Surface Characterization of the Activated Carbon Fibers After Plasma Polymerization of Allylamine

Na Lu, Shen Tang, Seung-Kon Ryu and Ho-Suk Choi♠

Department of Chemical Engineering, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon 305-764, Korea
♠e-mail: *hchoi@cnu.ac.kr*

Abstract

Plasma polymerization of allylamine subsequently after plasma pre-treatment was conducted on the activated carbon fibers (ACFs) for the immobilization of amine groups in the surface of ACFs. The change of structural properties of ACFs with respect to different polymerization conditions was investigated through BET method. The change of surface morphologies of ACFs with respect to different plasma polymerization power was also studied through AFM. It was found that the structural properties such as specific surface area and micropore volume could be optimized under certain plasma deposition conditions. It was reckoned that treatment and deposition showed adverse effect on plasma polymerization, in which the former developed the micro-structures of the ACFs and the latter tended to block the micro pores. The Fourier transform infrared spectroscopy (FTIR) revealed that the poly(allylamine) was successfully immobilized on the surface of ACFs and the amount of the deposited polymer layer was related to the plasma polymerization power. SEM results showed that the plasma deposited polymer layer were small and homogenously distributed. The size and the distribution of particles deposited were closely related to the plasma polymerization power, too.

Keywords : *Plasma polymerization, Activated carbon fiber, Micro-pore volume, Amine groups*

1. Introduction

Activated carbon fibers are traditional carbon materials widely used in adsorption industry. The hydrophobic surface of ACFs, however, always limited their application on this industry. Therefore, lots of research has been done to improve the surface properties of ACFs through various physico-chemical methods [1-4]. Among various surface modification methods, plasma surface modification is an efficient way to modify the surface properties of various materials [5-13] including carbon materials. After plasma surface modification, the surface of ACFs tended to be more hydrophilic and fitted for further application. Although the changes in the surface functionalities were very remarkable, the structural properties such as specific surface area and micropore volume always declined after plasma treatment. For example, Orfanoudaki *et al.* [14] once utilized the plasma deposition techniques to modify the surface properties of the ACFs, aiming for the formation of pore constrictions. They used propylene/nitrogen and ethylene/nitrogen as plasma reaction gases. Their results showed that plasma deposition made an external layer on the surface of ACFs and incorporated nitrogen groups on the surface of ACFs. Park *et al.* [15] investigated the surface properties and textural properties of ACFs after an atmospheric pressure plasma treatment. They noticed that plasma treatment made new oxygen-containing functional groups on the surface of the ACFs. However, the specific surface areas and pore volumes decreased due to blockages in pores after plasma treatment. In other paper by Park *et al.* [16], an atmospheric pressure plasma treatment (Ar/O$_2$ and Ar/N$_2$) was conducted on the activated carbon fibers for the application of the removal of hydrogen chloride. They proved that after plasma treatment the adsorption ability of the ACFs for the hydrogen chloride was improved due to the incorporation of new functional groups by plasma treatment. However, the decrease of specific surface area resulted in adverse effect, which was disadvantageous for the gas adsorption.

In this experiment, a novel result was found using an RF low pressure plasma treatment and plasma deposition. Usually after plasma modification, the structural properties such as specific surface area and micro-structure always declined, although the surface functionality was greatly improved. However, in our experiment, we improved not only the surface functionalities but also the structural properties using plasma treatment and plasma deposition. It is regarded that the burning and etching effect [17] of the low pressure plasma were lower although the kinetic energy of the low pressure plasma was higher than the atmospheric pressure plasma. Thus, the micro-structures of the ACFs could be more developed under low pressure plasma treatment. In our group, the effect of plasma treatment pressure was once

studied [18] and 250 mtorr was thought as an appropriate pressure. It is also shown through the BET results that plasma deposition can have a possibility to develop the micro-structures under certain treatment conditions, through the two competing processes of plasma treatment and plasma deposition. The morphology and the size of deposited poly-mers on the surface of ACFs strongly depended on the operation condition of plasma deposition process. The FTIR results showed that the amine groups could be successfully immobilized on the surface of ACFs through plasma deposi-tion of allylamine and the amount of the deposited layer on the ACFs was closely dependent on the plasma deposition power, too.

2. Experimental

2.1. Materials and sample preparation

Commercially available ACFs (KF-1500) were used as samples in this study and ultra pure O_2 (5.0 N UHP, Praxair Korea Co. LTD) was used to generate plasma. The allylamine (97%, Adrich), which was used as monomer, was obtained from Ardrich chemical Co. Before plasma treatment, the ACFs were dried in the oven at 200°C for 24 hrs.

2.2. Plasma treatment and deposition

Samples were vacuumed out with rotary and diffusion pumps at 10^{-4} mtorr for 10 minutes. The O_2 gas was intro-duced and the pressure was fixed at 250 mtorr. The samples were treated using a radio frequency plasma at 13.56 MHz (Model EPPs 2000, PLASMART Inc., Korea), as shown in Fig. 1. The flow rate of the O_2 gas was controlled using a mass flow controller (MFC; Model 5850E, Brooks, Japan).
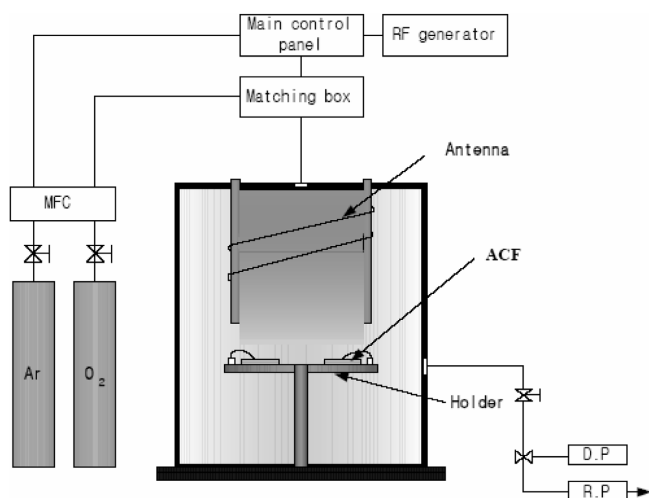

Fig. 1. Schematic diagram of the oxygen plasma system used in this work.

The plasma parameters were fixed, i.e. plasma treatment time of 30s and treatment power of 100W. After plasma treatment, the plasma chamber containing samples was vacuumed out again, followed by the introduction of the allyamine vapor. The plasma deposition time was fixed at 3 min and the pressure in plasma chamber was fixed at 300 mtorr. The plasma deposition power was studied at 30W, 50W and 70W, respectively.

2.3. BET Measurement

The porosities of the ACFs were characterized using N_2 adsorption at 77 K, from which the BET isotherm was obtained [19]. The amount of nitrogen adsorbed on ACFs was used to calculate the specific surface area using the BET equation. Total pore volume (V_t), micro-pore volume (V_{mi}), average pore diameter (A_p) and external surface area of ACFs were all obtained using the nitrogen-BET equation. The pore size distribution of the ACFs was calculated using the BJH adsorption model.

2.4. Characterization by SEM

SEM (Scanning electron microscopy) studies were carried out with an SM-500 (ETPSEMRA, Sydney, Australia) with an operational working distance of 5 mm and voltage of 10 kV. The ACFs samples were cut by 1×1 cm before SEM test, followed by gold coating on the surface. The scanning size was fixed at 250 nm.

2.5. Characterization by FTIR

The surface chemical functionality of the ACFs before and after plasma treatment was investigated using Fourier Trans-form Infrared (FTIR) spectroscopy. Small amount of KBr and ACFs samples were mixed, ground and then pelletized.

3. Results and Discussion

3.1. Structural properties of ACFs

The pore properties of the ACFs were characterized by BET methods through the adsorption isotherm of N_2 at 77 K. Fig. 2 shows the N_2 adsorption isotherms for the samples after plasma treatment and subsequent plasma deposition of allylamine at 30W, 50W, and 70W, respectively. The textural properties from the BET equation are listed in Table 1. It is seen in Figure 2 that most of the pores were filled at below the relative pressure (P/P$_0$) of 0.1, which are corresponding to the micro-structure of the ACFs. As shown in Table 1, the specific surface area, total pore volume and average micro-pore volume all increased after plasma treatment. These changes are thought to be caused by the plasma electron
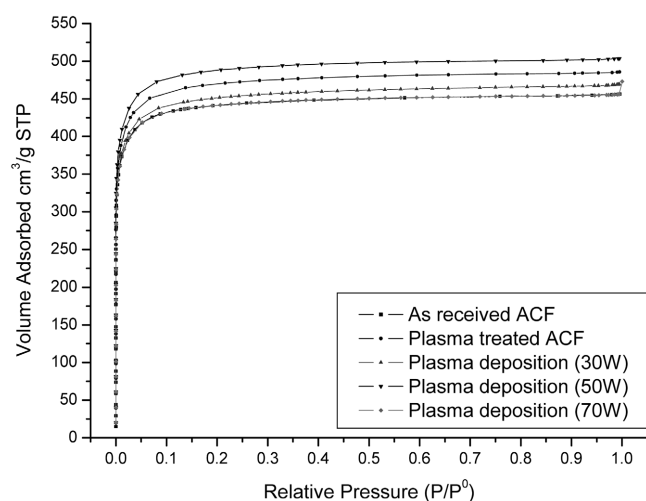
Fig. 2. BET N_2 adsorption isotherms of plasma treated and deposited ACFs.

Fig. 3. Pore size distribution of plasma treated and deposited ACFs.

bombardment, which develops the micropores on the ACFs. Comparing with the atmospheric pressure plasma, the kinetic energy of electrons emitted by the vacuum plasma is stronger. However, the burning effects are thought to be weaker. It is thought that strong burning effect may block or narrow the micropores and this is why the strong burning effect of the atmospheric pressure plasma decreased the specific surface area and micropore volume in aforementioned paper [15]. In contrast, under low pressure plasma treatment, the electrons are accelerated, which correspondingly increased the kinetic energy of the plasma. On the other hand, the burning effects under low pressure plasma are weaker due to the lower surface temperature during discharge. The above characteristics of low pressure plasma treatment are more possible to develop the micropores on the ACFs. Therefore, the specific surface area and micropore volume on the ACFs increased after the vacuum plasma treatment.

Plasma deposition is an efficient way for those vinyl monomers to be polymerized, which can be initiated by the plasma generated radicals. The surface functionalities could be dramatically changed with plasma polymerization of various vinyl monomers. For example, the deposition of acrylic acid can make carboxyl functionality on the substrate [20], and the choice of allylamine or allylalcohol can make amine
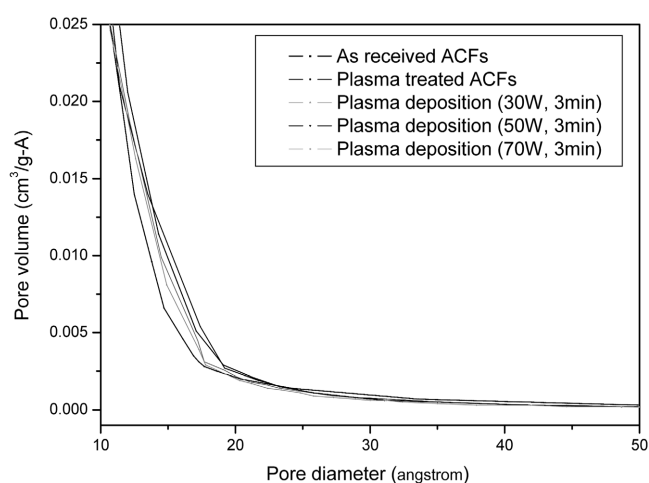
[21] and hydroxyl groups [22], respectively. On the plasma deposited samples, the properties of micro-structures changed with the plasma treatment power. It is thought that during plasma deposition, the effect of plasma treatment still existed while competing with the plasma deposition. When plasma deposition power is low, the effects of plasma treatment and deposition are both weak. With increasing deposition power, the competition of both treatment and deposition effects is more and more obvious until the plasma deposition dominates the whole reaction, which can form a polymer layer on the surface. As shown in Table 1, when plasma treatment power was 30W, the specific surface area and micropore volume slightly decreased, which was due to the plasma deposited particles on the surface of ACFs. At plasma deposition power of 50 W, it is thought that plasma treatment effect was more remarkable and the micro-pores were more developed. Therefore, the micropore volume and specific surface area increased. At plasma deposition of 70 W, it is thought that plasma deposition began to dominate in the whole reaction. The deposited polymer particles tended to cover the surface of the ACFs, which cause the decrease in the specific surface area and micropore volume. Comparing with the as-received sample, however, the properties of micro-structure deposited at 70W have still not shown decrement. Fig. 3 shows the pore size distribution of as-received, plasma-

Table 1. Structural Properties of the plasma treated and deposited ACFs

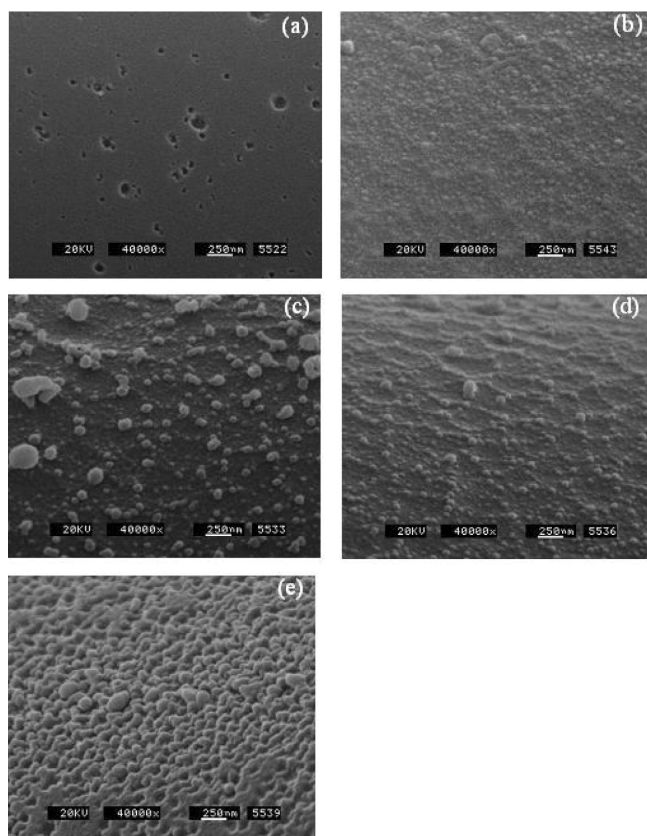| Samples	specific surface area (m^2/g)	V_t (cc/g)	V_{mi} (cc/g)	D_p (Å)	External surface area (m^2/g)
1	1752	0.71	0.69	16.1	5.1
2	1846	0.75	0.74	16.4	5.3
3	1704	0.73	0.71	17	6.9
4	1847	0.78	0.77	16.9	5.2
5	1660	0.71	0.69	17.6	4.6

Fig. 4. SEM images of plasma treated and deposited ACFs. (a) As-received ACFs, (b) Plasma-treated ACFs, (c) Plasma-deposited ACFs at 30 W, (d) Plasma-deposited ACFs at 50W, (e) Plasma-deposited ACFs at 70 W.

treated and deposited ACFs. It could have seen that the micropore volume with the diameter of 15~20 Å were increased on the plasma-treated sample and on the plasma-deposited samples. Comparing with the plasma-treated sample, the volume of the micropore at the above range on the plasma-deposited samples slightly decreased, but was still higher than that on the as-received sample. This result further reveals that plasma treatment could develop more micropores on the surface of ACFs and during plasma deposition, the plasma treatment and deposition simultaneously exist. Thus, the plasma power must be an important factor to control the effect of plasma deposition on the structural properties of ACFs.

Figure 4 shows the SEM images of the as-received, plasma-treated and plasma-deposited ACFs. It could be seen that the surface roughness of the ACFs increased on the plasma-treated sample (Fig. 4b), which was caused by the plasma etching effect. On the plasma-deposited samples shown in Fig. 4(c), (d) and (e), the plasma deposited particles were clearly seen. When the plasma treatment power was low like 30W, the size of deposited particles was rather big and the amount of particles was small. These particles may slightly

block inner micropores and result in the decrease of micropore volume. When the deposition power was 50 W, the particles became more and the size smaller due to prominent plasma treatment effect and comparatively weaker deposition effect, which developed the micropores. At plasma deposition power of 70 W, it is thought that the plasma deposition effect dominated in the reaction and large amount of deposited allylamine particles were seen. It is reckoned that these thick particles were deposited on the surface of the ACFs and accordingly resulted in the decrease of micropore volume on the ACFs. The above analysis of SEM results are corresponding to the BET results shown in Table 1, and it is believed that, if the deposition power kept increasing, the micropore volume would keep decreasing and block more micropores.

3.2. Surface chemical analysis of ACFs

The surface compositions obtained from FTIR were shown in Fig. 5. It could be seen that in case of the as-received ACFs, the representative peaks are the OH stretching groups at 3400 cm^{-1} and C=C stretching groups at 1640 cm^{-1} shown on curve A. After plasma treatment, the changes of curve B were not so obvious comparing with curve A, which was due to the short time plasma treatment. It was thought that in short treatment time, plasma effect on the surface functional groups of ACFs was not remarkable enough. Therefore, the obvious changes of the plasma treatment were not observed on curve A and B. On the plasma-deposited samples, the plasma treatment time is simultaneously extended and different representative peaks appeared due to the competition of the plasma treatment and deposition. On the curves of C and D, the typical plasma functional groups e.g. C=O stretching at 1724 cm^{-1}, O=C-O stretching at 1385 cm^{-1}, and C-O stretching at 1285 cm^{-1} were clearly seen. It is regarded that,
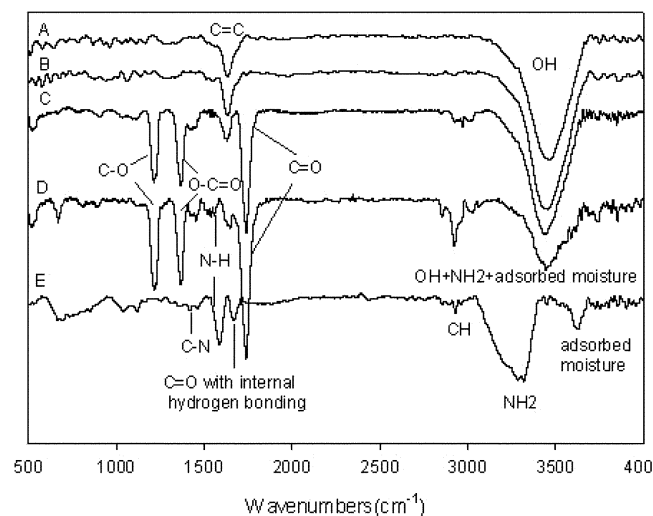

Fig. 5. FTIR spectra of the plasma treated and deposited ACFs.

at plasma deposition power of 30W-50W, the plasma deposition effect was comparatively weak and many functional groups were generated by plasma treatment. On curve C, the peak of OH stretching groups doesn't show large difference with curve B, and the typical peak of amine was not found. Referred to the SEM results in Fig. 4(c), it was analyzed that the effect of plasma deposition was weak and only small amount of polyallylamine particles was formed on the surface, which could not be fully detected by FTIR. On curve D, N-H bending vibration peak at 1550 cm^{-1} was found, revealing the existence of the plasma deposited allylamine on the ACFs. The peak at 3400 cm^{-1} largely decreased on curve D, and this peak was thought to be formed by a combination of the NH$_2$, OH groups and H$_2$O adsorbed in air. On curve E, it was found that the typical plasma treatment functional groups such as O=C-O, and C=O almost disappeared and the representative peaks of amine groups e.g. NH$_2$ shoulder stretching at 3300 cm^{-1}, C-N stretching at 1360 cm^{-1} appeared instead. The representative stretching peak of adsorbed moisture at 3700 cm^{-1} further testified the large amount of immobilized amine groups, which largely improved the surface hydrophilicity of the surface and adsorbed more moisture in air on the ACFs after plasma deposition. This result also indicated that, at plasma deposition power of 70W, large amount of allylamine was deposited on the surface of ACFs, which corresponded with SEM results in Figure 4 and verified the explanations of the BET results in Table 1.

4. Conclusion

The RF low pressure plasma treatment and subsequent deposition were conducted on the KF-1500 ACFs for the chemical and structural modification of surface. It was proved that not only the surface functionalities could be modified through plasma treatment and plasma deposition, but also the micro-structure of the ACFs could be developed with low pressure plasma treatment and subsequent plasma deposition at certain conditions. At relatively low deposition power of 30 W, the plasma treatment and deposition effects were both weak, and at intermediate deposition power of 50 W, the plasma treatment effect is predominant to the deposition effect. At higher plasma deposition power, the plasma deposition dominates in the whole reaction, and large amount of polyallylamine was deposited on the surface of ACFs.

Acknowledgements

Referneces

[1] (a) You, S. Y.; Park, Y. H.; Park, C. R. *Carbon* **2000**, *38*, 1453. (b) Mangun, C. L; Benak, K. R.; Economy, J.; Foster, K. L. *Carbon* **2001**, 39, 1809.

[2] Kawabuchi, Y. J.; Oka, H.; Kawano. S.; Mochida, I.; Yoshizawa, N. *Carbon* **1998**, *36*, 77.

[3] Roh, J. S.; Suhr, D. S. *Carbon science* **2004**, *5*, 51.

[4] Barranco, A.; Cotrion, J.; Yubero, F.; Gonzalez-Elipe, A. R. *Chem. Mater.* **2003**, *15*, 3041.

[5] Chen, Q. D.; Dai, L. M.; Gao, M.; Huang, S. M.; Mau, A. *J. Phys. Chem. B* **2001**, *105*, 618.

[6] Tang, S.; Kwon, O. J.; Lu, N.; Choi, H. S. *Surface and Coatings Technology* **2005**, *195*, 298.

[7] Kwon, O. J.; Tang, S.; Myung, S. W.; Lu, N.; Choi, H. S. *Surf. Coat. Technol.* **2005**, *192*, 1.

[8] Boudou, J. P.; Paredes, J. I.; Cuesta, A.; Martinez-Alonso, A.; Tascon, J. M. D. *Carbon* **2003**, *41*, 41.

[9] Chai, J. N.; Lu, F. Z.; Li, B. M.; Kwok, D. Y. *Langmuir* **2004**, *20*, 10919.

[10] Seo, M. K.; Park, S. J.; Lee, S. K. *J. Colloid Interface Sci.* **2005**, *285*, 306.

[11] Zhang, D.; Dougal, S. M.; Yeganeh, M. S. *Langmuir* **2000**, *16*, 4528.

[12] Dabhade, R. V.; Bodas, D. S.; Gangal, S. A. *Sens. Actuators. B, Chem.* **2004**, *98*, 37.

[13] Kim, J. S.; Kim, Y. E.; Lee, K. H. *J. Colloid and Interface Sci.* **2004**, *271*, 187.

[14] Orfanoudaki, T.; Skodras, G.; Dolios, I.; Sakellaropoulos, G. P. *Fuel* **2003**, *82*, 2045.

[15] Park, S. J.; Kim, B. J. *J Colloid Interface Sci.* **2004**, *275*, 590.

[16] Park, S. J.; Kim, B. J.; Ryu, S. K. *Carbon Science* **2004**, *5*, 103.

[17] Domingo-Garcia, M.; Lopez-Garzon, F. J.; Perez-Mendoza, M. *Carbon* **2000**, *38*, 555.

[18] Choi, H. S.; Kim, Y. S.; Zhang, Y.; Tang S.; Myung, S. W.; Shin, B. C. *Surf. Coat. Tech.* **2004**, *182*, 55.

[19] Gregg, S. J.; Sing, K. S. W. *Adsorption Surface Area and Porosity*; 2nd Edition, Academic Press, Inc., London, 1982.

[20] Lopez, L. C.; Gristina, R.; Ceccone, G.; Ross, I. F.; Favia, P.; d'Agostino, R. *Surf. Coat. Tech.* **2005**, *200*, 1000.

[21] Harsch, A.; Calderon, J.; Timmons, R. B.; Gross, G. W. *J. Neurosci. Meth.* **2000**, *98*, 135.

[22] Gancarz, I.; Bryjak, J.; Marek, B.; Gryzelda, P.; Tylus, W. *Eur. Polym. J.* **2003**, *39*, 1615.