JOURNAL OF MATERIALS SCIENCE 28 (1993) 4731–4734

Antibacterial activated carbon fibre derived from phenolic resin fibre by use of co-graftpolymerization

A. OYA*, M. KIMURA
Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan
T. SUGO, A. KATAKAI
Japan Atomic Energy Institute, Takasaki, Gunma 370-12, Japan
Y. ABE, T. IIZUKA, N. MAKIYAMA
Gun-ei Chemical Industrial Company, Ltd, Takasaki, Gunma 370, Japan

Phenolic-resin fibre was co-graftpolymerized with methyl methacrylate and methacrylic acid. The weight of the fibre increased by 26% after grafting. The grafted fibre was soaked in silver-nitrate solution to introduce silver ion on methacrylic acid in the graft by an ion-exchange reaction, followed by carbonization at 900 °C for 30 min under a nitrogen stream and activation at 900 °C under a steam stream. After activation for 40 min, the resulting fibre showed a silver content of 8.3 wt% a specific surface area of 1300 $m^2 g^{-1}$ and antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli*. The average crystallite size of the silver in this fibre was 30 nm, which suggests co-graftpolymerization is a useful technique to disperse fine silver particles in the activated carbon fibre. After soaking in flowing tap water for 10 and 20 days, this activated carbon fibre lost about 50 wt% of silver but kept its antibacterial activity.

1. Introduction

Fine silver particles have strong antibacterial activity [1, 2]. The present authors have reported on antibacterial activated carbon fibres containing finely dispersed silver particles [3]. Such a dispersion state was attained by mixing both methanol solutions of silver nitrate and spinnable phenolic resin. Since antibacterial activity is generally enhanced by decreasing the silver-particle size, the authors are interested in developing a new technique to disperse fine silver particles in activated carbon fibre.

Iizuka *et al.* [4] have found that activated carbon fibre is prepared favourably from methyl methacrylate (MMA) grafted-phenolic resin fibre. However, Ag^+ cannot usually be introduced into this graft by an ion-exchange reaction, whereas –COOH in methacrylic acid (MAA) is easily ion-exchanged by Ag^+ to convert to –COOAg. So, we thought to co-graftpolymerize the mixture of MAA and MMA into the phenolic-resin fibre and then introduce Ag^+ into the MAA part of the graft by an ion-exchange reaction. The purpose of the present work is to examine whether or not this technique is useful in preparing antibacterial activated carbon fibre, especially from the standpoint of the dispersion of silver particles.

2. Experimental procedure

2.1. Materials

The phenolic resin fibre (average diameter, 14 μm) used was the flame-resistant Kynol fibre produced commercially by the Gun-ei Chemical Company Ltd., further details have been described elsewhere [5–7]. The MMA and MAA were chemical grade and they were used after removal of hydroquinone as a polymerization inhibitor by using activated alumina. The other chemicals are all chemical grade.

2.2. Preparation procedures

A mixture of MMA and MAA (3:2 by volume ratio) was blended with an equal volume of methanol. The phenolic-resin fibre was soaked in a large excess of the resulting solution for one day at room temperature; this was followed by wringing to remain the solution of four-hold weight of the fibre. Next, the fibre was irradiated with an electron beam (3 MeV, 1 mA) by 200 kGy at room temperature under nitrogen. The fibre was then washed with a mixture of methanol and tetrahydrofuran (1:1 by volume ratio) to remove the ungrafted fractions and dryed under vacuum. Finally the fibre was soaked in a large amount of silver nitrate

* All correspondence should to be addressed to A. Oya

0022–2461

solution (1 mol l^{-1}) at room temperature for one day to introduce Ag^+ by an ion-exchange reaction, washed with deionized water and then dried under vacuum.

The grafted fibre (GF) was carbonized at 900 °C for 30 min under a stream of nitrogen. The carbonized fibre (CF) was further activated at 900 °C for 10 min and 40 min under a stream of steam (the partial pressure of steam was ca. 30%). They are denoted by ACF-10 and ACF-40 respectively, in this paper.

2.3. Measurements

Powder X-ray diffraction (XRD) was undertaken by using Ni-filtered CuK_α radiation. A transmission electron microscopy (TEM) and an electron probe X-ray microanalyser (EPMA) were used to observe the physical state of silver in the fibre. The silver content in the fibre was measured by an Inductively Coupled Plasma (ICP) emission spectroscopy. Here the fibre was burned and the residue was dissolved in nitric acid. The Brunauer-Emmett-Teller (BET) specific surface area was measured by a one-point method using the adsorption isotherm of N_2 at 77 K. Mechanical testing of the fibre was performed on an Instron testing machine using a cross-head speed of 0.2 cm min^{-1} and a gauge length of 2.5 cm. Antibacterial tests against *Staphylococcus aureus* and *Escherichia coli* were conducted by the halo method (further details were reported elsewhere [1, 2]. From the practical point of view, the fibre was finally subjected to an effusion test; that is, the antibacterial activity and the silver content of the fibre were examined after soaking in flowing tap water for 10 and 20 days.

3. Results

3.1. Carbonization and activation yields, Ag content, surface area and tensile strength

The weight of the phenolic resin fibre increased by 26.4 wt % after co-graftpolymerization. As shown in Table I, the GF showed 65 wt % and 33 wt % yields after carbonization and 40 min activation, respectively. The Ag content increased from 3.6 wt % for the GF to 5.2 wt % and 8.3 wt % for the CF and the ACF-40. The ACF-40 exhibited a specific surface area of 1300 $m^2 g^{-1}$. The tensile strength of the CF lowered remarkably after activation. The commercially available phenolic resin-based ACF with a 9–10 μm diameter and a specific surface area of 1500 $m^2 g^{-1}$ had a tensile strength of 400 MPa. The fibres before and after activation showed antibacterial activity against both types of bacteria.

3.2. SEM observation

Fig. 1 shows scanning electron microscopy (SEM) photographs of the fibre surfaces. The CF has a smooth surface, though with some dusts attached. Fine pores appeared in the ACF-10 and grew in the

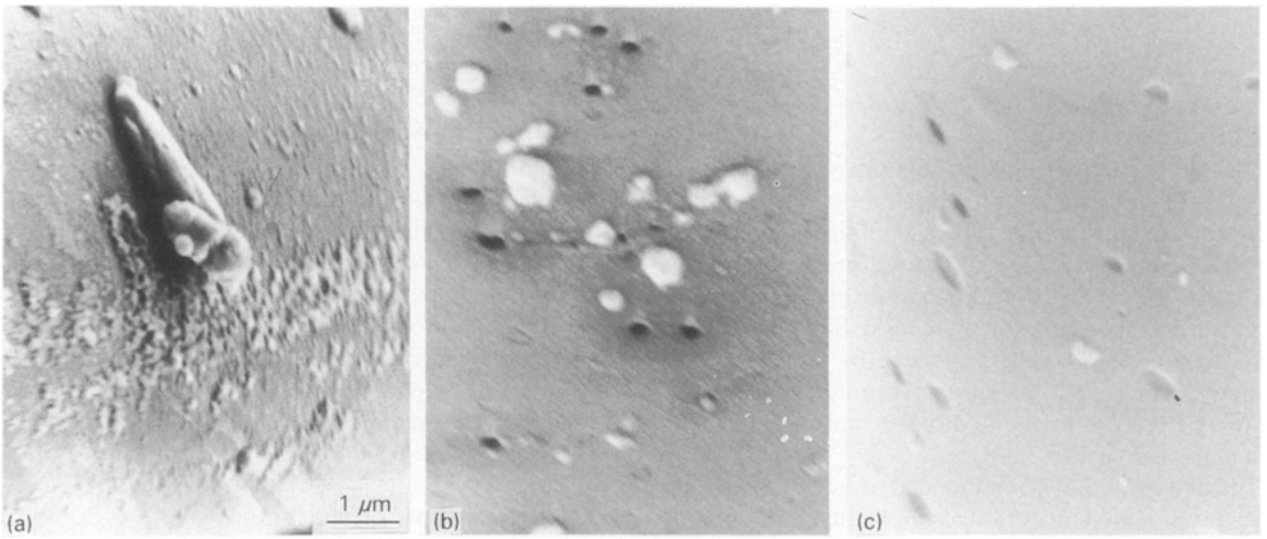

Figure 1 SEM photographs of the fibre surfaces at various stages: (a) CF, (b) ACF-10, and (c) ACF-40.

TABLE I Properties of the fibres

	Yield (wt %)	Ag content (wt %)	Surface area ($m^2 g^{-1}$)	Tensile strength (MPa)	Antibacterial activity	
					E. Coli	*S. Aureus*
GF	100	3.6				
CF	65	5.2	20	530	active	active
ACF-10	60	5.5	210	200	active	active
ACF-40	33	8.3	1300	190	active	active

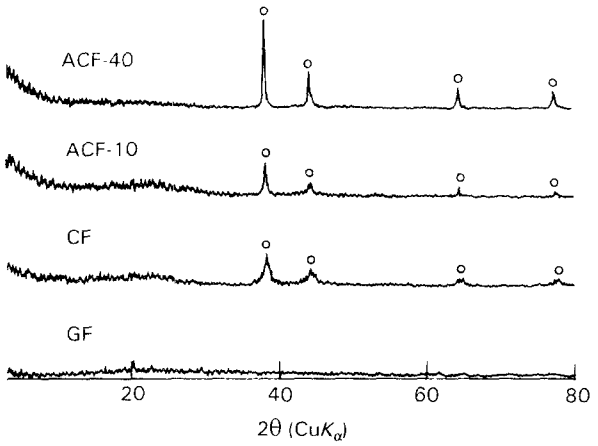

Figure 2 XRD profiles of the fibres at various stages: (○) Ag metal.

ACF-40. These pores must be formed by selective gasification catalysed by impurities on the surface.

3.3. X-ray diffraction

Fig. 2 shows the powder XRD profiles. Peaks of silver metal appeared in the CF and strengthened with proceeding activation. Sherrer's equation using a half band width of the (1 1 1) diffraction peak around 38° gave silver crystallite sizes of 14, 24 and 30 nm for the CF, the ACF-10 and the ACF-40, respectively.

3.4. TEM observation and EPMA

TEM photographs of the fibres are shown in Fig. 3. Many silver particles with sizes around 10 nm were observed in the CF. The silver particles grew somewhat in the ACF-10 and grew remarkably in the ACF-40. The largest reached about 150 nm. Fig. 4 is a SEM and an EPMA photograph of the CF. It is clear that the silver particles dispersed homogeneously throughout the fibre.

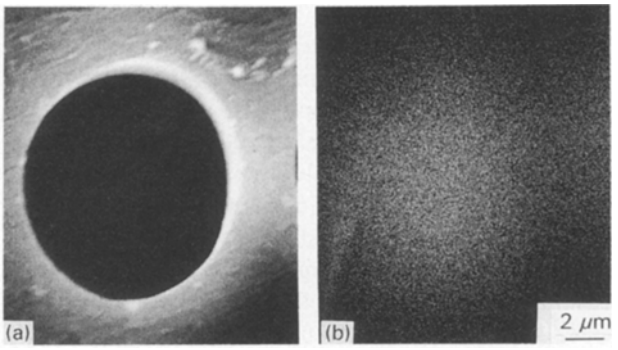

Figure 4 (a) SEM photograph, and (b) AgK_α image of the carbonized fibre (CF).

TABLE II Ag content and antibacterial activity before and after the effusion test

	Soaking time (days)	Ag content (wt %)	Antibacterial activity	
			E. Coli	*S. Aureus*
CF	0	5.2	active	active
	10	5.0	active	active
	20	3.6	active	active
ACF-10	0	5.5	active	active
	10	5.9	active	active
	20	2.9	active	active
ACF-40	0	8.3	active	active
	10	4.1	active	active
	20	6.4	active	active

3.5. Effusion test

Table II shows the silver content and antibacterial activity of the fibres after the effusion test. Although Table II shows some scatter, the removal of a relatively large amount of silver during soaking is real. After the effusion test, all fibres exhibited antibacterial activity against both types of bacteria.

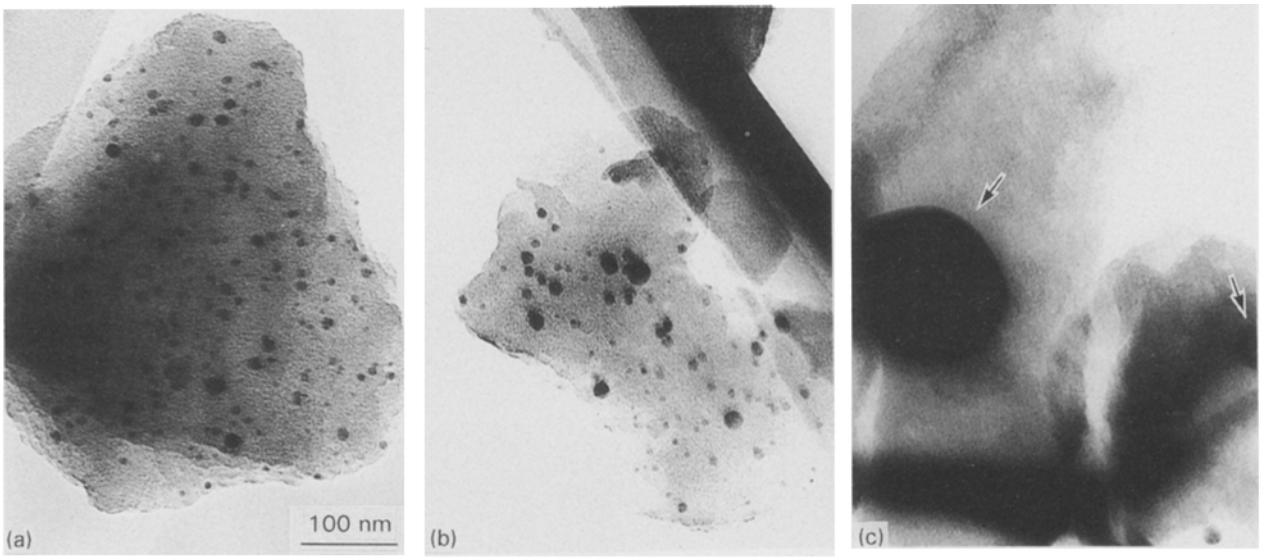

Figure 3 TEM photographs of the fibres at various stages: (a) CF, (b) ACF-10, and (c) ACF-40.

4. Discussion

The present authors are interested in preparing activated carbon fibres containing finely dispersed silver particles which exhibit strong antibacterial activity. As noted above, the antibacterial activated carbon fibre (AACF) has been previously prepared from the phenolic resin containing finely dispersed $AgNO_3$ [3]. The resulting carbonized fibre showed 0.67 wt % Ag and a specific surface area of 16 $m^2 g^{-1}$. After activation for 10 min and 60 min using the same method as used here, these values changed to 0.69 wt % and 280 $m^2 g^{-1}$, and 2.20 wt % and 1940 $m^2 g^{-1}$. Crystallite sizes of silver increased from 38 nm after carbonization to 51 nm and 52 nm after activation for 10 min and 40 min respectively. It is reasonable to consider that, in general, silver particles grow more favourably in fibres with a higher Ag content by heating. The carbonized fibre in the present work has a five times larger Ag content than in previous work [3]. Nevertheless, the former contained smaller silver crystallites. This suggests that co-graftpolymerization is a useful technique to disperse fine silver particles in the ACF.

However, the difference between the crystallite sizes of silver in the fibres in the previous and present works became smaller as carbonization and activation proceeded, which is reasonably explained by a preferential growth of silver crystallite in fibres with larger Ag content. Therefore, the co-graftpolymerized phenolic-resin fibre must be carbonized and activated at as low a temperature and in as short a time as possible in order to keep the fine silver particles in the ACF.

Another point to be noticed is that the AACF prepared in the present work has too large a silver content for practical use. Antibacterial activity is needed in the ACF but not in the CF. As suggested from the results of the effusion test, AACF with a high Ag content may cause pollution by the released silver.

The fractional ratio of MAA in the graft was not determined. However, since only MAA can ion-exchange with Ag^+, it is possible to deduce Ag content in the fibre by lowering the ratio of MAA in the MAA–MMA mixed solution, which means a large fractional part of MMA. The MMA-grafted phenolic-resin fibre favour the preparation of ACFs with a large surface area [4]. Another method to deduce Ag content is to shorten the soaking time of the GF in the MAA–MMA mixed solution. However, this may result in the supporting of silver only the fibre surface. These studies are now in progress.

Acknowledgement

The authors wish to thank Daiwa Chemical Company, Ltd for the antibacterial test.

References

1. A. OYA, T. BANSE, F. OHASHI and S. OTANI, *Appl. Clay Sci.* **6** (1991) 135.
2. A. OYA, T. BANSE and F. OHASHI, *Appl. Clay Sci.* **6** (1992) 311.
3. A. OYA, S. YOSHIDA, Y. ABE, T. IIZUKA and S. MAKIYAMA, *Carbon* **31** (1993) 71.
4. T. IIZUKA, Y. ABE, S. MAKIYAMA, M. SHIMADA, S. TAKIGAMI and Y. NAKAMURA, *Sen-i Gakkai Symp.* Preprint (1989) S-83.
5. F. S. HAYES, Jr, in "Kirk-Othmer: Encyclopedia of chemical technology", Vol. 16, 3rd Edn (John Wiley & Sons, New York, 1981) p. 125.
6. Y. ARITA, D. ARITA, R. FUJII, F. OGATA and M. IRISAWA, *Chemtech* (1989) 424.
7. Japanese Patent Publication 43911 (1978).

Received 30 April 1992
and accepted 3 February 1993