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Preparation of thin carbon fibers from waste wood-derived phenolic resin

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As is well-known, development of effective utilization techniques for waste wood is important from not only economical but also environmental point of view. Simple techniques as used in charcoal preparation have been predominantly used until now, and they have not brought about marked development in this field [1]. Even activated charcoal is in a similar serious situation [2]. We have thought that advanced techniques, leading to high price products, are required to enlarge the utilization fields of waste wood. This is why we are attempting to synthesize waste wood-based phenolic resin [3] and to derive advanced carbon materials from it. As reported previously, a phenolic resin (BPF) was synthesized by using phenol, of which one-third was replaced with cornstarch as a model material of waste wood, and carbon fibers were derived from it [4]. However, the carbon fibers included many pores of several hundreds nm in diameter, which were formed by catalytic gasification by MgO particles used as a neutralizer in synthesis of the phenolic resin. The details of synthesis procedure were reported elsewhere [4]. The resulting carbon fibers showed so poor mechanical properties as predicted from the porous structure that they were converted into activated carbon fiber, because activated carbon fibers are not so strongly required to have such properties [5].

On the basis of the above results, the present work was carried out to examine the following four possibilities: (i) to replace MgO particles by imidazole ($C_3H_4N_2$) to suppress the pore formation, because imidazole decomposes with no residue at carbonization process, (ii) to replace cornstarch by waste wood, (iii) to prepare thin carbon fibers as an advanced carbon material instead of conventional carbon fibers, (iv) to convert the resulting thin carbon fibers into activated carbon fibers.

A phenolic resin (WPF) was synthesized in Fuji Carbon Co. by using imidazole and waste wood powder instead of MgO particles and cornstarch, respectively, according to the same procedures reported elsewhere in detail [4]. The wood powder from American pine was supplied by a lumbermill. Thin carbon fiber was prepared by “polymer blend method”, the idea of which was explained elsewhere [6, 7]. The resulting WPF was dissolved into methanol and then subjected to spray-drying at 105 °C. As seen in Fig. 1, the particles were quite irregular in shape and their sizes ranged from several hundreds nm to 7 μm. The particles were dispersed in a toluene solution of high density polyethylene (HDPE), followed by evaporation of toluene with a rotary evaporator at 60 °C. The blending ratio of WPF:HDPE was controlled to be 3:7 by weight. The polymer blend was homogenized mechanically with a Laboratory Mixing Extruder (Atlas Electric Devices Co.), and then subjected to continuous melt-spinning at 165–185 °C, stabilization in an acid solution containing HCOH and HCl as main components and finally carbonization in a N_2 atmosphere at 1000 °C for 1 hr. A part of the thin carbon fibers was further activated at 800 °C for 30 min under steam to make clear the characteristic porous against those of conventional activated carbon fibers.

Fig. 2 shows SEM photographs of the stabilized polymer blend fibers. The fiber diameter was several tens of μm wide and far larger than those derived from BPF reported in the previous paper [4]. The stabilized polymer blend fibers were rigid and were broken easily by bending. The streaks on the surface (arrowed in Fig. 2a) may be attributable to the rigidity of WPF. An enlarged photograph of the fiber surface showed cracks which extended vertically to the fiber axis (arrowed in Fig. 2b). The length was less than 5 μm. The cracks must be formed by a larger shrinkage at the surface than the inside of the fiber in the stabilization process. The rigidity of WPF must be another cause.

Fig. 3 shows WPF-derived thin carbon fibers left after the removal of HDPE during the carbonization process. The fiber diameters were 1 μm with some scatter (Fig. 3a). Fig. 3b shows a TEM photograph of the thin carbon fiber. The similar surface was also observed in

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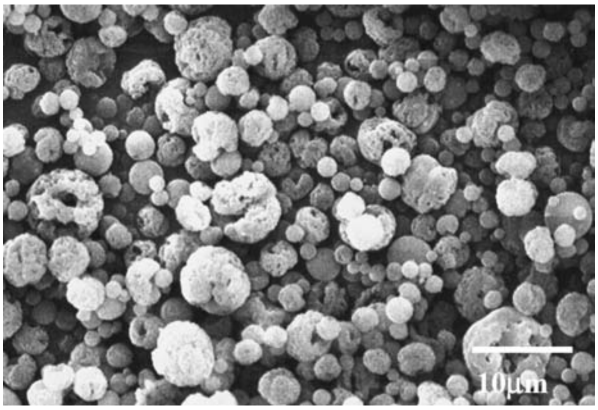

Figure 1 SEM photograph of WPF particles prepared by spray-drying.

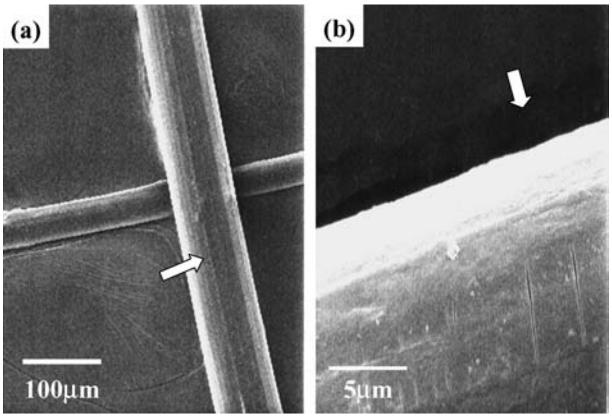

Figure 2 SEM photographs of WPF/HDPE polymer blend fibers after stabilization.

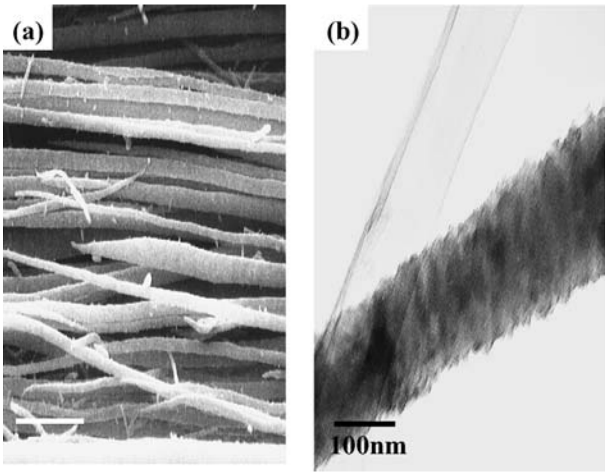

Figure 3 SEM photograph (a) and TEM photograph (b) of thin carbon fibers derived from WPF.

the non-graphitizing thin carbon fibers prepared from a commercially available phenol-formaldehyde resin [6]. One cannot expect high mechanical properties for the fibers shown in Fig. 3. Here it should be emphasized that no pores of several hundreds nm were observed in the thin carbon fibers, which was expected by replacing MgO particles by imidazole.

TABLE I Pore parameters of thin carbon fibers, before and after activation, derived from WPF

Sample	BET-SSA ($m^2\ g^{-1}$)	W ($cm^3\ g^{-1}$)	DH-PV ($mm^3\ g^{-1}$)	DH-SSA ($m^2\ g^{-1}$)
WPF-TCF	13	0.0031	31	17
WPF-ACTF	1048	0.42	120	129

Table I summarizes some data on porous structures of the thin carbon fibers, before and after the activation, obtained from N_2 absorption/desorption isotherm at 77 K. The thin carbon fibers before activation showed a small BET-specific surface area of 13 m^2/g, but the specific surface area increased drastically to 1048 m^2/g after the activation. This change is reasonably explained by the increase of micropore volume (W) after the activation. Mesopore surface area (DH-SAA) and mesopore volume (DH-PV) were calculated by using the DH method [8]. An interesting phenomenon was that mesopores formed favorably through the activation as seen in Table I [6]. WPF can be used as a unique precursor of mesoporous carbons different from conventional wood.

The results obtained in this work are summarized as follows: (i) imidazole used instead of MgO particles was effective in suppress pore formation, (ii) waste wood could be used as a raw material for phenolic resin, but the resulting resin was somewhat too rigid to spin smoothly, (iii) thin carbon fibers could be prepared from the waste wood-derived phenolic resin, (iv) the carbon fibers resulted favorably in the activated carbon fibers with mesopores. The present work suggested clearly a trigger to synthesize a phenolic resin by using waste wood and to use it as a precursor of advanced carbon materials. This is a preliminary work and many novel ideas will be required to complete the present work in future. Nevertheless, the present authors firmly believe that such a unique and challengeable work must be attempted actively to enlarge fields of utilization of waste wood.

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