Surface Modification and Characterization Studies of PMMA Sheets by Atmospheric Pressure Plasmas Treatment

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Abstract: In this work, a ring-type atmospheric pressure plasmas (APP) device is used for polymethyl methacrylate (PMMA) surface modification. The hydrophilic modification effects of Ar, O_2/Ar and N_2/Ar plasma are compared and investigated under the same condition by surface characteristics of PMMA and optical emission spectrometer (OES).It was observed that plasma treatment significantly improved the surface wettability with changing the concentration of N_2 and O_2 gas. Besides, the OES results demonstrate that both O_2/Ar and N_2/Ar plasma is composed with higher intensities of reactive species, like OH, O, NH and N2+ than that of Ar plasma and show a better modification effect.

Keywords: PMMA, surface treatment, atmospheric pressure plasma, OES, surface morphology

1. Introduction

Poly(methylmethacrylate) (PMMA) has been widely used in the optical and biological applications, due to its excellent optical properties, high molding precision and low cost. However, its' low surface energy property results in poor wettability and bad biocompatibility. Many surface modification techniques like wet-chemical, UV-lamps , vacuum plasma [1] and atmospheric pressure plasma (APP) [2] treatment have been applied to create the hydrophilic functional group (such as NH_x or OH) on surfaces to enhance their wettability properties. Among these technologies, APP treatment has attracted much attention due to its dry process, low vacuum equipment cost and high productivity.

The properties of plasma treatment are strongly dependent on process parameters, which like the kinds of gas and ratio. Indeed, the chemical composition and surface roughness are strongly influenced the surface characteristics. In this study, the surface characteristics of PMMA sheets treated in Ar, O_2/Ar and N_2/Ar plasmas under atmospheric pressure were investigated. Besides, the relationship between the chemical structure and physical properties of atmospheric pressure plasma treated PMMA were also discussed.

2. Experimental

A self-assemble 13.56 MHz RF APP reactor and process conditions were shown in Fig.1. PMMA sheet with 2 x 2 cm as the substrate was put on a movable-stage with the stage moving at 4 cm/s. All the runs, the RF-APP head-to-sample distance and power source were fixed at 5 mm and 80 W, respectively. Optical emission spectroscopy (OES) was used to investigate the influence of plasma species on the surface modification of PMMA sheets. The X-ray photoelectron spectrometer (XPS), contact angle analyzer were used to examine the effect of process variables on film surface characteristics.

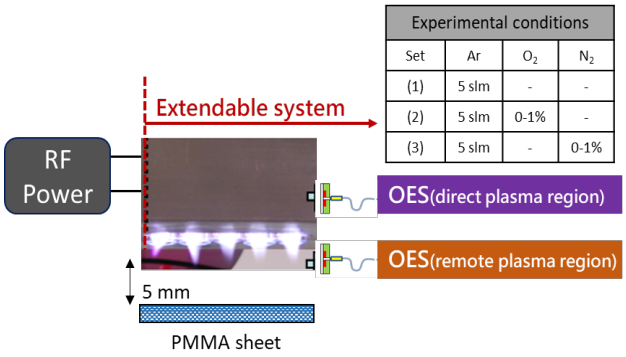

Fig.1 Schematic of self-assemble RF-APP system.

3. Results and discussion

The properties of plasma treated PMMA sheets are strongly dependent on process parameters such as the kinds of gas, source power and substrate conditions. Among these factors, the kinds of gas are very important because it can create unique functional groups during plasma discharge. Therefore, we investigated the various gas conditions (pure-Ar, O_2/Ar and N_2/Ar) that influence the treated surface properties such as the chemical composition of PMMA.

Fig. 2 shows the OES spectra of the pure-Ar, 1%O_2/Ar and 1%N_2/Ar plasmas. It was found that the OH $_{(308.9\ nm)}$ radicals [3] were detected of all plasmas. This finding is not surprising because all of discharge processes are under atmospheric pressure. Moreover, this results can be explained why the pure-Ar APP also has hydrophilic treatment function (see the contact angle

result in Fig. 3). Besides, the higher emission intensity of O (777 nm) atom and N-based species [NH (336 nm), N_2^* (336 nm), N_2^+ (336 nm)] [3,4] were observed at O_2/Ar and N_2/Ar plasma, respectively.

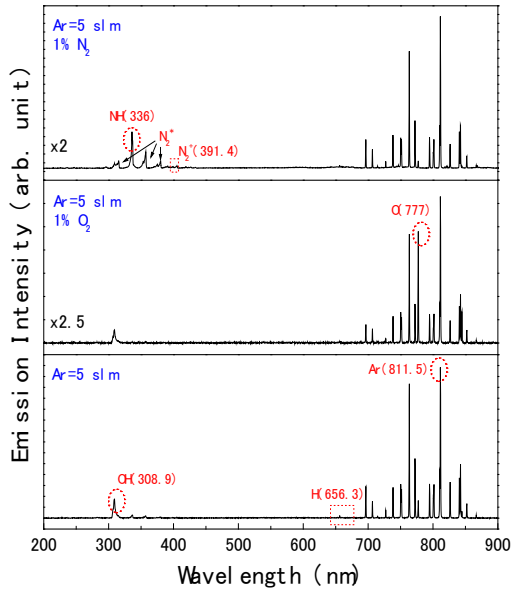

Fig.2 OES spectra of the pure-Ar, O_2/Ar and N_2/Ar Plasmas.

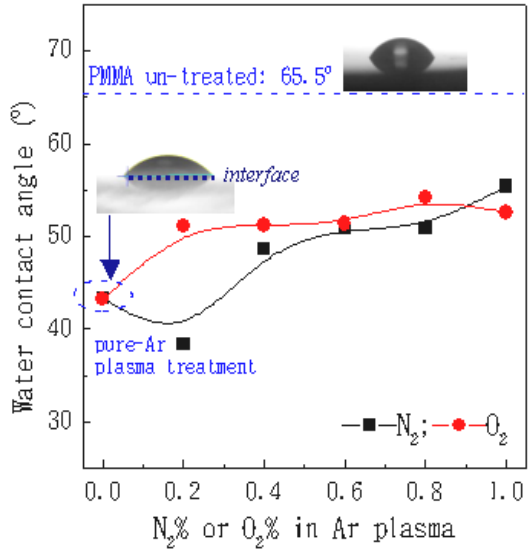

Fig.3 Water contact angle of PMMA as a function of gas ratio.

Fig. 3 shows the water contact angle of PMMA sheets as a function of N_2 (or O_2) percentage in Ar APP. As can be seen in this figure, it shows the N_2/Ar has better treatment result than O_2/Ar APP, especially in 0.2%N_2/Ar plasma. It is suggested that the NH, N_2^*, N_2^+ species (see Fig, 2) are generated as the small amount N_2 add to Ar plasma. However, too much N_2 addition was decreased NH species (NH maybe depleted by R1 and R2 reactions.) in remote plasma region. This suggestion is consistent with the result by Fig. 4. The NH specie of N_2/Ar plasma as a function of N_2 percentage under direct and remote APP region is shown in Fig. 4. As the percentage of nitrogen additive increased, the NH intensity increased at first, reached a maximum and then decreased at remote plasma region. This trend is almost consistent with the hydrophilic property (see Fig. 3) from the contact angle result. Although the NH intensity increased with increasing N_2 additive in direct APP region, the characteristics of remote plasma region were more important in surface treatment.

(R1) $NH + N \rightarrow N_2 + H$

(R2) $NH + H \rightarrow N + H_2$

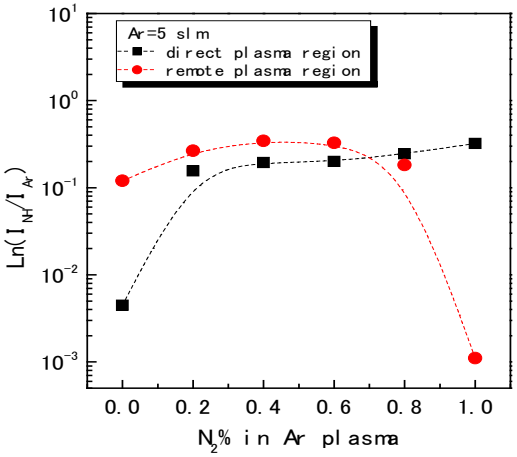

Fig.4 Relative intensity of NH under various N_2/Ar ratios.

4. Conclusion

Poly(methylmethacrylate) (PMMA) has been widely used in various applications. However, its' low surface energy property results in poor wettability. In this study, the surface characteristics of PMMA treated in Ar, O_2/Ar and N_2/Ar plasmas under atmospheric pressure were investigated. It was observed that plasma treatment significantly improved the surface wettability with changing the concentration of N2 and O2 gas. Besides, the better wettability PMMA can obtain in N_2/Ar APP treatment. However, too much N_2 addition reduces the NH radical and influences the treatment result.

References

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