Efficiently Activated Carbon Fiber Derived from Grafted Novoloid Fiber

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SYNOPSIS

Graft copolymerization of methyl methacrylate onto novoloid fiber was carried out by the electron beam mutual irradiation method. The characteristics of the grafted fiber were almost the same as those of the original novoloid fiber. The grafted fiber was carbonized and activated to yield an efficiently activated carbon fiber. The yield and the specific surface area of the activated carbon fiber, derived from the grafted novoloid fiber, were much greater than those derived from the original novoloid fiber. This is because grafted poly(methyl methacrylate) decomposes into monomer and gaseous products, forming pores on the surface and inside of the novoloid fiber on heating. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Novoloid fiber is a type of phenol fiber that is derived from phenol and formaldehyde under acidic conditions. The fiber turns into a carbon fiber when burnt, generating a small amount of gas. The activated carbon fiber, from the novoloid fiber, has excellent characteristics, including high adsorption ability, high tensile strength, strength for twist, and high pliability. If such an activated carbon fiber is obtained in a high yield, the application of the fiber will increase.

The effects of inorganic compounds, such as alkali metals, alkaline earth metals, iron, cobalt, nickel, and their salts, on the yield of activated carbon were widely examined and these additives showed excellent catalytic abilities in order to produce activated carbon fibers with high efficiency.[1-6] Since the metal compounds remain in carbon fibers after activation, the fibers cannot be used as adsorbents in liquid systems.

Poly(methyl methacrylate) is known as a typical polymer, which is decomposed into a monomer in high yield when heated.[7-9] The polymer is completely decomposed into gaseous products and leaves nothing if decomposed at 900°C.

Poly(methyl methacrylate), grafted onto the novoloid fiber, is expected to be decomposed into its monomer and gaseous products, making pores on the surface and inside of the novoloid fiber, and it is expected to leave nothing. As a result, an activated carbon fiber with high specific surface area is expected from the methyl methacrylate grafted novoloid fiber, with a higher yield than those derived from the novoloid fiber without grafting. It is also expected that the activated carbon fiber will be used for liquid systems.

EXPERIMENTAL

Materials

A commercial novoloid fiber, Kynol (KF-0270M), produced by Gun-ei Chemical Industry Co., Ltd., was used in the experiment. The diameter of the fiber was 14 μm.

Methyl methacrylate (MMA) was purified by passing the monomer through a column filled with activated aluminum oxide. Other reagents were used without further purification.

Graft Copolymerization

The novoloid fiber was dried under reduced pressure and was weighed. The fiber was then immersed in a mixture of MMA and methanol at room temperature for 1 h. The excess solution on the fiber was removed by squeezing the sample with glass rods to give a wet pick-up of 300%. The sample was packed in a polyethylene bag and nitrogen gas was introduced into the bag. The sample was irradiated with electron beams at a dose rate of 1×10^3 Gy/sec for 200 sec at 35°C. After irradiation, the sample was extracted with hot acetone for 15 h to remove homopolymer. The sample was dried under reduced pressure and was weighed. The extent of grafting was calculated as follows:

$$\text{Extent of Grafting (\%)} = \frac{W_G - W_0}{W_0} \times 100$$

where W_0 and W_G are the weights of the sample before and after graft copolymerization, respectively.

The ratio of MMA and methanol was changed and the graft copolymerization reaction was carried out in a similar manner.

Carbonization

The carbonization of the sample was carried out in an apparatus as shown in Figure 1. The nitrogen stream was introduced into an electric oven through route a at a flow rate of 180 mL/min, and the temperature of the electric oven was raised at a rate of 5°C/min. The sample was heated to 900°C, was maintained at the temperature for 30 min, and then was cooled gradually under nitrogen atmosphere. Thus, a carbonized fiber was obtained.

The yield of the carbon fiber was calculated in the following two ways:

Yield of carbon fiber based on weight

$$\text{of novoloid fiber (\%)} = \frac{W_C}{W_0} \times 100$$

Yield of carbon fiber based on weight

$$\text{of grafted fiber (\%)} = \frac{W_C}{W_G} \times 100$$

where W_C is the weight of the carbon fiber after the carbonization.

Activation of Carbonized Fiber

The carbonized fiber was activated using the same apparatus as shown in Figure 1. The carbonized fiber was heated to 900°C in dry nitrogen stream through route a; nitrogen gas was then introduced into hot water (80 ± 1°C) through route b at a rate of 450 mL/min. The steam was brought by nitrogen and it activated the carbonized fiber for 40 min. The water content of the stream was 33 vol %. Dry ni-
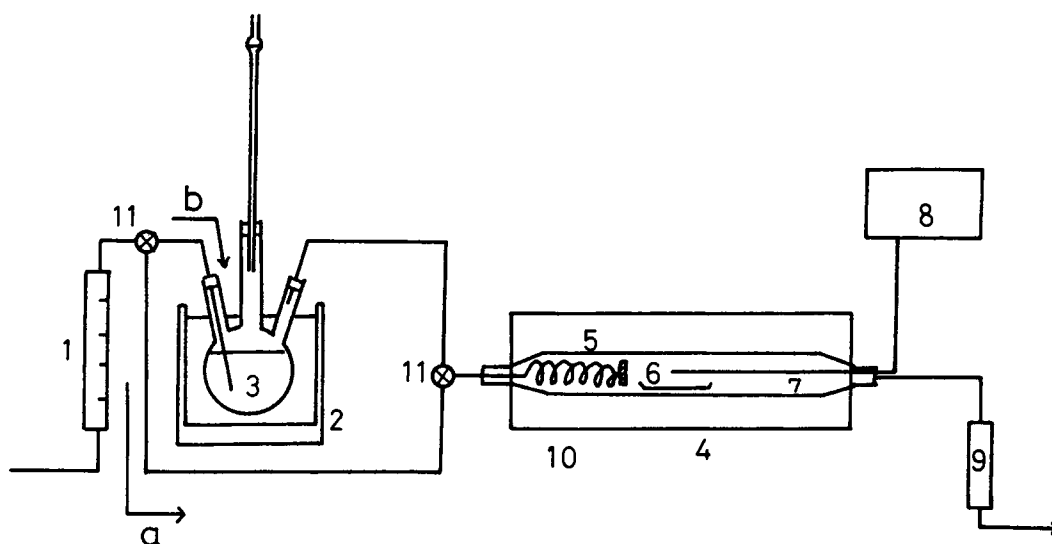

Figure 1 Apparatus for carbonization and activation of sample. (1) Flow meter, (2) oil bath, (3) water, (4) electric oven, (5) quartz tube, (6) sample holder, (7) thermocouple, (8) temperature controller, (9) trap, (10) quartz filter, (11) three-way cock. For carbonization and activation, nitrogen was introduced through route a and b, respectively.

trogen gas was then introduced through route a at a rate of 50 mL/min in order to cool the fiber. The activated carbon fiber was then weighed.

The yield of the activated carbon fiber was calculated in two ways; one was based on the weight of the novoloid fiber before grafting and the other was based on weight of the carbon fiber before activation.

Measurement of Physical Properties

Diameters of the fibers, before and after the graft copolymerization and the carbonization, were measured with a Search denier computer Model DC-11B (Search, Japan).

Specific surface areas of the carbonized and the activated samples were measured with a Micromeritics Flow Sorb Model 2300 II (Micromeritics, USA).

Surfaces of the samples, before and after graft copolymerization, carbonization, and activation, were observed with a JEOL Scanning Electron Microscope, Model JSM T 220 A (JEOL, Japan).

Tensile strength of the grafted and the carbonized fibers was measured by an Orientech TENSILON Model RTM-25 (Orientech, Japan).

RESULTS AND DISCUSSION

Graft Copolymerization of MMA on Novoloid Fiber

The extent of grafting onto the novoloid fiber, by the mutual irradiation method, depended on the composition of the monomer solution as shown in Figure 2. The graft copolymerization reaction by the post irradiation method was also performed, but little weight increase was observed.

Scanning electron micrographs, before and after the grafting reaction, are shown in Figure 3. A novoloid fiber, with 21.7% extent of grafting, showed a thicker diameter by 10% as compared with that
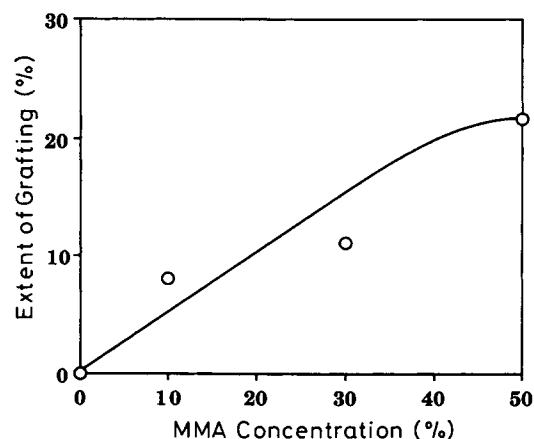

Figure 2 Effect of monomer concentration on extent of grafting.

of the original novoloid fiber. Therefore, it is considered that poly(methyl methacrylate) (PMMA) was introduced not only on the surface but also inside the fiber by the grafting reaction.

The relations between the extent of grafting and tensile strength are summarized in Table I. Graft copolymerization did not change the tensile strength per filament, but decreased that per denier. The phenomena can be explained by the increase of filament diameter by the graft copolymerization. As grafted PMMA is unoriented and amorphous, it has little effectiveness in increasing strength.

Carbon Fiber Derived from Grafted Novoloid Fiber

The yield of the carbon fiber from the grafted fiber is shown in Figure 4. The yield, calculated from the weight of the grafted novoloid fiber, decreased as the extent of grafting increased. This is because PMMA, introduced as a branch polymer on the novoloid fiber, is easily decomposed into monomer and gaseous products on heating, as compared with the novoloid fiber. The yield, based on the original

Table I Tensile Strength of Grafted Fiber

Sample: Extent of Grafting (%)	Tensile Strength	
	Per Filament (g)	Per Denier (g/d)
0	3.39	1.58
8.1	3.43	1.51
11.1	3.55	1.51
21.7	3.46	1.42

Table II Tensile Strength of Carbon Fiber

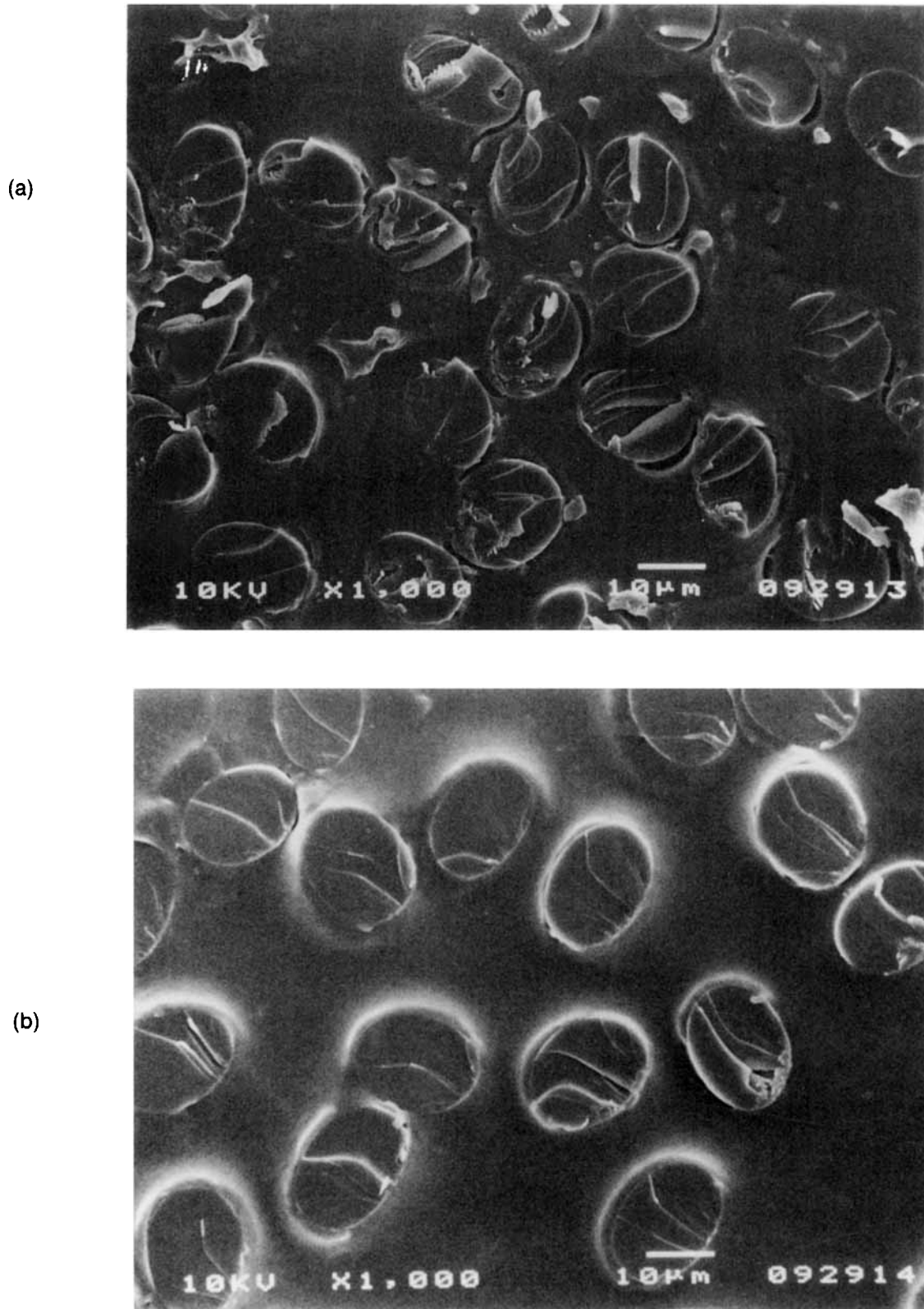| Sample: Extent of Grafting (%)	Tensile Strength	
	Per Filament (g)	Per Denier (g/d)
0	5.18	3.10
8.1	5.12	2.83
11.1	5.15	3.20
21.7	4.90	2.74

Figure 3   Scanning electron micrographs. (a) Novoloid fiber, (b) grafted novoloid fiber with 21.7% extent of grafting.
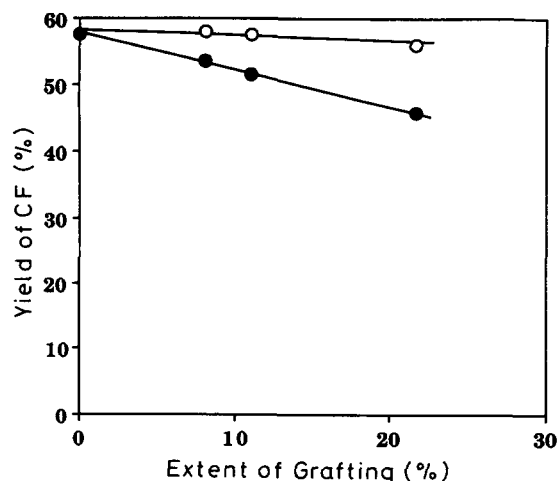
Figure 4 Yield of carbon fiber from grafted fiber. (O) Calculated on the basis of novoloid fiber, (●) calculated on the basis of grafted fiber.

weight of the novoloid fiber, is almost the same, regardless of the extent of grafting. This means that PMMA decomposes into the monomer and gaseous products and does not affect the carbonization yield of the novoloid fiber.

The pores, which might be on the surface of the novoloid fiber due to the grafting of MMA and the decomposition of PMMA by heating, were not observed on scanning electron micrographs. No difference was observed between the carbon fibers derived from the novoloid fiber and the grafted fiber.

The specific surface area of the carbonized fiber from the novoloid fiber was about 1.2 m^2/g, while that from the grafted fiber, with the 21.7% extent
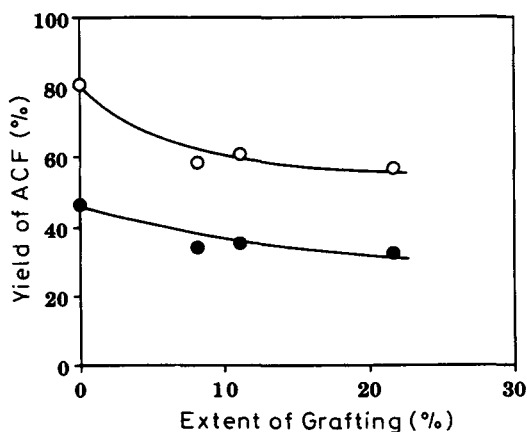

Figure 5 Yield of activated carbon fiber derived from grafted fiber. (O) Calculated on the basis of novoloid fiber, (●) calculated on the basis of carbon fiber. Carbon fiber was derived from grafted novoloid fiber.
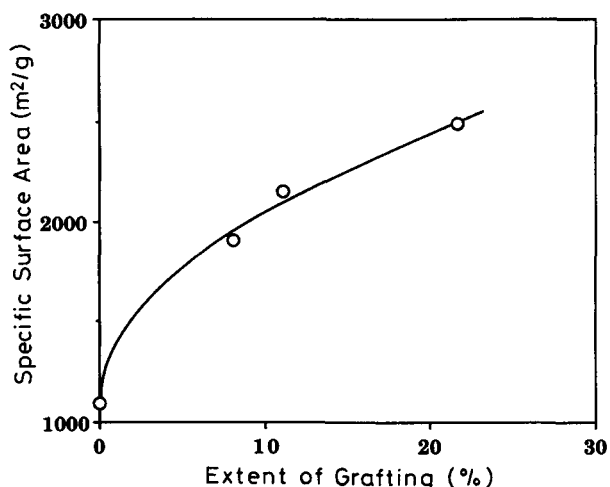

Figure 6 Effect of grafting on specific surface area.

of grafting, was 100 m^2/g. Therefore, it can be said that the grafted PMMA deposits not only on the surface, but also inside of the novoloid fiber.

The tensile strength of the carbon fiber derived from the grafted novoloid fiber is shown in Table II. The strength did not change much by the grafting reaction, except for the fiber with the extent of grafting of 21.7%. PMMA is decomposed into the monomer almost completely by heating to 300°C,[7-9] while the novoloid fiber begins to decompose at 338.5°C.[10] Therefore, the grafted PMMA is decomposed into the monomer and gaseous products, making pores in the novoloid fibers during the carbonization reaction. The amount of the monomer generated increases with the extent of grafting. Therefore, the carbonized fiber, derived from the 21.7% grafted fiber, became porous and weak in strength.

Activated Carbon Fiber Derived from Grafted Novoloid Fiber

The yield of the activated carbon fiber (ACF), derived from the grafted novoloid fiber, is shown in Figure 5, on the bases of the original novoloid fiber and carbon fiber. The yield decreases on both bases as the extent of grafting increases. As the activation conditions were the same for all samples, the structure of the carbon fiber derived from the grafted fiber has a great effect on the yield; if the carbon fiber has a porous structure, the yield of the activated carbon fiber will be low because steam is distributed quickly into the carbon fiber through the pores. However, the pores were too small to be observed on scanning electron micrographs.
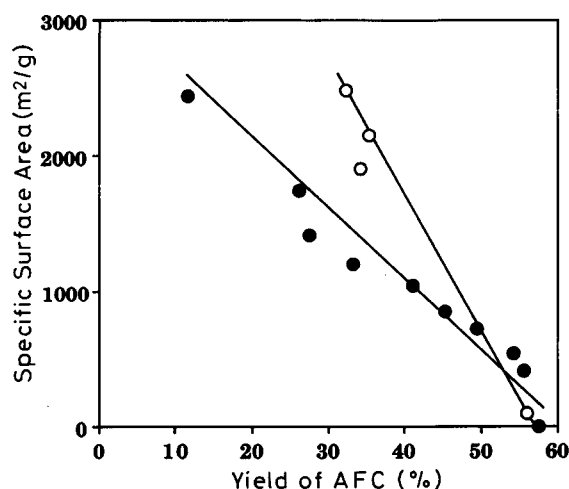
Figure 7 Relation between yield of activated carbon fiber, calculated on the basis of novoloid fiber and specific surface area. (O) Activated carbon fiber (ACF) derived from grafted novoloid fiber, (●) activated carbon fiber derived from novoloid fiber.

As the extent of grafting increases, the specific surface area of the activated carbon fiber increased, as shown in Figure 6. The results show that the grafted PMMA deposited not only on the surface, but also inside of the novoloid fiber. The PMMA decomposed into the monomer and gaseous products, and made pores on the surface and inside of the novoloid fiber on heating. The more the PMMA deposits, the more the total volume of pore will be. Though the total volume did not affect the yield of the activated carbon fiber much, it affected the specific surface area of the activated carbon fiber. Therefore, the nature of the carbon fiber before activation affects the nature of the activated carbon fiber.

Effective Way to Produce Activated Carbon Fiber

The relations between the yield based on the weight of the novoloid fiber and the specific surface area of the activated carbon fiber, derived from the novoloid

fiber and grafted fiber, are shown in Figure 7. The activation time for the carbon fiber, derived from the novoloid fiber, was changed to give activated carbon fibers with different specific surface areas. The activation conditions for the carbon fibers, derived from the grafted fiber, were the same for all samples. As the yield decreases, the specific surface area increases linearly in both series. However, the slopes of both lines are different; the carbon fibers, derived from the grafted samples, showed a steeper slope than the carbon fibers from the novoloid fibers. The specific surface area of the activated carbon fiber, derived from the grafted fiber, was much larger than that obtained from the novoloid fiber, if activated under the same conditions. This means that the graft copolymerization of MMA onto the novoloid fiber is effective in producing the activated carbon fiber with a large specific surface area and high efficiency. In other words, the process is energy conservative.

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