is shown in **Figure 15**.

When the nitrogen ions or radicals reach the surface of the polystyrene, a number of reactions can take place. The styrene monomer is composed of an aromatic ring of  $C_6H_5^-$  and a vinyl  $-CH=CH_2$ . The polymerization separates the double bond into  $-CH_2$ , resulting in a chain of the polystyrene. The energetic nitrogen ions or radicals substitute the  $-CH_2$ . Depending on the ions and radicals energy, the substitution reactions can either break or combine the polymer chain. The larger  $M_w$  polystyrene results in the larger number of nitrogen incorporated by the plasma treatment.

## 4. Conclusions

This work concludes the possibility of nitrogen plasma treatment to control the wettability of polystyrene surface. In general, the plasma effectively reduced the contact angle and hence increased the wettability or reduced the hydrophobicity of the surface. The solvents utilized during the deposition procedure affected the surface roughness of the resulted thin film. A solvent with a higher HSP or a vapor pressure produced the film with a higher surface roughness. The plasma treatment greatly reduced the surface roughness by 107 nm in average. The contact angle of the surface after the treatment drastically reduced, depending on the surface

roughness before treatment. Further results of the plasma treatment on the film produced with various molecular weights revealed that the plasma treatment has more effect on changing the surface roughness but less effect on changing the wettability of the larger molecular weight. This indicates that the plasma treatment resulted in the modification of the surface microstructure and morphology beside the surface roughness. The modification was controlled by the incorporation of the nitrogen from the plasma into the polystyrene's molecules.

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