21PB-055

Improvement of Hydrophilic Polymer Material Surface By Atmospheric pressure RF Plasma Using Mixed Gas He/O_2

He/O_2大気圧RFプラズマによる高分子材料表面の親水化処理

Shota Takahashi, Takumi Araya, Takashi Shibata, Seiji Mukaigawa and Koichi Takaki
高橋祥大, 荒谷琢, 柴田崇史, 向川政治, 高木浩一

Faculty of Technology, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020—8551, Japan
岩手大学工学部, 〒020-8551　岩手県盛岡市上田4-3-5

In this study, we generated radio frequency atmospheric-pressure plasma using He/O_2 mixed gas using a dielectric barrier discharge type reactor, and we improved the surface properties using an organic polymer surface treatment. We determined the optimized condition of the surface treatment by changing the ratio of the mixed gas flow rate. The lowest contact angle of polyethylene significantly decreased from 93.3° to 23.4°. Surface analysis of X-ray photoelectron spectroscopy spectra in polyethylene revealed the formation of an oxygen-containing group.

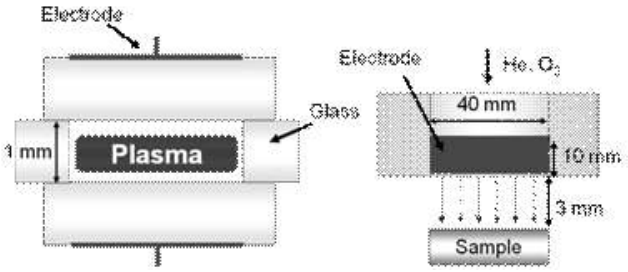
1. Introduction

Organic polymer materials are widely used as industrial materials, medicine, and household products; surface processing requires high adhesion. Recently, improvement of the hydrophilicity of the polymer surface using plasma has attracted attention. [(1)-(3)] This study aimed to improve the hydrophilicity due to be added to hydrophilic groups on the polymer surface by plasma surface treatment. Stable glow discharge was generated using dielectric barrier discharge (DBD), enabling surface treatment in atmospheric pressure. Using the DBD plasma surface treatment method, cost can be reduced because a vacuum system is not necessary; this method also has a low environmental impact because it uses only a small amount of chemicals. In addition, line processing is easy. [(1)]

In plasma surface treatment, the composition of the feed gas affects the surface treatment and plasma characteristics. In this study, to efficiently generate oxygen-containing groups such as carboxyl and hydroxyl, which is a factor to improve hydrophilicity, we mixed oxygen with the feed gas. In particular, OH groups on the polymer surface could be applied to the molecular adhesion Triazine thiol.

2. Experimental Setup

The plasma reactor is shown in Fig.1. The glow discharge was DBD plasma consisting of two glass plates inside two parallel copper electrodes (40×10 mm^2, working) with a gap 1 mm long and 40 mm wide. The specimen used was polyethylene (PE). The downstream side of the plasma region in the plasma reactor was opened, and the PE was placed 3 mm from



(a) Front view　　(b)Top view

Fig.1 Plasma generator

the open side of the plasma reactor. Voltage was supplied to the powered electrode through the matching circuit. The power and frequency were 100 W and 13.56 MHz, respectively. We used helium and oxygen mixed gas in the plasma system, with a total gas flow of 3.0 L/min, controlled to 0%, 0.7%, 1.3%, and 2.0% of oxygen concentrations using mass flow controllers. The surface treatment time was 10, 20, 30, and 40 s.

3. Experimental Results

3.1 *Surface hydrophilicity*

Fig.2 shows the oxygen concentration dependency of the contact angle at the PE surface. The contact angle at the untreated PE was 93.3°. The hydrophilicity of the PE treated with helium and oxygen mixed gas improved compared with that of the PE treated with helium gas only. When the treatment time was 10 s, the contact angle was reduced to 60° in the case of 0% oxygen concentration. The oxygen gas was added to the feed gas, and the contact angle was reduced to approximately 50°;　the effect of oxygen addition was

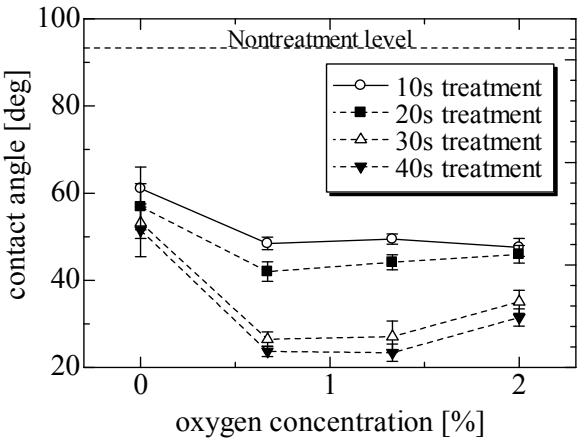


Fig.2. Oxygen concentration dependency of contact angle on PE surface

obtained. When the treatment time was 40 s, the contact angle decreased up to 23.40° in the case of 0.7% oxygen concentration. Emission spectroscopy revealed that oxygen radicals were mostly generated in the case of 0.7% oxygen concentration. Therefore, long-term treatment, rather than brief treatment, was more likely to affect oxygen radicals.

3.2 *XPS analysis*

Table 1 shows the corresponding contributions of the different carbon- and oxygen-containing chemical bonds. Table 2 gives the atomic composition of each PE surface. We identified five peaks in the C1s spectra of each specimen: a major peak at 284.6 eV, assigned to aliphatic carbon atoms(C－C); a peak at 286.1 eV, corresponding to the carbon atoms in the C－O bonds; a peak at 286.5 eV, corresponding to the carbon atoms in C－OH bonds; a carbon double bond (C=O), appearing at the binding energy of 287.4 eV; and a peak at 288.8 eV, arising from the carbon atoms in the carboxyl group (COOH). [4] The molecular structure of PE is $(-CH_2-CH_2-)_n$, it has a structure of ethylene polymerization. PE surface treated at 0.7% oxygen concentration and 40 s showed great improvement in hydrophilicity, absorbing oxygen better than any other treated surface.

In Table 1, COOH was the largest chemical bond of the oxygen-containing groups on the PE treated at 1.3% oxygen concentration and 40 s. The proportion of COOH was 20.1%. The largest number of OH groups was found on PE treated with the same conditions, totaling 9.9% in a relative area corresponding to the different chemical bonds. Significant increase in the number of COOH and OH groups significantly impact the contact angle measurements.

Table.1. Data of deconvolution of C1s peaks for PE surface untreated and treated with plasma

		C-C	C-O	C-OH	C=O	COOH	
Binding energy		284.6	286.1	286.5	287.4	288.8	(eV)
Nontreatment		97.2	2.8	—	—	—	
[10 s]	0%	90.4	1.9	1.8	3.9	2.0	
	0.7%	76.0	6.7	3.8	7.2	6.3	
	1.3%	71.6	3.4	8.5	7.5	9.0	
	2.0%	72.2	2.3	9.1	11.4	5.0	
[40 s]	0%	79.0	4.6	8.7	6.3	3.9	
	0.7%	52.9	3.9	9.0	14.0	19.3	
	1.3%	50.6	6.8	9.9	13.5	20.1	
	2.0%	62.6	4.7	8.7	8.6	15.4	(%)

Table.2. XPS analysis of PE surface untreated and treated with plasma

		C1s	O1s	N1s	
Non treatment		97.5	2.3	0.2	
[10 s]	0%	82.8	17.2	0	
	0.7%	72.5	25.7	1.8	
	1.3%	71.7	27.5	0.8	
	2.0%	70.4	28.0	1.6	
[40 s]	0%	81.9	17.9	0.2	
	0.7%	60.8	38.0	1.2	
	1.3%	60.7	38.3	1.0	
	2.0%	64.9	32.3	2.8	(%)

4. Conclusion

After atmospheric pressure glow discharge was generated by the radio frequency atmospheric plasma reactor, we performed plasma surface treatment on PE by controlling the oxygen gas concentration of the feed gas. The hydrophilicity of the PE treated in 1.3% oxygen concentration and 40 s was greatly improved, and the PE absorbed more COOH than the treated PE.

References

[1] Takuya Sato, Takahiro, Seiji Mukaigawa, Koichi Takaki, Tamiya Fujiwara：“Polymer materials surface treatment using RF atmospheric pressure plasmas under controlled conditions of relative humidity”, Joint Technical Meeting on Pulsed Power Technology and Electrical Discharge, IEE Japan, PPT-11-19, pp.21-24(2011)H. Yamada and S. Hamaguchi: J. Appl. Phys. 96 (2004) 6147.

[2] Dongsoo Lee, Sang Hee Hong, Kwang-Hyun Peak, Won-Tae Ju：“Adsorbability enhancement of activated carbon by dielectric barrier discharge plasma treatment”, Surface and Coatings Technology 200(2005) 2277-2282

[3] Yu Ren, Yuyan Hong, Jie Sun, Yiping Qiu：“Influence of treatment duration on hydrophobic recovery of plasma-treated ultrahigh modulus polyethylene fiber surface”, Journal of Applied Polymer Science, Vol.110, pp.995-1001 (2008)

[4] J.S.Brinen, S.Greenhouse, L.Pinatti：“ESCA and SIMS studies of plasma treatments of intraocular lenses”, Surface and Interface Analysis. vol.17, pp.63-70 (1991)