Hydrophilization of Polycarbonate by Ar Glow Discharge

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In order to enhance a hydrophilicity of polycarbonate (PC) surface, PC sheet was irradiated by DC glow plasma with Ar, Ar+O_2 (10%) or Ar+N_2 (10%) for (1-10) min. The durability of the hydrophilic property in a vacuum, air or water was also evaluated. The water contact angle was largely decreased by the plasma irradiation for only 2 min. The water contact angle decreased from 63-71^o to 23-32^o, 18-25^o and 21-27^o after the irradiation for 10 min with Ar, Ar+O_2 and Ar+N_2 plasmas, respectively. The contact angle after the every plasma irradiation did not change during the preservation in the air for 1 hr, but increased to approximately 40^o during the preservation in the vacuum up to 168 hr. While the contact angle after the Ar+O_2 irradiation for 10 min followed by the preservation in the water for 20 min recovered the value before the irradiation, the water contact angle after the preservation up to 336 hr in the air or the vacuum kept still a smaller value than that before the irradiation.

Keywords: plasma processing, polycarbonate, surface modification, hydrophilization, glow discharge.

1. Introduction

Micro Electro Mechanical System (MEMS) is an important technique for micro-TAS devices. For this system, micro channels with a diameter of a few - 100 micrometers are fixed on the surface of the micro-TAS. In the micro channel, liquid specimens such as reagent solutions and bloods are flowed. If the inside wall of the micro channels is hydrophobic, fluid hardly flows in the micro channel. Therefore, the material used for micro-TAS must have a hydrophilic surface.

Polycarbonate (PC) is considered as a candidate for the micro-TAS. PC has a high level crashworthiness, thermostability, and dimension stability, so that is widely used for electronic components, precision machine and building material [1].

It is well known that the plasma irradiation to the polymer such as PC results in the surface modifications [2] owing to the introduction of functional group [3]. In the present study, PC sheet was irradiated by DC glow plasma in order to enhance the hydrophilicity of PC surface owing to the surface modification. Ar, Ar+O_2 or Ar+N_2 were used as discharge gas, and the irradiation effects were compared. In addition, the durability of the hydrophilic properties in the air, vacuum or water after the plasma irradiation was also evaluated,

2. Experiment

DC glow discharge apparatus, shown in fig.1, was used for the plasma irradiation to PC sheet. A cylindrical chamber made of stainless-steel was taken as the cathode. A copper anode was inserted at the center in the chamber. PC sample with a size of 1.2cm x 1.2cm x 0.1cm was placed on an alumina plate. The base pressure of the apparatus before the plasma irradiation was approximately 10^{-5} Pa. After the pumping, a discharge gas was introduced into the chamber and then the plasma irradiation experiment was conducted. The gas of Ar, Ar+O_2 (10%) or Ar+N_2 (10%) was used as the discharge gas. The total pressure was 100 Pa. The discharge voltage was approximately 300 V. The irradiation time was taken in the range from 1 to 10 min.

Water contact angle was measured to evaluate the hydrophilization of the PC surface. Ion-exchanged water (10 μl) was dropped on the PC sheet, and the contact angle was measured from the lateral view of the drops.

In order to examine the durability of the hydrophilic properties, the irradiated PC sheet was kept in the air, vacuum desiccator (~10 Pa) or water, and after that the contact angle was measured.

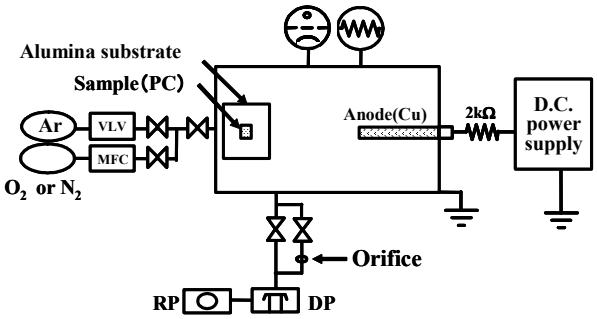

Fig.1 DC glow discharge apparatus.

3. Results and Discussion

3.1 Hydrophilization of PC surface by plasma irradiation.

Figures 2 show the lateral view of the water drop on the PC sheet before irradiation or after irradiation for 10 min, respectively. Before the irradiation, the contact angle of the PC was 63-71°. The contact angle decreased to 23-32°, 18-25° and 21-27° after the irradiation for 10 min using Ar, Ar+O_2 and Ar+N_2, respectively.

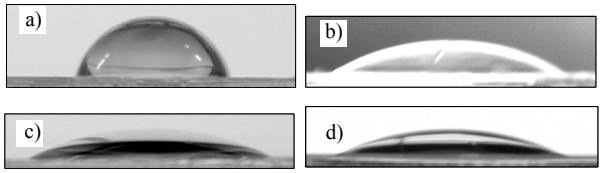

Fig.2 Lateral view of water dropped PC sheets before the plasma irradiation, (a), after the Ar plasma irradiation, (b), after the Ar+O_2 plasma irradiation, (c), and after the Ar+N_2 plasma irradiation, (d).

Figure 3 shows water contact angle of irradiated PC surface as a function of the irradiation time. After the irradiation for 2 min, the water contact angle dropped to approximately 27°. Even if the irradiation time was taken more than 2 min, the water contact angle did not decrease for the every plasma irradiation.

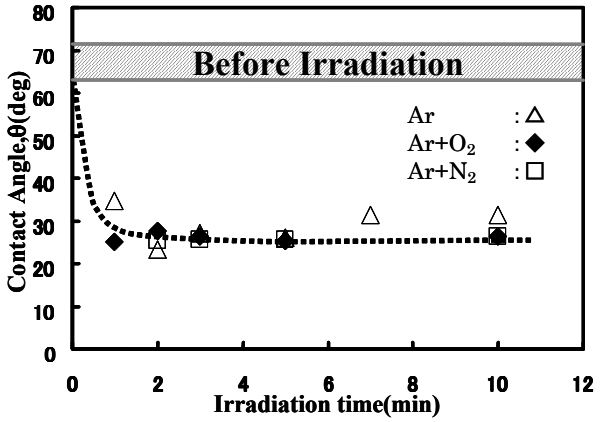

Fig.3 Irradiation time dependence of contact angle for PC surface.

In the present study, the hydrophilization of PC surface was independent on the discharge gas species. It is reported that the hydrophilization of PC occurs in a few seconds or 30 s [3, 4]. The present tendency on the contact angel is consistent with the previous works.

3.2 Durability of hydrophilization of PC surface after plasma irradiation

Figure 4 shows the aging time evolution of water contact angle for PC sheet after the plasma irradiation for 10 min. PC sheet was preserved in air until 1 hr and then in a vacuum desiccator. The water contact angle did not change during the preservation for 1 hr. After the preservation longer than 1 hr, the water contact angle gradually increased with the preservation time, and became approximately 40° in the preservation up to 168 hr. This tendency was shown in the every plasma irradiation in the present study.

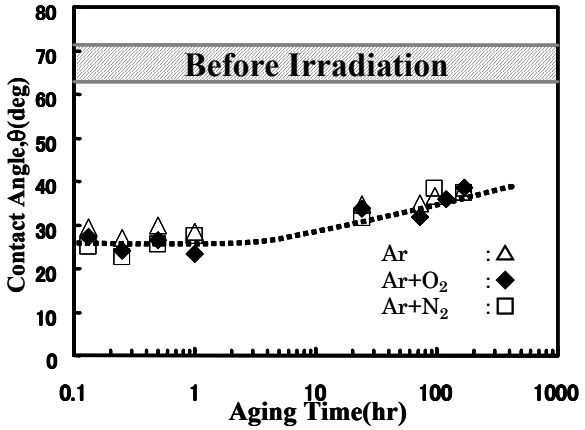

Fig.4 Aging time dependence of contact angle for PC after the plasma irradiations.

It is explained that the recovery of the hydrophobic occurs due to a combination of surface reorientation effect, migration of mobile species from the bulk toward the surface, and external contamination [5]. Since these are attributed to PC properties, the durability of the hydrophilic property might have not depended on the discharge gas species in the present experiment.

Figure 5 shows the change in water contact angle of plasma-irradiated PC sheet during the preservation in the vacuum, the air or the water. All PC samples were irradiated by Ar+O_2 plasma for 10 min. For the case of the preservation in the water, the PC sample was dried in the vacuum desiccator for 1 min and the contact angle was measured. The preservation in the water for a short time resulted in the large increase of the water contact angle. After the preservation in the water for 20 min, the

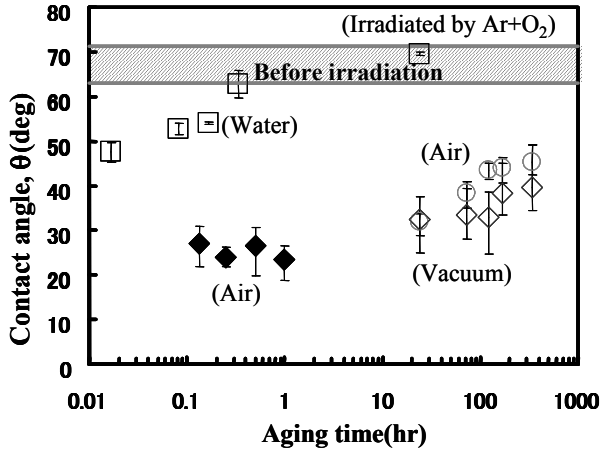

Fig.5 Contact angle for polycarbonate versus exposure time in the vacuum, the air or the water.

contact angle recovered to the value before the plasma irradiation. This phenomenon is generally attributed to chain scission reaction producing low molecular weight oxidized material on the surface [5]. The water contact angle after the preservation in the air or the vacuum up to 336 hr did not recover to the value before the plasma irradiation. Namely the water content in the air or the vacuum may have a small effect on recovering of the water contact angle of the plasma-irradiated PC surface.

4. Conclusion

The water contact angle of PC surface decreased to 23-32^{o}, 18-25^{o} and 21-27^{o} after the irradiation for 10 min using Ar, Ar+O_2 and Ar+N_2, respectively. The PC surface became hydrophilic surface after the every plasma irradiation. After the irradiation for 2 min, the water contact angle of the PC surface largely decreased. Even if the irradiation time was taken longer than 2 min, the water contact angle did not decrease. The water contact angle did not change during the preservation in the air for 1 hr. After the preservation in the vacuum above 1 hr, the water contact angle gradually increased with the preservation time, and became approximately 40^{o} in the preservation for 168 hr. These tendencies appeared in the every plasma irradiation. The preservation of PC in the water after irradiation resulted in the water contact angle recovering to the value before irradiation for a short time. Therefore water has an effect on recovering of the contact angle of plasma- irradiated PC surface. The preservation of PC in the air after irradiation resulted in a slight increase of water contact angle. In the application of plasma irradiated PC to micro channels, the preservation in the air or the vacuum is appropriate.

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