Surface modification of polypropylene by nitrogen-containing plasma

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Abstract−Polypropylene was treated with low pressure glow discharge plasma for the introduction of functional groups in its surface using plasma of different types. For this purpose plasma containing nitrogen and hydrogen and coating by deposition of thin plasma polymerized layers of functional group carrying monomer with NH_2 on it were used. The surface elemental composition was changed stoichiometrically by adjusting the plasma conditions depending on the feeding and plasma density. The optimum power plays an important role in the control of surface reactions between surface reactive species and plasma reactive species. Plasma-Polymerized-Allylamine (PPAa) thin film prepared with r.f. continuous and pulse wave power was characterized to study surface amine functionality. The surface amine content of PPAa at r.f. pulse wave power could be retained more efficiently than that of PPAa at r.f. continuous wave power because of less fragment of monomer. The stability test of r.f. pulse wave plasma polymerization indicated that the deposits of PPAa at the high r.f. pulse wave power were more stable than those at low r.f. pulse wave power after soaking it in tetrahydrofuran (THF).

Key words: X-Ray Photoelectron Spectroscopy, Pulse-plasma, Radio Frequency (RF) Plasma, Polypropylene, Nitrogen-containing Gases

INTRODUCTION

Polymers have many distinct advantages as engineering materials, but sometimes it is necessary to modify their surfaces in order to add other properties such as biocompatibility, printability and adhesive property [1]. They have been modified with various plasma techniques, such as corona [2], acetonitrile plasma [3], CO_2 plasma [4] and dichloromethane plasma [5]. Cold plasma treatment for modifying polymer surface can initiate surface reactions in polymers to lead scission reaction at near-surface C-C or C-H bonds. Free radicals created can further react with reactive species in the gas phase [6,7]. Subsequently, a surface reacting with active nitrogen such as N_2^+ and N_2^* [8] can react with other molecules such as metals [9, 10], macromolecules [11] and so on. Nitrogen plasma can give rise to amine (-NH_2), imine (-CH=NH), cyano (-CN) and amide (-CO-NH) groups [12]. On the other hand, plasma polymerization is well known as an easy way to produce a thin polymer layer having functional groups. Hydroxyl, carbonyl, carboxyl and amino functional groups can contribute to enhance cell attachment on plasma deposited films [13]. Plasma polymer (polymer synthesized through plasma polymerization), however, invariably contains a variety of functional groups which can make the study of cell attachment to the surface complex [13].

In this study, a polypropylene surface was modified with nitrogen containing plasma like N_2/H_2, NH_3/N_2 mixture and allylamine monomer. Primary amine groups generated by plasma techniques onto a polymer surface can immobilize molecules for separation or diagnostic purposes. The polymer modified with plasma can be applied to biomedical field, biomolecular (e.g., protein, enzyme) immobilization and cell adhesion devices [14]. The surface functional groups can be utilized as anchoring sites for binding specific spacer molecules. To achieve this, plasma surface modification was systematically conducted to get the insight about different types of nitrogen-containing plasma. The surface chemical changes and quantities modified with nitrogen-containing plasma were characterized by using elemental analysis and derivatization method with XPS, respectively. From experiments depending on an individual system, the influence of plasma conditions and the surface functionality were studied. Also, the weak physical and chemical properties of plasma polymer were investigated by testing the stability of plasma polymer in solvent.

EXPERIMENTAL

1. Materials

Polypropylene (PP) foils with a thickness of 100 μm (Goodfellow, UK) were cleaned with diethyl ether in ultrasonic bath for 30 min and dried in vacuum desiccator. Ultra-high purity gases (purity of NH_3, N_2, H_2 >99.9%) were used without further purification. Allylamine monomer (>99%) from Merck, Darmstadt, Germany was purified by distillation. Tetrahydrofuran (THF) and acetone, supplied by Messer-Grieshem GmbH, Germany, were used as received.

2. Plasma Surface Treatment

The reactor, as shown in Fig. 1, was equipped with a radio-frequency (r.f., 13.56 MHz) generator with an automatic matching unit and r.f. bar antenna (length: 35 cm). Polypropylene film was placed on a continuously rotating, grounded steel cylinder at 10 cm distance to the r.f. powered electrode. The rotating sample was only intensively exposed to the plasma glow, i.e., about 25% of a rotation. The total flow rate was kept at 20 sccm. $N_2 : H_2$ and $NH_3 : H_2$ gases were mixed in different feed proportions (the ratio of $N_2 : H_2$; 20 : 0, 10 : 10, 5 : 15, 2 : 18 sccm). The discharge pressure was kept at 10 Pa by controlling a turbo pump. Power used was 3, 10, 50 and 100 W

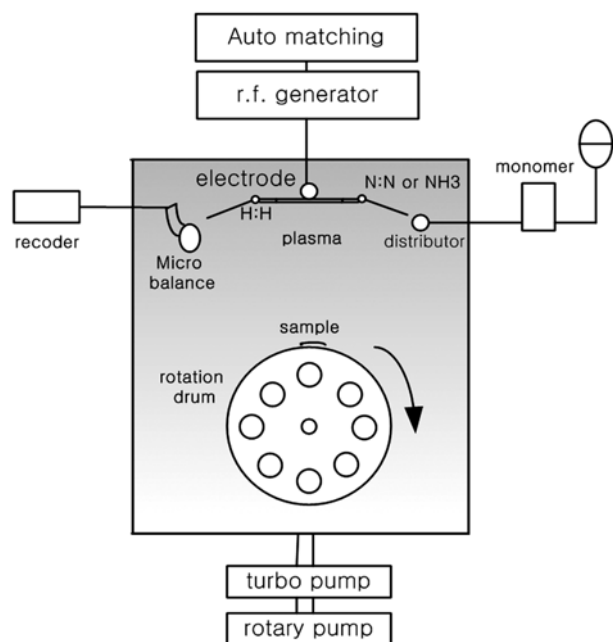†To whom correspondence should be addressed.
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Fig. 1. Schematic diagram of plasma reactor.

Fig. 2. The surface N/C ratio results for $N_2 : H_2$ and $NH_3 : H_2$ mixture gas plasma treatments as a function of H_2 feed rate at power of 100 W.

in the present study. The sample was then irradiated by nitrogen-hydrogen mixed plasma for 30 s. For plasma polymerization, ally-lamine monomer liquid purified was fed into the reactor by liquid flow meter (LFM, MKS). The line was preheated to 50-55 °C to evaporate the monomer. The distributor in the reactor was also heated. The flow of liquid controlled by LFM was kept with 5 g/h. The r.f. power of continuous wave (CW) plasma ranged from 3 to 80 W. The power of pulse wave (PW) plasma was varied from 300 to 600 W with duty cycle ($D=t_{on}/(t_{on}+t_{off})$) of 0.1 and a pulse frequency of 10^3 Hz was applied to reduce fragmentation. The plasma polymerization with allylamine was conducted for 5 min to make plasma-polymerized-allylamine (PPAa). After deposition, all parts deposited were separated from the reactor inside and cleaned with acetone. A micro balance was used to monitor the thickness of the thin film deposited during plasma process near electrode.

3. Analytical Techniques

After plasma surface modification, the chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS). The surface was analyzed by using a SAGE 150 (SPECS, German) photoelectron spectrometer, with Mg Kα X-rays (hv=1253.6 eV), operated at 225 W, and a take off angle of 90° with respect to the surface normal. All samples were measured by XPS within 2 hours to reduce post-treatment reactions of long-lived radicals or unstable functional groups created during treatment with molecular oxygen and water vapor present in the atmosphere. Three points on all samples treated were measured.

Fluorine atoms of PFBA (pentafluorobenzaldehyde) have been utilized to label -NH$_2$ among other groups, following a derivatization procedure designed to titrate them by means of XPS. Polypropylene substrates were exposed to vapor from a solid of PFBA placed on glass plate in desiccator kept at 45 °C for 40 min. After degassing, substrates were analyzed by XPS. Primary amine concentrations were derived as follows:
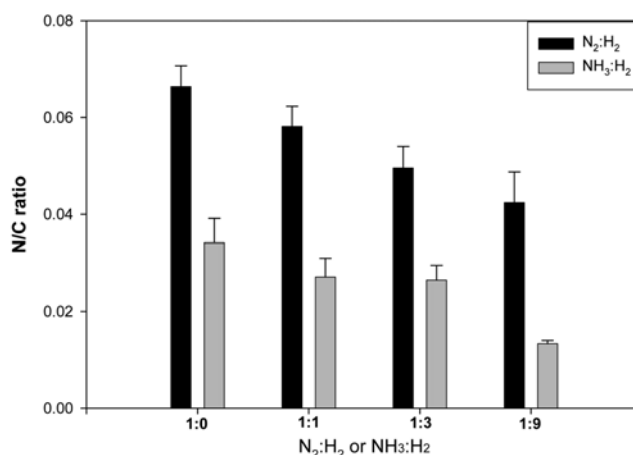
$$[NH_2] = \left[\frac{[F]}{5}/([C]-7[F]/5)\right] \times 100\% \qquad (1)$$

where [F] and [C] are the fluorine and carbon contents determined by XPS after the reaction with PFBA [15]. To check out the stability of plasma polymer layer in solvent, samples treated were immersed and shaken in THF for 25 min.

RESULTS AND DISCUSSION

1. Plasma Surface Modification with $N_2 : H_2$ and $NH_3 : H_2$ Mixtures

Fig. 2 shows the ratio of N/C on polypropylene surface treated with $N_2 : H_2$ and $NH_3 : H_2$ mixture plasma at 100 W r.f. power. As shown in Fig. 2, the surface N/C ratio decreased with increasing H_2 content in the feed. The surface N/C ratio after $NH_3 : H_2$ mixture plasma treatment also decreased with increasing H_2 ratio while sustaining the half value of the surface N/C after $N_2 : H_2$ mixture plasma treatment. The difference in the surface N/C ratio results from the difference in nitrogen content between the N_2 and NH_3 feed. The stoichiometric change of N/C ratio of substrate surface could show the possibility of controlling the surface chemical composition more precisely through plasma treatment. At r.f. power less than 50 W, there was no trend and regularity due to the insufficient ion flux. At high power such as 200 W, the functional groups grafted on the surface were decomposed due to etching effect, and therefore the nitrogen content decreased. The 100 W r.f. power, however, could generate more nitrogen content on PP surface with reproducible N/C ratios at the pressure of 10 Pa and the feed rate of 20 sccm. It was thought that a high power would be damaging to the topography and the surface chemical properties. The high pressure (means high ion density) could yield higher surface N/C ratio [16]. Favia [17] showed that, when H_2 was added to the feed, the grafting selectivity of -NH$_2$ increased. When the N/C ratio was 21.1%, the amount of amine group indicated 3.3% of the NH$_2$/C. A density of 3-4% primary amino groups is the best value ever reported in literature [14]. In this study, however, the percent of amine groups would be small because of the low N/C ratio of 6%. It would be a

matter of course that the grafting amine group on polypropylene also amounts to a few.

2. Plasma Polymerization by r.f. CW and PW Plasma

Through plasma polymerization, a thin film of plasma-polymerized-allylamine (PPAa) was formed on the surface of propylene. Fig. 3 represents the change of thin film thickness with respect to r.f. CW and PW power. The thin film thickness was obtained from
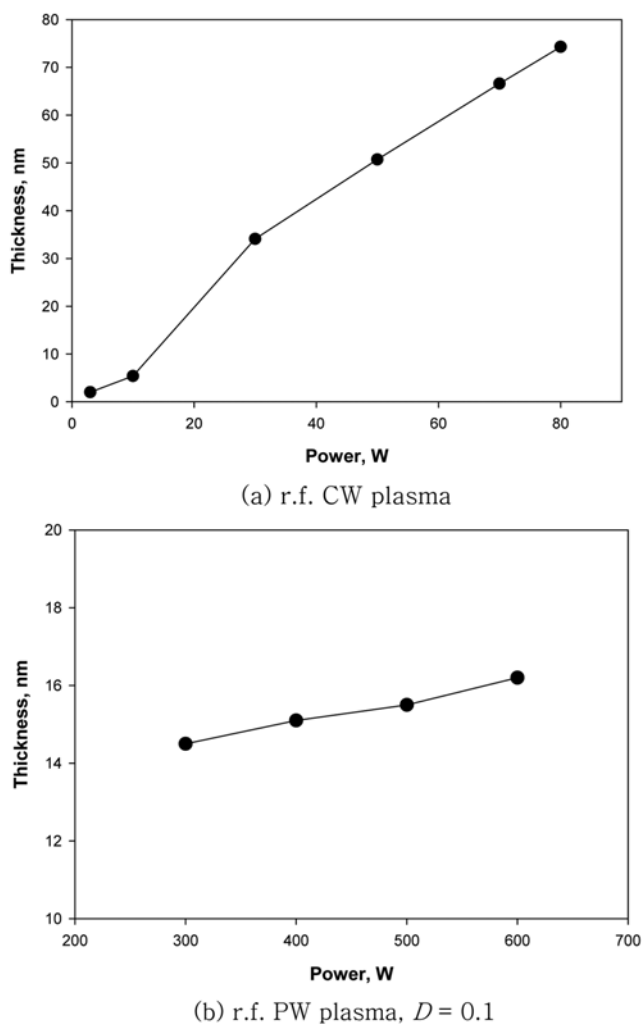

(a) r.f. CW plasma

(b) r.f. PW plasma, $D = 0.1$

Fig. 3. Deposition rate about (a) r.f. CW and (b) r.f. PW plasma.

the deposition rate estimated by micro balance. It shows that the thickness of PPAa thin film increased with increasing r.f. CW and PW power. During deposition, the resulting oligomers polymerized diffuse to the surface of substrates (and reactor wall) and covered it in continued polymerization. For r.f. PW plasma, the deposition rate was lower than the r.f. CW because of lower plasma energy. Plasma polymerization depends on input power for creating activated species. The two plasma processes could provide the different structural and chemical characteristics of plasma polymer. The r.f CW power is more appropriate for creating cross-linked structure than the r.f. PW power. The degree of fragmentation of monomer by ion bombardment mainly causes the different property of plasma polymer.

In Table 1, the elemental compositions of PPAa from XPS are summarized for r.f. CW and PW plasma. PPAa contains carbon and nitrogen atoms started from allylamine monomer. Allyamine monomer has theoretically 25% nitrogen and 75% carbon. In case of r.f. CW power below 10 W, an N/C ratio of less than 9% could not give sufficient information of PPAa's chemical property because of thin thickness. To utilize the XPS, the thickness of the layer should be over 10 nm. A signal for XPS measurement was detected with 69% within 3 nm and 99% within 9 nm. So, the XPS data could not provide a precise analysis about the surface composition of PPAa prepared at below 10 W. The XPS results of PPAa over 30 W were required for analyzing the reliable composition of PPAa. The surface N/C ratio of PPAa shows a little divergence in the range of 40-80 W. As the power increased, the amount of nitrogen usually increased, but the concentration of other functional groups, such as secondary and tertiary amines and imines, increased. In this case of gas-phase, allylamine does not fragment into more different species. So, the surface chemistry of PPAa does not show any significant variation over the power range studied [18]. In case of r.f. PW plasma, the surface N/C ratio of PPAa prepared at 300 and 400 W with D=0.1 presented lower values than those at 500 and 600 W with D=0.1. The relatively weak energy of plasma causes a less dense surface of PPAa leading to the lower surface N/C ratio.

The quantification of amine functional groups on the surface of PPAa was performed by using derivatization method with PFBA. After derivatization, the N/C ratios decreased because of PFBA immobilized after labeling the primary amine on the surface of PPAa. The increase of fluorine content corresponds to the increase of primary amine groups on the surface of PPAa. At r.f. CW power over

Table 1. The N/C ratio and fluorine percent on propylene treated with r.f. CW and PW plasma. The percent of amine group is also shown

Type of plasma	Power, W	N/C %	N/C % After derivatization	F %	NH$_2$ %
CW	3	4.19±0.16	3.54±0.35	6.07±2.79	1.73
	10	9.30±0.15	7.51±0.22	5.53±0.56	1.50
	30	25.48±0.68	19.42±0.28	14.83±1.31	6.85
	50	27.91±0.26	19.79±0.45	11.15±0.15	4.37
	70	26.27±0.25	18.66±0.36	15.57±0.54	7.10
	80	25.37±0.35	18.44±0.79	14.87±0.59	6.52
PW D=0.1	300	17.06±0.60	13.19±1.23	12.0±1.77	4.86
	400	18.50±1.17	13.21±1.34	13.87±2.82	6.41
	500	22.47±1.25	17.80±0.98	8.27±1.67	2.99
	600	27.05±9.38	13.83±3.20	5.83±2.38	1.97

Table 2. The N/C ratio, F and the percent of amine group on the surface of PPAa by r.f. PW plasma after soaking in THF

Type of plasma	Power, W	N/C % after soaking in THF	N/C % after derivatization	F %	NH$_2$ %
PW D=0.1	300	13.95±0.64	5.64±0.34	4.53±0.17	1.25
	400	14.49±0.28	7.39±0.88	5.9±1.64	1.70
	500	18.45±0.51	7.35±0.98	5.9±1.57	1.68
	600	17.48±0.89	12.67±1.01	11.3±0.53	4.11

30 W, the N/C ratio was between 25 and 28% without showing any significant difference. The corresponding amine percent of PPAa surface was 4.37-7.10%. In r.f. PW plasma, the N/C ratio increased with increasing the r.f. PW power presenting an amine percent of 4.86-6.41%. The PPAa prepared with r.f. PW power showed relatively low N/C ratio of 17.06-18.50% at 300-400 W with duty cycle 0.1, but resulted in a relatively high amine percent of 4.86-6.41%. This means that the surface amine percent of PPAa at r.f. PW power could be retained more efficiently than that of PPAa at r.f. CW power. The highest primary amine concentration reached about 8% at the plasma polymerized diaminocyclohexane with pulse plasma [15]. A value of 2.2% was calculated on NH$_2$ content evolution around 30 W of r.f. power [19].

3. Stability of PPAa Prepared at r.f. PW Plasma

The stability of PPAa in THF solution has been investigated by checking the surface amine group after soaking it in THF. Table 2 represents the XPS results after soaking samples in THF and subsequent derivatization with PFBA. After soaking, N/C ratio was decreased because some soluble PPAa molecules with low molecular weight were washed out. After derivatization with PFBA, however, the sample prepared at the r.f. PW power of 600 W showed higher N/C ratio and fluorine content. Although the r.f. PW plasma resulted in less cross-linked network structure of plasma polymer than the r.f. CW plasma, the increase of r.f. PW power can still result in the increase of cross-linking degree of surface PPAa. Thus, the high power PPAa deposits lose less material after soaking than low-power plasma deposits [20], and consequently retain more amine groups.

CONCLUSIONS

The present work investigated the plasma surface modification of polypropylene by means of plasma containing nitrogen and amine group. The r.f. CW Plasma using both N$_2$: H$_2$ and NH$_3$: N$_2$ gas mixtures could stoichiometrically control the surface N/C ratios with respect to the feed gas ratios. The 100 W r.f. power could generate more nitrogen content on PP surface with reproducible N/C ratios at the pressure of 10 Pa and the feed rate of 20 sccm.

Plasma polymerization was also carried out on both r.f. CW and PW plasma. The thickness of PAAa deposited increased with increasing both r.f. CW and r.f. PW power. The deposition rate of r.f. PW plasma with D=0.1 was lower than that of the r.f. CW plasma because of less activation of monomers. From XPS results in r.f. CW plasma, the surface N/C ratio of PPAa revealed no significant difference at the power range of 30-80 W because the power of 30 W and the reaction time of 5 min was enough for the completion of plasma polymerization of allylamine. In case of r.f. PW plasma, the surface N/C ratio of PPAa gradually increased with increasing r.f. PW power with D=0.1. The PPAa prepared with r.f. PW power

showed a relatively low N/C ratio of 17.06-18.50% at 300-400 W with duty cycle 0.1, but resulted in a relatively high amine percent of 4.86-6.41%. The surface N/C ratio of PPAa prepared at r.f. PW power was decreased after soaking it in THF solution, but both N/C ratio and fluorine content were highly retained for the sample prepared at the r.f. PW power of 600 W. Thus, the high power PPAa deposits retain more amine groups.

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