Surface Cleaning of Polyethylene Terephthalate Film with Non-equilibrium Atmospheric Discharge Plasma

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The dampness by treating the surface with polyethylene terephthalate (PET) film was measured to grasp the plasma parameters and was observed the surface condition with an atomic force microscope (AFM) to find the causes of the dampness. Also, the vibrational and rotational temperatures in the plasma were calculated after identifying the radicals within the plasma by analyzing the emission spectral with an emission spectrum. The hydrophilic properties were enhanced, by treating the surface of the PET film with non-equilibrium atmospheric discharge plasma. When the rotational temperature was 0.22 to 0.31 eV within the plasma, surface modification control could be easily carried out to surface treatment of PET film on non-equilibrium atmospheric pressure plasma.

Keywords : Atmospheric non-equilibrium plasma, Polyethylene terephthalate film, Surface cleaning, Vibrational temperature, Rotational temperature

1. INTRODUCTION

The application of dry process technology using non-equilibrium atmospheric pressure discharge plasma is expanding from the electronic industry to materials and machinery as well as into the physiology and medical industries[1-3]. In addition, various forms of plasma electrons such as microwave power source as the non-equilibrium atmosphere pressure plasma source, non-equilibrium atmosphere pressure plasma-making technologies, jet type, and dielectric barrier discharge (DBD) has similarly been introduced[4-7]. However as the gas temperature is significantly low compared to the electron temperature in the plasma, local thermal equilibrium states are not formed within the plasma characteristics of these atmospheric pressures. Also it is difficult to find the basic characteristics using probe measurements and such because the mean free path of the electron is shorter than the sheath thickness when in atmospheric pressure. Therefore radical density is a vital parameter, when applied to the dry process technology, as the basic characteristic in the non-equilibrium atmospheric pressure plasma. At the same time, it is necessary to establish accurate and easy measurement methods of electron temperatures and electron density to characterize the plasma. Presently surface modification technology for polymeric film using non-equilibrium atmospheric pressure plasma[8] is the most practical dry process technology. Polymer film is an indispensable material not only in the packaging field but also in the food and medical industries. Reports generally on the improvement in dampness and adhesiveness, have been made on the diversity of functions that would follow if a plasma treatment were given to polymer films[9]. Thus grasping various parameters during a surface modification control of plastic materials can make an overall examination of the basic characteristics in non-equilibrium atmospheric pressure plasma.

In this work, we are aiming at establishing the plasma parameters in non-equilibrium atmospheric pressure discharge plasma as well as to establish various parameters to apply on actual dry process technologies. We are also aiming to implement dry process technologies to new non-equilibrium atmospheric pressure plasma industries using DC pulse power source and plasma jet electrons by carrying out an emission spectral analysis. This will be conducted to grasp the characteristics of the non-equilibrium atmospheric pressure plasma using plasma generating DC radio frequency pulse power sources and plasma jet electrons.

2. EXPERIMENTAL

We used DC radio frequency pulse power source for plasma generation and atmospheric pressure plasma jet

electrons to generate plasma. The experimental apparatus has been described in detail our previous report[10], and can be briefly described as follows. The plasma gas was a mixed gas with argon at a constant 8 L/min. and different arbitrary amounts of nitrogen. The plasma torch consisted of a tungsten rod at the center and a SUS pipe surrounding the rod. In the upper part of the torch, a quartz tube was placed between the tungsten rod and the SUS pipe, generating dielectric barrier discharges to produce reactive species. In the lower part of the torch where dielectrics are not introduced, arc discharges were generated. By using the electromagnetic pumping effect, the reactive species generated in the upper part of the torch were effectively emitted. It is difficult to make experimental measurements of plasma parameters in the non-equilibrium atmospheric pressure plasma. It has been reported that a number of functions can be attached to the material itself by exposing the plasma to polymer substances and modifying the surface[10,11]. In general it is known that the dampness and adhesiveness improves by activating the surface of the material when the polymer material is exposed to plasma. Thus we measured the dampness by treating the surface with non-equilibrium atmospheric pressure plasma on polyethylene terephthalate (PET) film (Teijin dupont films, HS-100) and polyethylene naphthalate (PEN) film (Teijin dupont films, Q51) to examine the radical species that is produced in the plasma. Both PET and PEN films were 10 x 10 mm large and the thickness was 100 μm and 51 μm respectively. Figure 1 shows an emission spectrum using plasma gas with 20 L/min. Argon gas plus 0.5 L/min. Nitrogen gas, a pulse frequency of 10 kHz a wavelength range of 300 to 900 nm under a power source of 100 W. We were able to obtain the transition from $B^3\Pi g$ to $A^3\Sigma g^+$ in the same diagram. We determined the vibrational temperature from the tilt of the Boltzmann plot as well as using the collisional radiative model by theoretically finding the number densities of vibrational level after measuring the emission spectrum with the spectrograph using a sensitivity calibration in the wavelength range of 630 to 720 nm in the 1st positive system of the nitrogen molecule. The rotational temperature, as an approximation value of the vibration temperature and translational temperature in the plasma, was determined experimentally by comparing the emission spectrum obtained through the experiment and considering the apparatus function describing the spectrograph resolution that was calculated in advance using the vibrational temperature determined by the overlap of the rotational spectral[12].

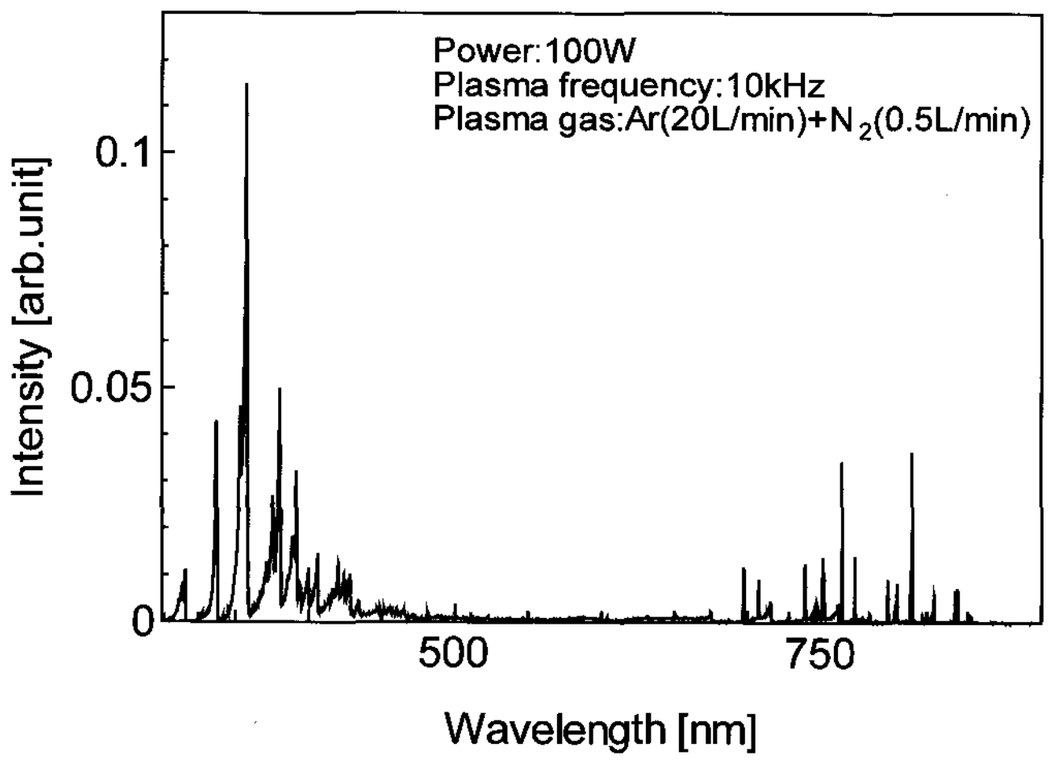

Fig. 1. Emission spectrum in 300-900 nm of Ar (20 L/min.) + N_2 (0.5 L/min.) of metastable state at 100 W and 10 kHz.

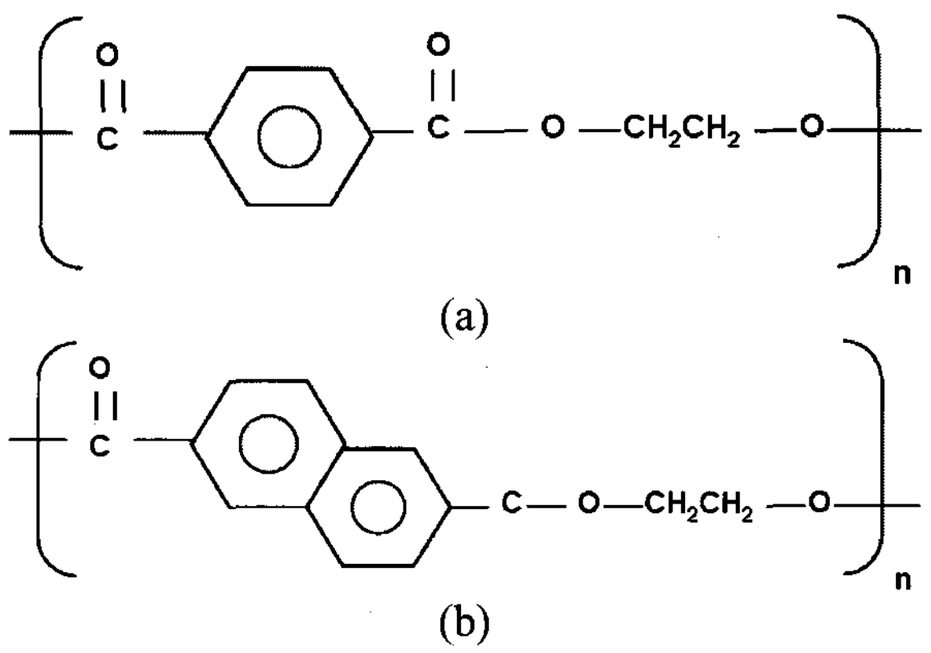

Fig. 2. Chemical structure model of the PET film (a) and PEN film (b).

Figure 2 shows the molecular structure of both PET and PEN film used in the experiment. PET films are generally well known and need no introduction but PEN films are stronger, heat resistant, and more hydrolysis resistant than PET films. The dampness analysis was conducted after the plasma surface treatment was done on the sample for 24 hours. We measured the contact angle by dropping 3.4 mg of water using a contact-angle meter (Type CA-D, Kyowa Interface Science Co., Ltd.). We also observed the surface structure of the sample using an atomic force microscope (AFM) to check the surface structure of the PET and PEN film after the plasma surface treatment. A number of indicators in the plasma are needed when conducting a plasma surface treatment on the material and it is thought that the vibration excitation level in the radical species within the plasma play an important part[13]. Therefore we examined the vibrational and rotational temperature of the plasma gas and the radical species using the emission spectroscopy method[14] by analyzing the emission spectrum in the non-equilibrium atmospheric pressure plasma with a spectrograph. Optical fiber tips were set up 40 mm from the lower part of the nozzle of the plasma jet electron to measure emission spectrum with a spectrograph.

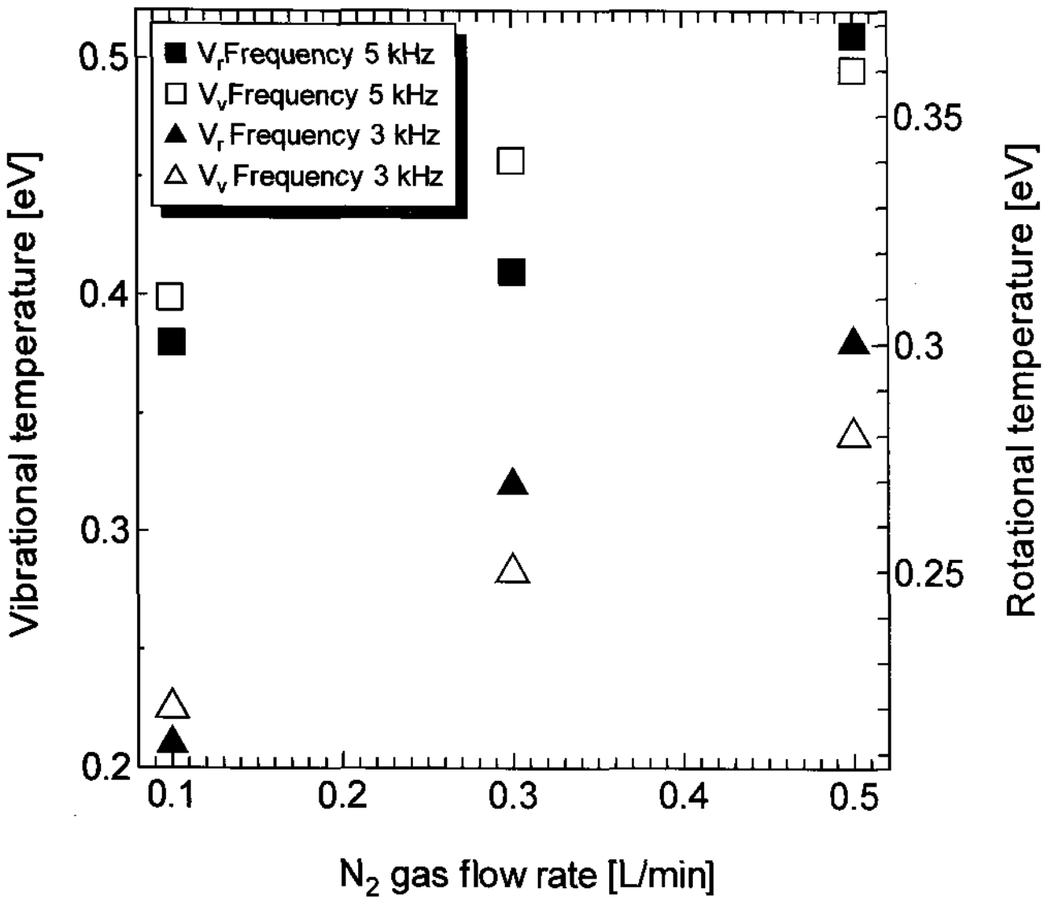

Fig. 3. Relationship between nitrogen gas flow rate and vibrational and rotational temperatures at atmospheric pressure argon and nitrogen plasma measured by optical emission spectroscopy.

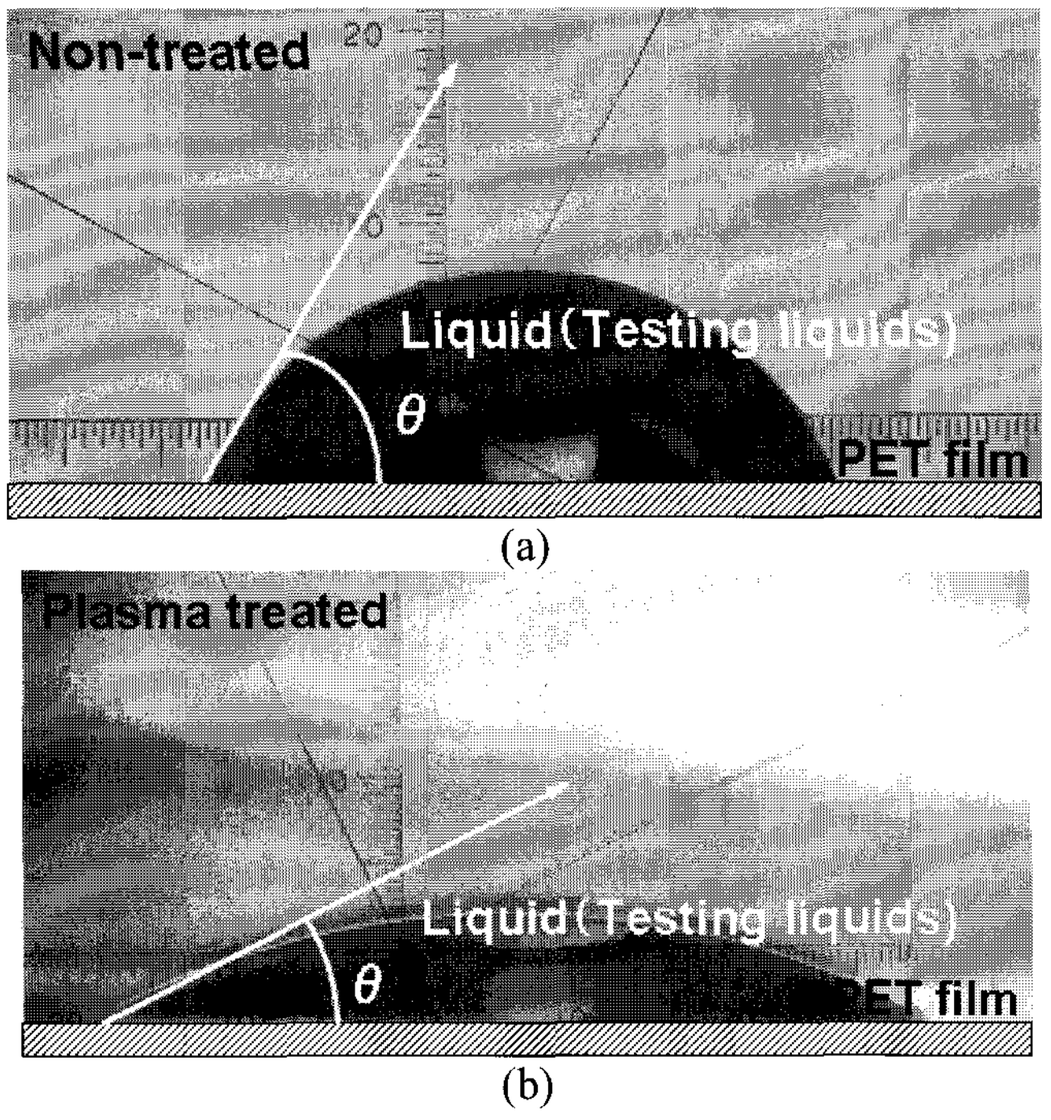

Fig. 4. Photograph of water droplets on PEN films. (a) without treatment and (b) with treatment.

3. RESULTS AND DISCUSSION

Figure 3 shows the relationship between the plasma vibration and rotation temperature when the plasma gas is a mixture of Argon gas at a constant 10 L/min. and the Nitrogen gas shifting between 0.3 to 0.5 L/min. depending on the conditions, with a power source of 150 W and the plasma frequency at 3 kHz and 5 kHz. The rise in both the vibration and rotation temperature occurring with the rise in the amount of nitrogen can be detected from the same diagram. Also similarly the vibrational and rotational temperature rises with the rise of the plasma frequency. This is because as the amount of nitrogen gas rises, the electron density increases proportionately with the increase of nitrogen molecules in the second positive and 1st positive system. As the collision between the electrons and nitrogen molecules and the collision frequency between the nitrogen molecules increases, the vibrational and rotational temperature rises. The plasma vibrational temperature was approximately 0.21 to 0.38 eV and the rotational temperature was approximately 0.22 to 0.28 eV when the power source was 150 W and the plasma frequency was 3 kHz in an atmospheric pressure plasma jet using plasma generating DC radio frequency pulse power source. In addition it was found that the plasma had a relatively low electron temperature as the plasma vibrational temperature was approximately 0.38 to 0.51 eV and the rotational temperature was approximately 0.31 to 0.36 eV when the plasma frequency was 5 kHz.

Figure 4 shows a photograph of the dampness in PEN film after a surface treatment using plasma gas mixed with 8 L/min. of Argon gas and 0.3 L/min. of Nitrogen gas, a power source of 100 W and 10 kHz of plasma frequency. Both the PEN and PET film had gone through a plasma process where the plasma electron was placed 50 mm below the nozzle. From the diagram you can see that the contact angle and the water shedding are large when there is no surface treatment. Also you can see that the contact angle is small and that the hydrophilicity improves after a plasma treatment. We were able to determine that the hydrophilicity of the PET film improved with a surface treatment using non-equilibrium atmospheric plasma with a mix of argon and nitrogen gas.

Figure 5 shows a three dimensional photograph, with an observation size of 1.0 μm, using AFM on the PET film surface showing the causes of hyprophilicity improvements under the same previously mentioned conditions. In the same diagram we cannot observe any eminent changes in the rough surface when it has not gone through any surface treatment. However it is obvious that the surface has changed (about 7 nm) after a plasma treatment. It is thought that a chain scission reaction has begun with the scission of the chain on the weaker part of the chemical bond on the PET film by the nitrogen radical generated from the plasma[11]. The surface then breaks and is removed with the effects of the chain scission and the plasma gas temperature improving the hydrophilicity of the PET film.

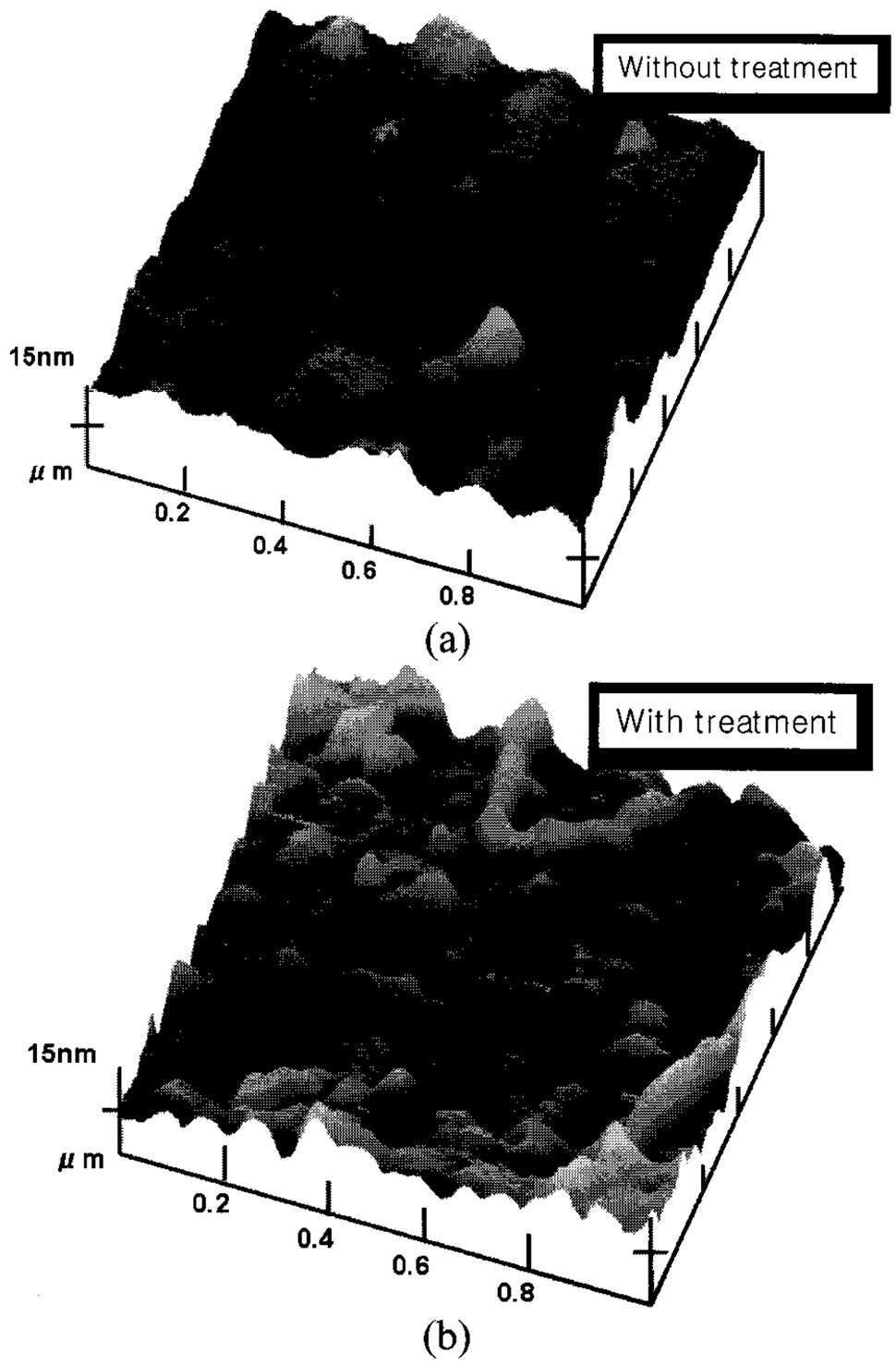

Fig. 5. AFM 3D photograph images of PEN film surfaces by non-treated surface (a) and plasma treated surface (b).

Figure 6 shows the relationship between the time taken for the plasma treatment and the contact angle when conducting a plasma treatment between 1 to 5 s on the PET and PEN film to compare and observe the effects of the plasma treatment based on the differences in PET film characteristics. We determined that the contact angle was larger when the time taken for plasma treatment was longer for both PET and PEN films. Both PET and PEN films showed characteristics that were adequately above melting point than 258 to 269 °C and the plasma gas temperature (approximately 150 °C). Therefore it can be deduced that the surface of the PET and PEN film are not processed by the plasma temperature but by the effects of the nitrogen radical in the plasma. It is thought that the reason why the contact angle is larger as the plasma processing time is longer is because after the plasma process, the percentage of C-O binding is comparatively larger than the C-O and COO binding on the surface of the PET and PEN film because of the nitridation effects from the nitrogen radicals. The hydrophilicty improves because of the polymerization reaction by the plasma and the reaction of the Benzene

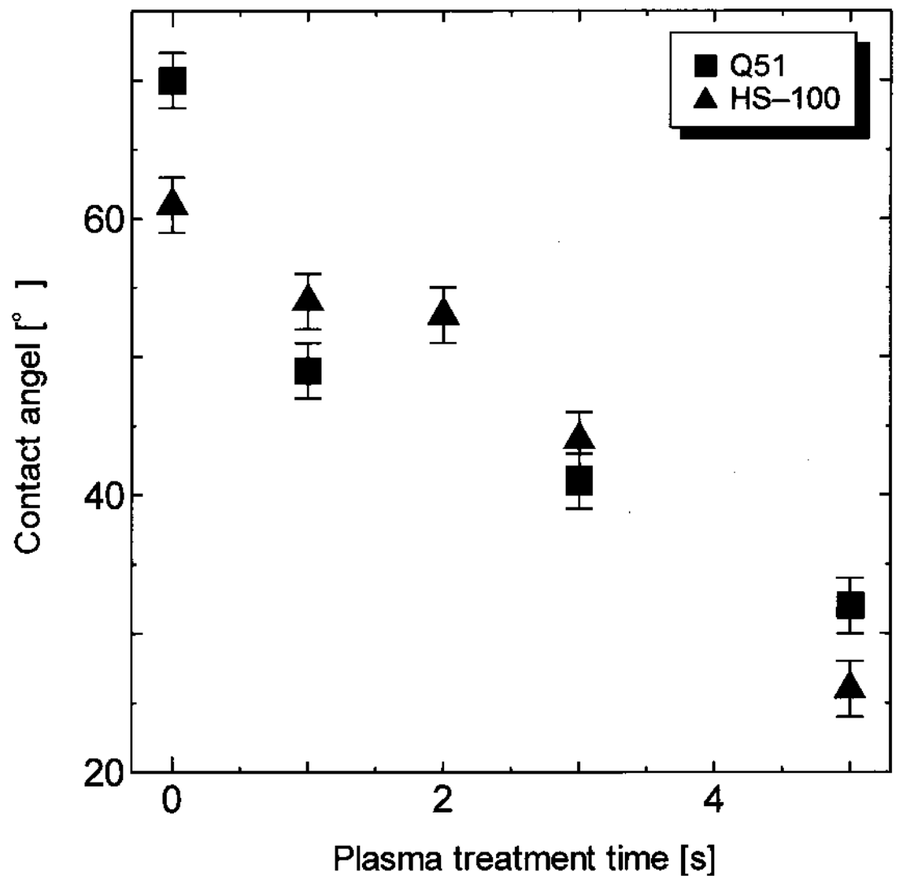

Fig. 6. Water contact-angle of various PET and PEN films just after treatment.

ring contained in the surface of the PET film. Thus the identification of the nitrogen radical and the calculation of the various plasma parameters will be an important element in grasping the basic plasma characteristics.

4. CONCLUSION

In this work, the hydrophilicity was improved by surface treatment of the PET film using non-equilibrium atmospheric plasma with DC radio frequency pulse power source and plasma jet electrons and an AR/N_2 mixture gas. These parameters were very important in grasping the plasma characteristics in the non-equilibrium atmospheric plasma. Particularly it was found that nitrogen gas has significant effects to the surface modification on the PET film. In addition, the non-equilibrium atmospheric plasma was a relatively low electronic temperature as the vibrational and rotational temperature in the non-equilibrium atmospheric plasma of the radio frequency pulse power source and plasma jet electron was approximately 0.21 to 0.51 eV and 0.22 to 0.31 eV. Therefore, the effective surface modification control of the PET film could be carried out with the processing time and plasma flow amount when the rotational temperature was around 0.22 to 0.31 eV.

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