Hydrophilic Modification of Plastic Surface by Using Microwave Plasma Irradiation

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Plastics that have a hydrophobic surface are generally given printable or adhesive properties through the modification of their surfaces to be hydrophilic. Although conventional surface modification methods such as corona discharge treatment provide the hydrophilic property, long-lasting hydrophilic surface has been hardly obtained. Therefore, we studied the modification process of plastic samples by using microwave plasma irradiation to achieve a long-lasting hydrophilic surface. We optimized the conditions of the plasma treatment and developed a process consisting of a two-step treatment using argon plasma and argon/oxygen plasma. It was established that the two-step plasma processing technology gave plastic surfaces hydrophilicity lasting at least 80 days and more.

1. Introduction

Plastics offer many advantages, such as light weight, strength, transparency combined with flexibility in coloring, electrical and thermal insulation, and superior hygienic properties. These and other unique characteristics make plastics are extremely versatile. To expand the applications of plastics even further, the surfaces of plastics are modified by various methods such as ① plasma irradiation, ② chemical vapor deposition, ③ ultraviolet irradiation, and ④ etching. In particular, plasma irradiation by corona discharge, which is the most common method, is commercially used to make hydrophobic plastic surfaces into hydrophilic ones in order to provide printable or adhesive properties.

However, the hydrophilic properties provided by corona discharge irradiation diminish soon after the treatment and are lost over time.[(1)] Many studies have been conducted on the modification of plastic surfaces by plasma irradiation,[(2)-(4)] however the life-span of hydrophilic properties has hardly been evaluated. In this regard, we paid attention on evaluating the life-span of hydrophilic properties and investigating its degradation mechanism. Moreover, we focused on establishing a process able to achieve long-lived hydrophilic properties on the surface of plastic samples by using microwave.

2. Experimental method

2.1 Plasma surface treatment

In this study, an Electron Cyclotron Resonance (ECR) plasma generator was used for plasma surface treatment. The schematic view of the ECR plasma generator is shown in **Fig. 1**. The plasma is generated by microwaves (2.45 GHz) and a magnetic field.

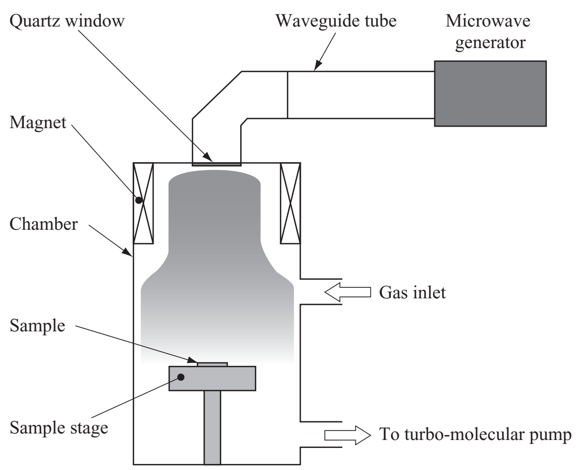

Fig. 1 Schematic view of the electron cyclotron resonance (ECR) plasma generator

In this study, polystyrene (PS) was used for the plastic samples (thickness of 2 mm). After ultrasonic cleaning with ethanol, the PS plates were put on the stage in the chamber. Then, the chamber was evacuated to 6.7×10^{-4} Pa, and the source gas was introduced into the chamber until the appropriate pressure was reached. The microwave power was set to 350 W to generate the plasma and then the surface of the PS sample was irradiated by the plasma.

2.2 Characterization of plasma treated PS sample

Hydrophilic properties of the PS samples after the plasma surface treatment were evaluated by water contact angles. The water contact angle was measured with a drop of 2 μl of ion-exchange water. **Figure 2** shows the water contact angles and corresponding wettability. The water contact

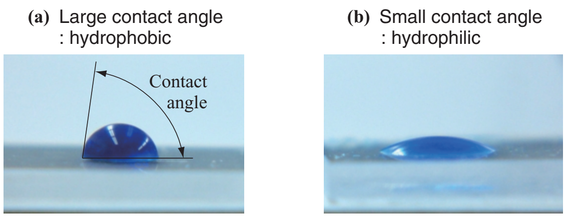

Fig. 2 Water contact angle and wettability

angle is an indicator of the wettability. A larger water contact angle indicates hydrophobic properties which means water is repelled as shown in **Fig. 2-(a)** whereas a smaller water contact angle indicates hydrophilic properties which means that water is flat as shown in **Fig. 2-(b)**. The water contact angles were measured every few days to evaluate the life-span of the hydrophilicity of the treated surfaces.

The surface chemical state of the PS samples after the treatment was evaluated by X-ray Photoelectron Spectroscopy (XPS).

3. Results of plasma surface treatment process

3.1 Condition of source gases and pressures

The plasma state changes depending on the gas and process pressure in the chamber. We investigated different gases and pressure conditions to find the best treatment conditions that give hydrophilic properties to the surface of the plastic samples.

The PS samples were treated using plasma generated from various gases such as ① hydrogen, ② argon, ③ nitrogen/hydrogen, ④ oxygen, and ⑤ argon/oxygen and evaluated the water contact angles after the treatment. **Figure 3** shows the water contact angle of PS surfaces treated with various gases. Hydrophilic properties differ depending on the kind of gas. The plasma generated using the gas containing oxygen provided the higher hydrophilicity.

Then, the water contact angles of surfaces plasma treated with different oxygen concentrations were evaluated. The pressures applied in the treatment process were also studied. The results are shown in **Fig. 4**. Enhanced

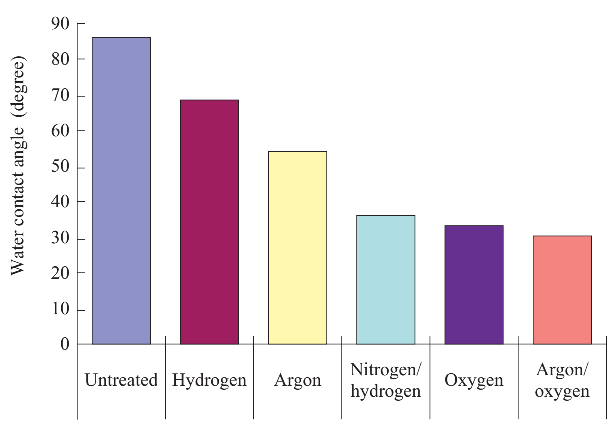

Fig. 3 Water contact angle of PS surfaces treated with various gases

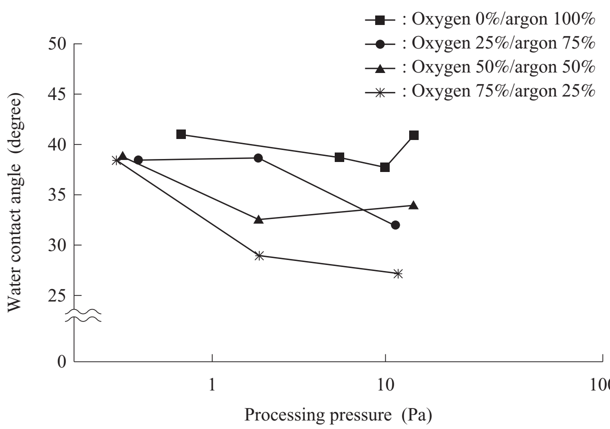

Fig. 4 Water contact angle of PS surfaces, as a function of oxygen content and process pressure of plasma irradiation

hydrophilic properties were observed after treatments with higher concentrations of oxygen and higher processing pressures. More specifically, at an oxygen concentration of 75% and processing pressure of 12 Pa, the water contact angle decreased to 30 degrees,(5) which is one criteria of hydrophilicity.

3.2 Optimization of surface treatment by plasma irradiation

Plasma generated using the source gas containing oxygen provided hydrophilic properties to the PS surface. However, this treatment process could not cause the plastic to keep the hydrophilic properties for a long time. So, we tried a new approach to keeping the hydrophilicity of the PS surface. The new process consists of a two-step treatment. The first step is a pretreatment by irradiation with a argon plasma at a process pressure of 0.4 Pa, and the second step is plasma treatment with a mixed gas of argon and oxygen at 13.3 Pa.

In order to confirm the effect of the two-step treatment, three kinds of treatments were performed to compare the changes in water contact angles over time after respective treatments — namely, ① treatment by argon plasma (0.4 Pa, 4 min), ② treatment by argon-oxygen plasma (up to 13 Pa, 4 min), and ③ two-step treatment. The results are shown in **Fig. 5**. The water contact angles of all PS samples after plasma irradiation decreased, and this result indicates the obvious hydrophilic transformation of the treated PS samples. The water contact angles after the two-step treatment and treatment by the argon-oxygen plasma were both below 40 degrees. Notably, the two-step treatment succeeded in keeping a water contact angle of 30-40 degrees and thus superior hydrophilic properties even many days after the treatment. The pretreatment by argon plasma in the first step of the two-step treatment is likely to have exerted a good effect for maintaining the hydrophilic properties of the surface of the PS sample.

Eventually, as shown in **Fig. 6**, we were able to establish a two-step plasma treatment process that results in the long-term retention of hydrophilic properties as evidenced by a water contact angle of less than 30 degrees even 80 days after treatment. The surface of a untreated PS

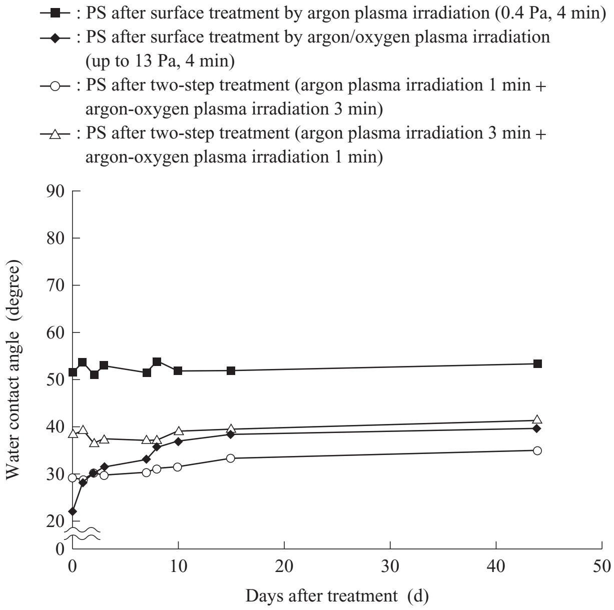

Fig. 5 Water contact angle of PS surfaces, as a function of exposure time after plasma irradiation

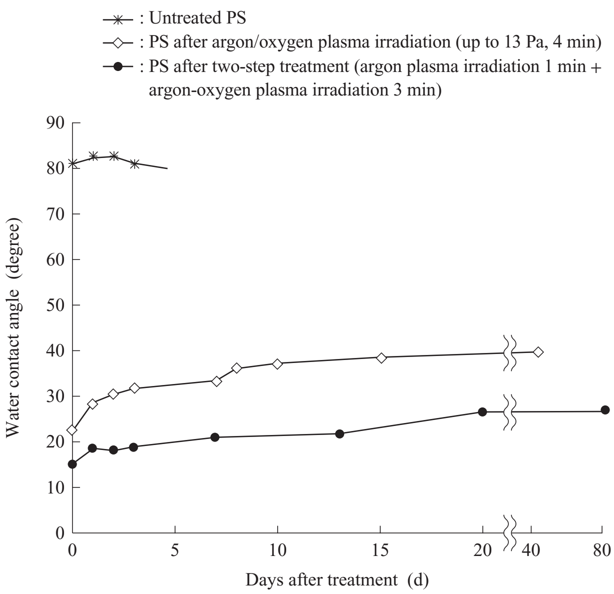

Fig. 6 Water contact angle of PS surfaces, as a function of exposure time after optimized plasma treatment

sample continuously had a water contact angle of around 80 degrees. The state of untreated surface of PS sample is considered to remain constant regardless of the passage of time. The water contact angle of the PS sample treated only with an argon-oxygen plasma was less than 30 degrees, but the water contact angle increased with time. In contrast, the optimized two-step treatment on the PS sample kept a low water contact angle as about 27 degrees for 82 days although there was a slight increasing of the angle. The pretreatment by argon plasma in the first step of this two-step treatment is performed under a low pressure of around 0.4 Pa in the chamber. In the low pressure condition providing large mean free path of gas molecules and ions the plasma can easily be diffused throughout the chamber so that the ions in the plasma effected physical action to the surface of samples. The likely reason for the hydrophilic properties kept for a long time after the two-step treatment is the enhanced reaction efficiency of the oxygen radicals and increased surface area as a result of the increase in reactive sites on the PS sample achieved by pretreatment with argon plasma under low pressure.

4. Chemical state of PS surface treated by plasma irradiation

The chemical condition of the surface of the PS sample was investigated using XPS analysis in order to study the mechanism by which the hydrophilic properties are imparted by the plasma irradiation. **Figure 7** shows the carbon spectra (C1s) from the XPS analysis of the untreated and treated PS samples by the two-step treatment (argon plasma irradiation under 0.4 Pa for 1 minute + argon-oxygen plasma irradiation under pressure up to 13 Pa for 3 minutes). In the spectrum of the untreated PS sample, the C1s peaks of 285.0 eV and 291.5 eV, which are ascribed to a C–C or C–H bond and a π–π^* shake-up transitions (in the aromatic ring of PS) respectively. However, a broader peak was observed in the sides of the high binding energy on the surface treated by plasma irradiation, which is assigned to functional groups as they commonly contain oxygen.[(6)-(8)]

Peak resolution was performed to examine in detail the broad peak observed on the PS surface after plasma irradiation. The broad peak can be separated into six peaks shown in **Fig. 8**, and the C1s peaks of 284.4, 285.0, 286.6, 288.0, 289.1, and 291.5 eV are ascribed to C=C, C–C/C–H, C–O, C=O, O–C=O, and π–π^* respectively, which indicates the appearance of functional groups containing oxygen (i.e., C–O, C=O, and O–C=O) on the PS surface provided by the plasma irradiation. These results of the water contact angle measurement and the XPS analysis shows that these functional groups containing oxygen (i.e., C–O, C=O, and O–C=O) as provided by the plasma irradiation has contributed to the hydrophilic properties of the PS sample.

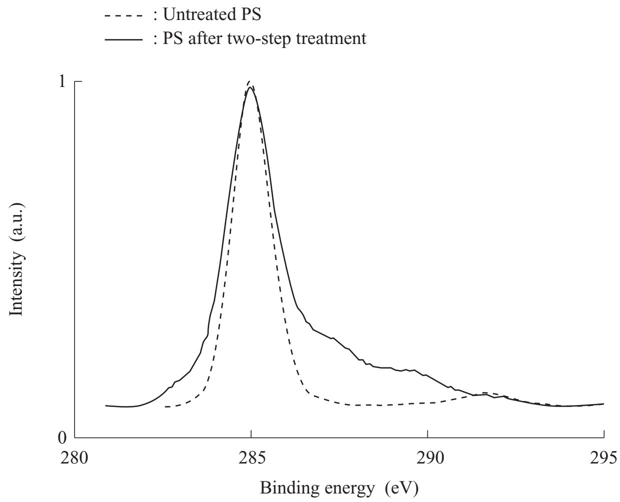

Fig. 7 C1s XPS spectra of the untreated and treated PS surfaces

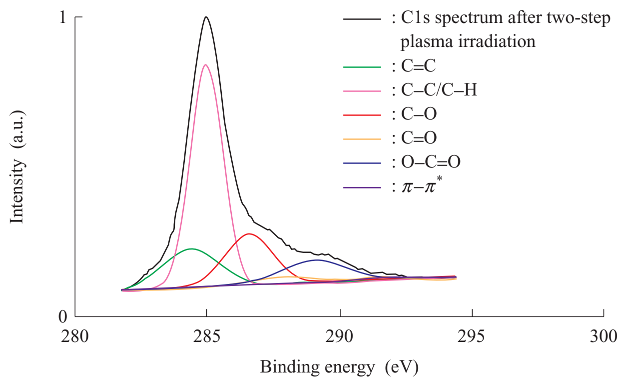

Fig. 8 C1s XPS spectra of the PS surface treated with plasma irradiation

One of the possible reasons for the degradation of hydrophilic properties over time is changes in the state of the functional groups on the surface of PS. Accordingly, XPS analysis was conducted over the course of a few days to examine the change in the proportion of functional groups present on the surface of the PS sample. Then, the relationship between the functional groups and the hydrophilic properties of the PS sample was evaluated. The proportion of the peak area attributed to each functional group corresponds to the abundance ratio of the functional groups present. **Figure 9** shows the peak area ratio attributable to each functional group over time. The slight reduction in the abundance ratio of O–C=O as compared with C–O and C=O suggests that O–C=O is related mainly to the hydrophilic properties after the surface treatment. Therefore, the reason for the hydrophilic properties of PS samples achieved by the two-step treatment lasting so long is considered to be the physical action of the pretreatment with argon plasma slowing the decline of O–C=O, which plays an important role in providing hydrophilic properties.

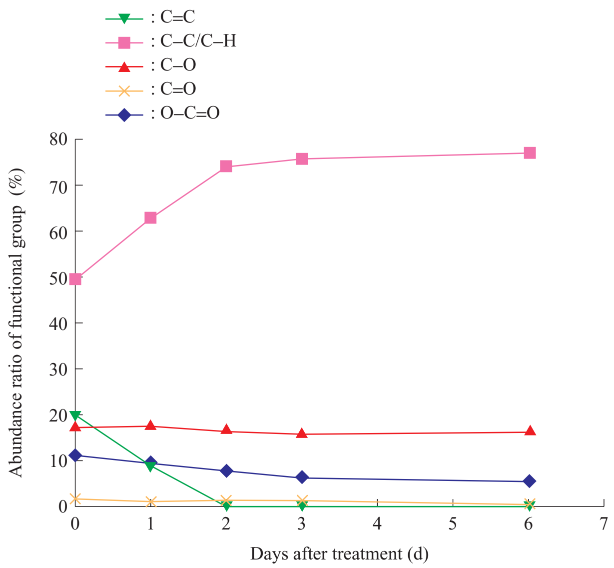

Fig. 9 Temporal changes in the area ratio estimated by the XPS spectra of the treated PS surface

5. Conclusion

This paper discussed plastic surface treatment as an application of IHI's microwave plasma technology in pursuit of a surface treatment process that achieves lasting hydrophilic properties on the surface of plastics. Examination of the microwave plasma irradiation process was conducted with samples made of PS among other commonly used plastics. As a result, a two-step treatment consisted with argon plasma as pretreatment and argon-oxygen plasma was identified as a process that can achieve sustained hydrophilic properties for long time. In the pretreatment with argon plasma of this two-step treatment, argon ions are considered to exert a physical action that increases the reactive sites on the surface of PS samples, thereby improving reaction efficiency of oxygen radicals in the subsequent main treatment.

And, the mechanism of the appearance and subsequent disappearance of the hydrophilic properties of PS samples could be presumed by XPS analysis focused on the functional groups containing oxygen. The analysis revealed that C–O, C=O, and O–C=O appear on the surface of PS samples as a result of plasma irradiation. Among these functional groups containing oxygen, O–C=O was identified to be the most important functional group in the disappearance of hydrophilic properties.

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REFERENCES

(1) T. Ogawa : New Development of Surface Treatments for Polymers CMC Publishing Co., Ltd. (2007. 2) pp. 40-42

(2) J. Lai, B. Sunderland, J. Xue, S. Yan, W. Zhao, M. Folkard, B. D. Michael and Y. Wang : Study on hydrophilicity of polymer surfaces improved by plasma treatment Applied Surface Science Vol. 252 No. 10 (2006. 3) pp. 3 375-3 379

(3) H. Liu, Y. Pei, D. Xie, X. Deng, Y. X. Leng, Y. Jin and N. Huang : Surface modification of ultra-high molecular weight polyethylene (UHMWPE) by argon plasma Applied Surface Science Vol. 256 No. 12 (2010. 4) pp. 3 941-3 945

(4) A. A. Meyer-Plath, B. Finke, K. Schröder and A. Ohl : Pulsed and cw microwave plasma excitation for surface functionalization in nitrogen-containing gases Surface and Coatings Technology Vol. 174-175 (2003. 9-10) pp. 877-881

(5) Central Glass Co., Ltd. : HYDROPHILIC COATING FILM AND METHOD FOR FORMING THE SAME Sugimoto T.(Central Glass Co., Ltd.). Jpn. Kokai Tokkyo Koho JP 2007308602 A, 20071129, 2007. (2007. 11)

(6) L. Wanga, L. Yan, P. Zhao, Y. Torimoto, M. Sadakata

and Q. Li : Surface modification of polystyrene with atomic oxygen radical anions-dissolved solution Applied Surface Science Vol. 254 No. 13 (2008. 4) pp. 4 191-4 200
(7) N. Vandencasteele and F. Reniers : Plasma-modified polymer surfaces : Characterization using XPS Journal of Electron Spectroscopy and Related Phenomena Vol. 178-179 (2010. 5) pp. 394-408
(8) M. Kral1, A. Ogino, K. Narushima, N. Inagaki, M. Yamashita and M. Nagatsu : Low-temperature nitrogen introduction onto polyurethane surface using surface-wave excited N_2/H_2 plasma Japanese Journal of Applied Physics Vol. 46 No. 11 (2007) pp. 7 470-7 474