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OPTICAL EMISSION SPECTROSCOPY STUDIES DURING NITROGEN PLASMA OF POLYSTYRENE SURFACES MODIFICATION

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ABSTRACT: Nitrogen plasma treatment was successfully performed to modify polystyrene surfaces from hydrophobic into hydrophilic. The objective of the work was to achieve better wettability of the polystyrene surfaces. Various surface characters of the polystyrene were obtained by synthesising the polystyrene layer from different molecular weight (Mw) solution using a spin coating method. The solution prepared for the coating procedure was made by dissolving monomers which have Mw of 35,000 g/mol, 192,000 g/mol, and 280,000 g/mol into toluene solvent at the concentration of 6%. The polystyrene surfaces then treated by means of the nitrogen plasma using a 2 MHz plasma generator with the power of 40 watts and the gas flow of 20 ml/minutes for 2 minutes. The optical emission spectroscopy (OES) provided the measurement of plasma species and the calculated electron temperature (T_e) and electron density (n_e). The species N_2^+ ion was identified from the intensity emission of OES. The existence of the N_2^+ ion and corresponding to the condition of T_e and n_e in the plasma plays a key role in the polystyrene's surface changes as found in the polystyrene surface after plasma treatment. After plasma treatment, nitrile functional group (C≡N) was found in the polystyrene surface which is indicated by the Fourier Transform Infrared (FTIR) fingerprint of the nitrile functional group at the vibration peak of 2300-2400 cm^{-1}. The existence of the C≡N represent the surface changed from hydrophobic to hydrophilic. This result was in agreement with a lower contact angle of the polystyrene surface.

Keywords: Nitrogen Plasma, N_2^+ ion, OES, Nitrile and Polystyrene

1. INTRODUCTION

Plasma-based approach has gained considerable popularity for modifying interfacial polymers to enhance bondings with subsequent molecular immobilization layer designed to contact with specific biological responses [1]. This is because the plasma has the ability to change physical and chemical properties of surfaces without affecting bulk properties [2] . In addition, this method also requires a shorter period of process than any other method of surface modification. When the plasma is exposed to polymer surfaces, formation of new functional group, graft polymerization, coating, and molecular crosslink is occurred [2]. In general, modification using plasma will increase the surface energy and cause the surface of the polymer increasingly hydrophilic [3]. Modification of polymers using a plasma nitrogen can also cause the formation of polar groups such as amine, imine, amide, and nitrile on the polymer surface [4]. The existence of such functional groups is originated from the chemical interactions between the plasma species (ions, electrons, neutrals, and radicals) with the polymer chains.

A non-invasive in-situ plasma diagnosis can be achieved by an Optical Emission Spectroscopy (OES) in UV-vis regions. Since most of the plasma is generated in a vacuum chamber, the OES system measure the emission via an optical fiber attached to the chamber. These emissions are the result of the particle de-excitation [5]. It provides valuable information such as electron temperature, ion density, and electron density. Where the data are presented in the form of line-ratio. That is, each line spectrum shows an optical transition between two levels of quantum energy [6].

Polymeric materials are widely used in many applications due to their mechanical properties (including flexibility) of thermal conductivity, transparency, chemical inertia, etc. However, some applications require certain surface properties (wettability, adhesion, biocompatibility), which can be achieved by plasma treatment [7, 8]. Polystyrene (PS) is one of the most widely used materials for applications included in sensor development. The polystyrene can be used as itself and also combined with other materials. One of the objectives of the polystyrene modification in the sensor world is to achieve better adsorption of biomolecules on the surface. In the present paper, OES was used to diagnose and determine the state of the nitrogen plasma which characterize by the plasma species, electron temperature T_e and electron density n_e during the plasma treatment process. This characterization is important to control the nitrogen plasma processing on polystyrene′s surface. The relationship between the species plasma, T_e and n_e with the surface wettability and functional polar group is discussed.

2. EXPERIMENTAL DETAIL

Samples in this work were a layer of polystyrene thin film deposited on a QCM surface. The raw materials were polystyrene granules with various molecular weight of 35,000 g.mol^{-1}, 192,000 g.mol^{-1}, and 280,000 g.mol^{-1}. The granules of each Mw were dissolved in toluene solvent to make of 6% solution of the polymer. The polystyrene solution was deposited on the QCM surface with spin coating technique with a rotational speed of 3000 rpm and a deposition time of 60 seconds.

Modification polystyrene surface was performed using a 2 MHz plasma generator at 40 watt radio frequency (RF) power, 40 Pa pressure, 20 ml / min gas flow rate and treatment time for 2 min. During the plasma treatment process, the plasma spectrum was characterized by optical emission spectroscopy (AURORA-4000). The experimental set-up for identifying the plasma species is shown in Fig. 1. An optical sensor was fixed to the chamber window and connected to an optical spectrometer. The active plasma species then analyzed using a computer controlled system with software spectral analysis which appear the graph between wavelength (λ) vs. the intensity. The measurable wavelength detected in the spectrometer is from 200 nm to 1000 nm. Then the emission spectra was performed with NIST's Atomic Database to determine species plasma, the temperature (T_e) and density (n_e) of electron.

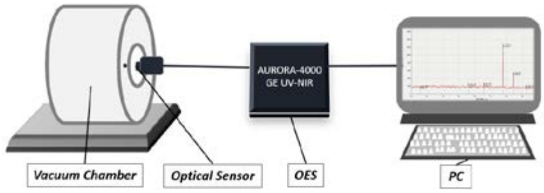

Fig. 1 Scheme of the optical emission spectroscopy for measurement of species in the plasma process

In this work, the NII was selected for the estimation of the temperature electron. Based on the experimental results the NII was found at the spectral line at wavelength of 387.8 nm, 424.1 nm, and 467.4 nm. The relative intensity for selected spectral line of the NII was used to calculate temperature electron by using Boltzmann's equation:

$$\ln\frac{I\lambda}{gA} = Const - \frac{E_i}{kT} \quad (1)$$

Where:
I = observed emission intensity
λ = wavelength of the emission line
g = statistical weight
A = transition probability for spontaneous emission
E_i = excitation energy
K = Boltzmann constant
T = temperature

T_e is calculated from the slope of the straight line $(-\frac{1}{kT})$ fitted to a plot of the left-hand side of equation (1) against E_i.

The calculated electron density was determined by from spectral line broadening by the Stark-effect [9, 10]. This method was selected due to the appeared relative emission intensities only singly ionized species. Deduction of the Stark broadening and determination of its full width half maximum (FWHM) which in turn resulted in the electron density can be carried out by using the equation (2) and (3):

$$\Delta\lambda_{1/2} = 2\omega\left(\frac{n_e}{10^{16}}\right) \quad (2)$$

$$n_e = \left(\frac{\Delta\lambda_{1/2}10^{16}}{2\omega}\right) \quad (3)$$

$$n_e \geq 1{,}6\ x\ 10^{16}T_{1/2}(\Delta E)^3 \quad (4)$$

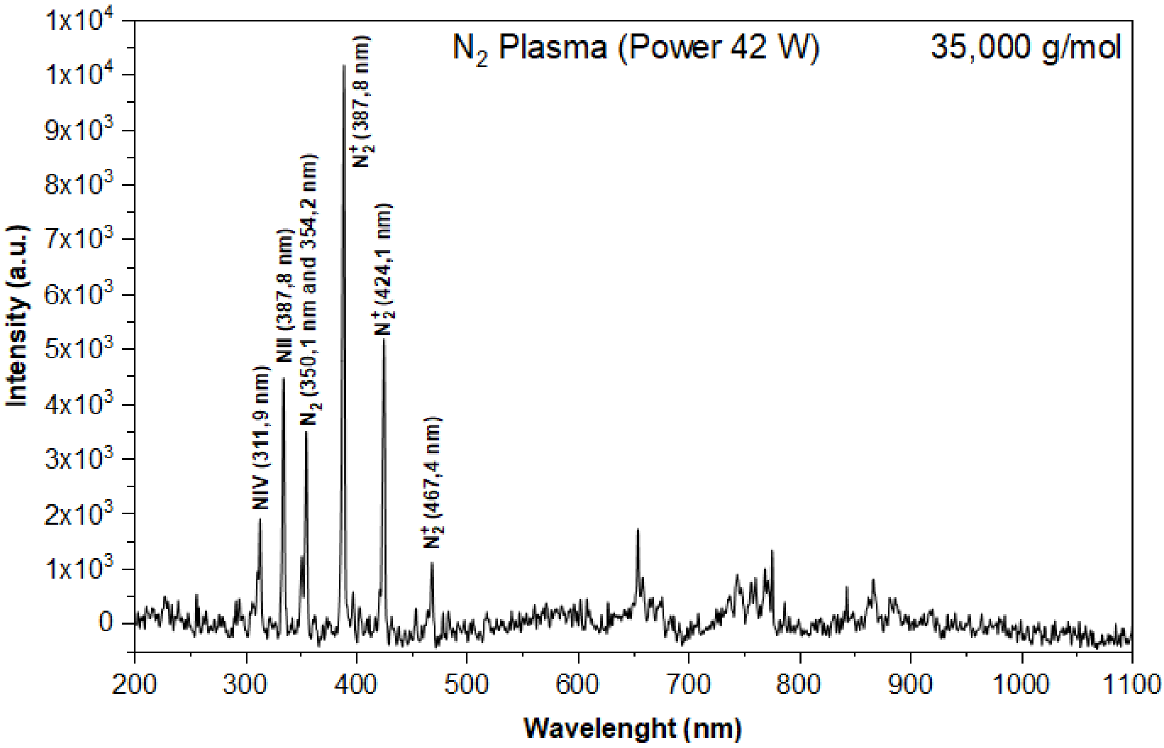

Fig. 2 Emission spectra of nitrogen plasma at Mw of 35,000 g/mol

n_e = electron density in m^{-3}, $\Delta\lambda$ = full-width at half-maximum (FWHM) in nm, ΔE = energy of the emitting level

The contact angle was measured using the contact angle measurement [11]. and the polar functional groups are observed with FTIR before and after treated by nitrogen plasma.

3. RESULTS AND DISCUSSION

In nitrogen plasma, the active species that interact with polystyrene surfaces, electron temperature and electron density are observed with OES. Fig. 2 shows a typical emission spectrum of nitrogen plasma as a function of wavelength and intensity obtained from Mw with 35,000 g/mol.

As seen in Fig. 2, the main emitted species are observed at the wavelength of 387.810 nm, 424.123 nm and 467.7 nm. Based on the *Atomic Database NIST* spectrum, this main emission spectrum is NII which show ion $\boldsymbol{N_2^+}$ [12]. The presence of $\boldsymbol{N_2^+}$ species has a very important role in the polystyrene surface modification process.

The $\boldsymbol{N_2^+}$ ionic state is largely the result of the electron collision processes [13], the reaction mechanism can be seen below:

$$e + N_2(X, 0) \rightarrow e + e + N_2^+ (B, v') \qquad (5)$$

As shown in Fig 3, the intensity of emission of N_2^+ ions in a variation of Mw indicates a decreasing intensity change. This corresponds to the increasing number of N_2^+ ions reacting with the C atom to form the C$\equiv$N group. The appearance of ion $\boldsymbol{N_2^+}$ in the OES spectra is attributed to the observation with FTIR as shown in Fig. 4. The FTIR spectra show the new peaks at the wavelength of 2300-2400 cm^{-1} after treated by plasma nitrogen. This peaks represent to the nitrile functional group (C≡N) which is the polar group. The presence of such polar groups indicates a thin layer of polystyrene having wettability due to changes in functional groups which make the polystyrene surface properties more reactive. The presence of a polar group indicates that the surface is hydrophilic as indicated by the low angle of contact as shown in Fig. 5. The contact angle reduced with the higher molecular weights after treated by plasma treatment. The higher the molecular weight the absorbance intensity of the C$\equiv$N increases.

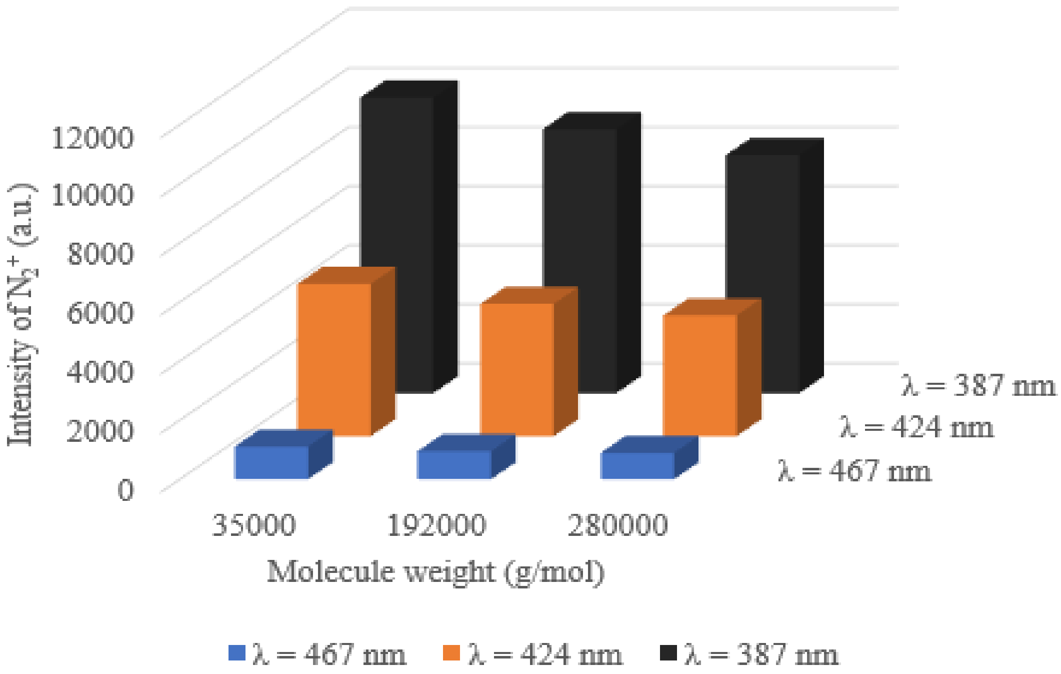

Fig 3. The OES intensity of emission spectral ion N_2^+ in the polystyrene surfaces during plasma process with different Mw

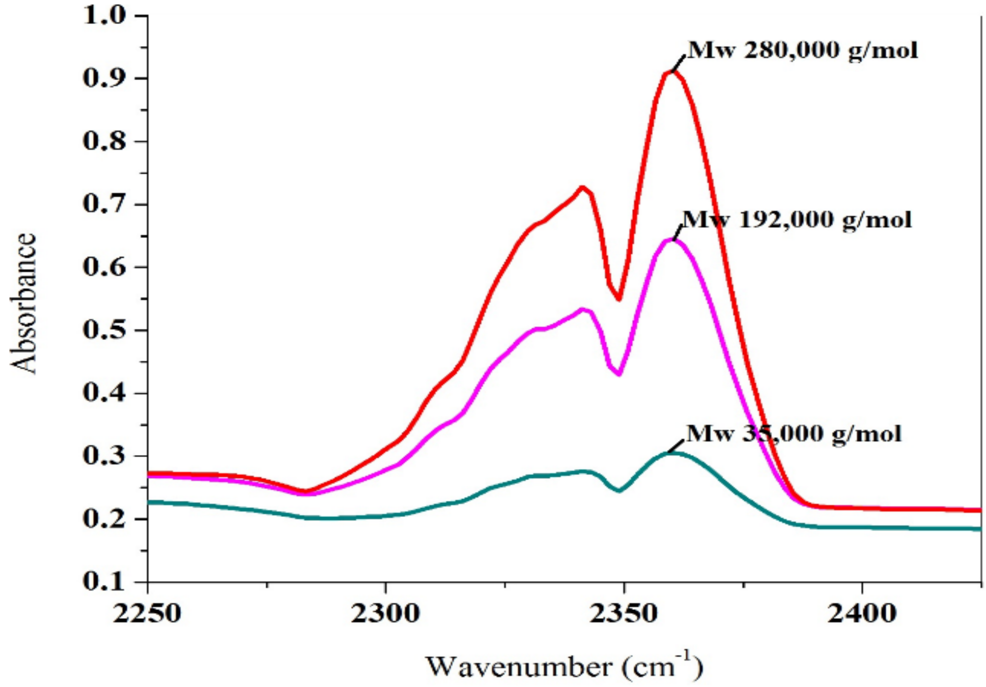

Fig. 4 The FTIR nitrile spectra of the polystyrene surface treated by nitrogen plasma with different Mw

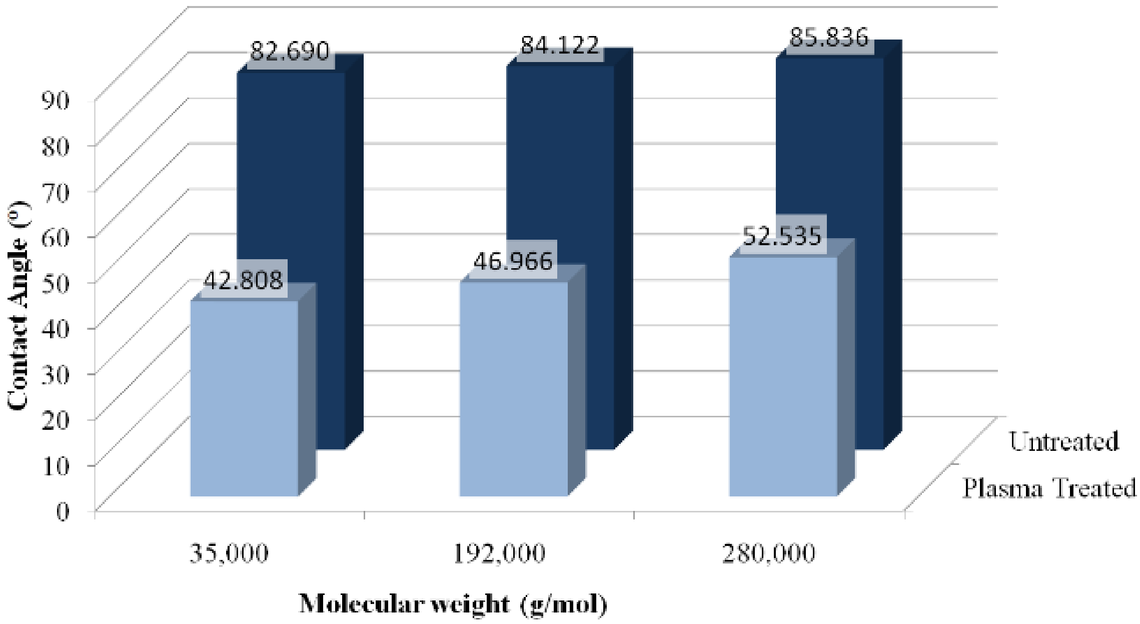

Fig. 5 The effect of various Mw on the hydrophobicity of the polystyrene surface before and after plasma treatment

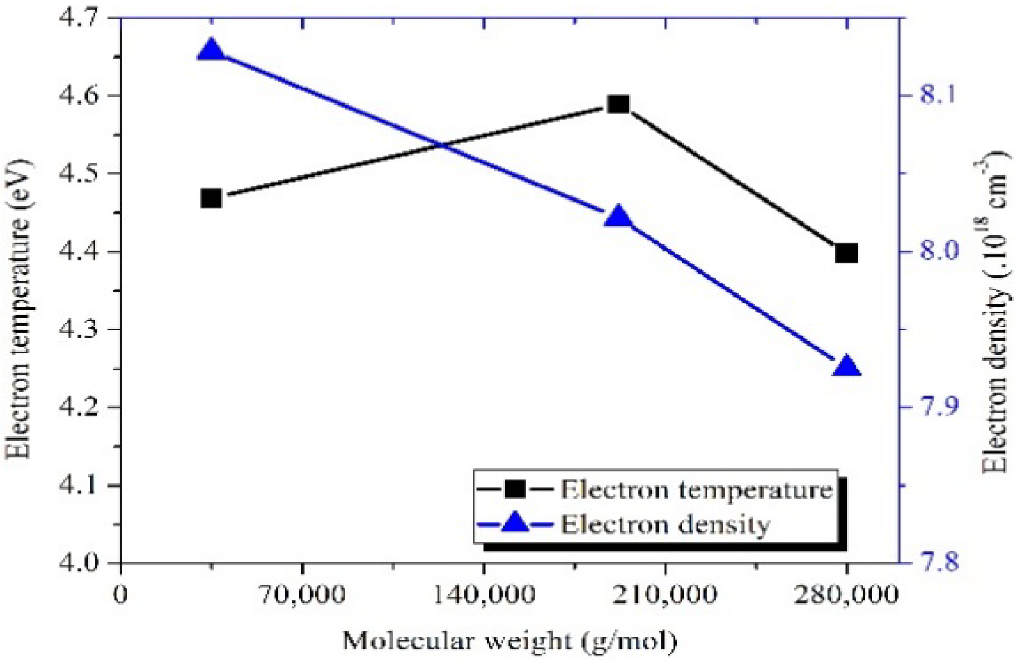

Fig. 6 The relationship between electron temperature (T_e) and electron density ($\boldsymbol{n_e}$) for variation molecular weight

Fig. 6 shows the plotted graphic between electron temperature (T_e) and electron density ($\boldsymbol{n_e}$) and various Mw. The electron temperature indicates the high energy electrons that promote dissociations and ionizations. Plasmas containing the high energy electron raise the ion $\boldsymbol{N_2^+}$ bombardment of the surface of the polystyrene. It is recognized that the energies are enough to break the C atom from polystyrene to form the C-N bond. The higher the T_e, the more the ion bombardment occurred and affected by the ionization process. The higher the ionization, the stronger the bond between N and C atom. The electron temperature is increased until Mw of 192,000 g/mol then slightly decreased at 28,000 Mw. However, the FTIR absorption spectra show the increasing of the C≡N functional group. This phenomenon cannot be described clearly due to complex plasma chemistry and will be investigated in the future. On the other hand, the electron density show decrease with the increasing Mw. This phenomenon due to the more the formation of C≡N bond results in the reduction of the species ion N^{2+} due to the N ion incorporate with C atom to form C-N bond.

4. CONCLUSION

The wettability of the polystyrene′s surface changes from hydrophobic to hydrophilic after treated in nitrogen plasma using 2 MHz RF generator. The results proved that the enhanced wettability due to reaction of the C≡N and the N_2^+ ion detected with corresponding $\boldsymbol{T_e}$ and $\boldsymbol{n_e}$ of the plasma. The intensity of the N_2^+ ion and electron density decrease with the increasing the Mw. However, the T_e was slightly increase with the Mw then decreasing. This phenomenon cannot be described clearly due to the complex plasma chemistry and will be studied in the future.

5. ACKNOWLEDGMENTS

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