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Preparation of carbon fibers from biomass-based phenol-formaldehyde resin

C. YOSHIDA, K. OKABE
Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan
T. YAO, N. SHIRAISHI
Fuji Carbon Co. Ltd., Kohka, Shiga 520-3401, Japan
A. OYA*
Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan
E-mail: oya@chem.gunma-u.ac.jp

The work was carried out to get information how to use wasted biomass, particularly waste woods, as a raw material for fine and advanced carbon products. A phenol-starch-formaldehyde resin was synthesized by using phenol of which one third was replaced by cornstarch as a model material for waste wood. The resin was spun, stabilized and finally carbonized at 900°C. A commercial novolac-type phenol-formaldehyde resin was used as a reference. There was no essential difference in the microscopic structures between the carbon fibers derived from the synthesized and the commercial resins, but the former resin showed some disadvantages against the latter: one is a poor spinnability to result in thick and irregular carbon fibers, and another one is the formation of macropores in the resulting carbon fibers, leading to low mechanical strength. These disadvantages are thought to be caused by the remaining MgO particles used as a neutralization agent in the synthesis of the resin. A possibility to achieve the final purpose is discussed briefly.

1. Introduction

Waste wood is mostly disposed of by burning or landfilling. Only a small part is converted to charcoal which is used primitively as a soil conditioner, a humidity controller, a water purifier for rivers and ponds, in addition to the use as a fuel. In order to increase the use of waste wood, novel utilization methods must be developed. Since waste wood can be thought of as a kind of natural polymer material, we suppose that it can be used as a raw material for advanced products.

We have developed such fine carbon materials as antibacterial activated carbon fibers [1], very thin carbon fibers [2], carbon nanotubes [3] etc. from commercially available novolac-type phenol-formaldehyde resin. Recently a novolac-type phenolic resin was developed from biomasses such as waste wood [4]. It would be very interesting if it could be used as a raw material for advanced carbon products. However, the presence of a small amount of unreacted wood in the waste wood-derived phenolic resin brought about difficulty in the spinning for the preparation of carbon fiber. In a preliminary study, phenolic resin was developed from starch which was used in part instead of phenol, and it was used successfully to prepare carbon fibers. The present paper describes the structure and mechanical strength of the resulting carbon fibers. Of course, our final target is to develop fine and advanced carbon materials by using a phenolic resin prepared from waste wood, but the present study using cornstarch instead of waste wood gave an important clue how to complete the target.

2. Experimental

2.1. Raw materials and synthetic procedure of resin

Cornstarch powder with a chemical structure as shown in Fig. 1 was mixed with phenol containing 1.5 wt% H_2SO_4 as a reaction catalyst. The ratio was cornstarch/phenol = 1/3 by weight. The mixture was liquefied by holding at 150°C for 30 min with stirring. Possible chemical structures of the resulting compounds are shown in Fig. 1. The unreacted phenol was analyzed quantitatively by high performance liquid chromatography, from which the ratio of starch/phenol for the resulting resin was determined to be 0.85 by weight. One-third of the sulfuric acid in the reaction mixture was neutralized with NaOH solution.

Subsequently, formaldehyde as a cross-linking agent was added to the solution by 1.2 times the molar quantity of unreacted phenol and was heated to 80°C for 60 min to convert the unreacted phenol to resin. The solution was neutralized with MgO and finally

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*Author to whom all correspondence should be addressed.

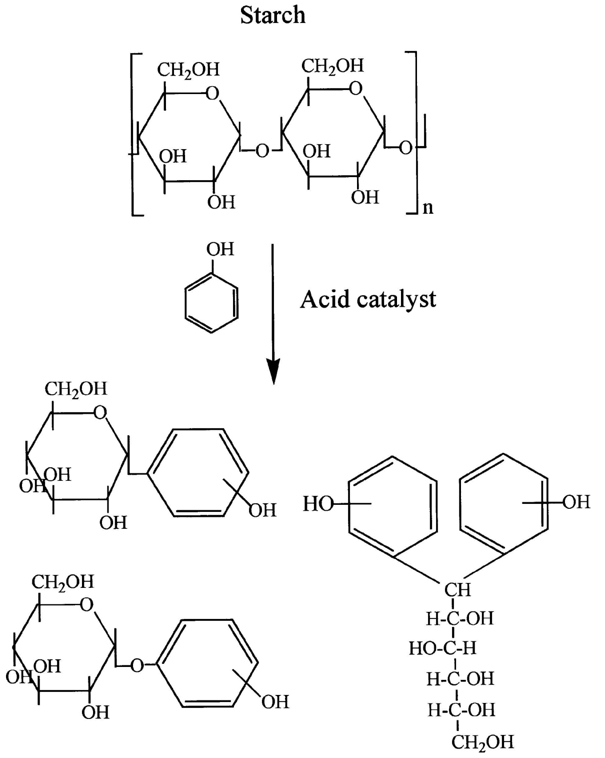

Figure 1 Chemical structure of starch and possible chemical structures of BPF resin.

concentrated in vacuum at 120°C to remove the remained unreacted phenol. The resulting resin is noted as BPF resin in the text.

2.2. Preparation of carbon fiber

BPF resin was spun centrifugally, stabilized by soaking in an acid solution containing HCHO and HCl as main components at 95°C for 24 h, neutralized with aqueous ammonia, washed with deionized water and finally dried. These procedures were reported in more detail elsewhere [1].

The stabilized fibers were carbonized at 900°C for 1 h in a nitrogen atmosphere, and parts of this material were further heat-treated at 2000°C under vacuum and at 3000°C in an Ar atmosphere for 1 h. The fibers are designated as BPF followed by the heat-treatment temperature, e.g., BPF-900 means the BPF resin-derived carbon fiber heated at 900°C. A commercially available novolac-type phenol-formaldehyde resin (PF resin) was used as a reference. The preparation procedures of carbon fiber are the same as those used for BPF resin.

2.3. Measurements

Thermogravimetric (TG) analysis was carried out with a Rigaku Thermo plus TG8120 instrument with a heating rate of 5°C/min in a nitrogen atmosphere. Structural change of the fibers by heat-treatment was traced with a Nicoletmagna-IR550 spectrometer and a Rigaku X-ray diffractometer. The fibers were also observed with a scanning electron microscope JSM-5300 and a transmission electron microscope Jeol JEM1200EXS. Specific surface area was obtained from a nitrogen adsorption isotherm taken at 77 K with a Belsorp 28SA. Tensile strength was measured with Orientec STA-1150 instrument under a span distance of 5 mm and a crosshead speed of 0.5 mm/min. The data shown are average value for 20 fibers.

3. Results

3.1. IR spectra

Fig. 2a and b shows IR spectra of PF- and BPF-fibers after stabilization and heated at 200 and 300°C. The most distinct differences between the spectra of both fibers

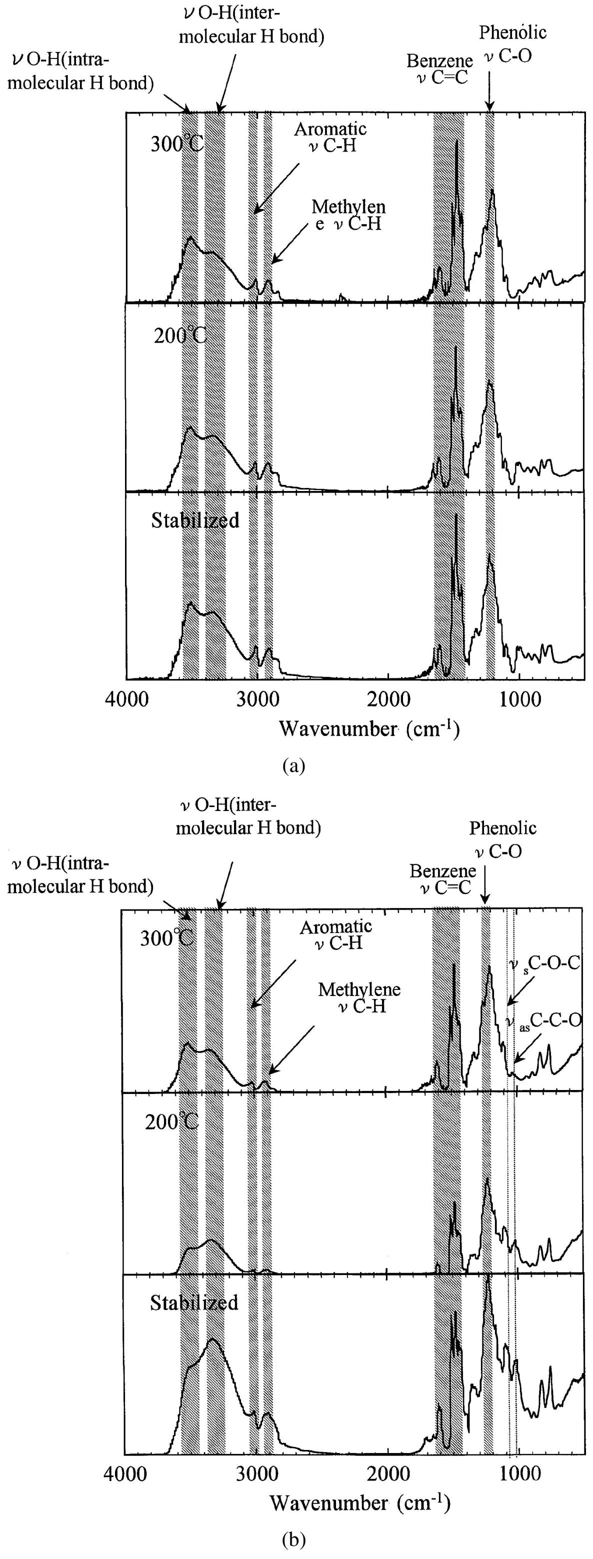

Figure 2 IR spectra of PF (a) and BPF (b) resins after stabilization and carbonization at 200 and 300°C.

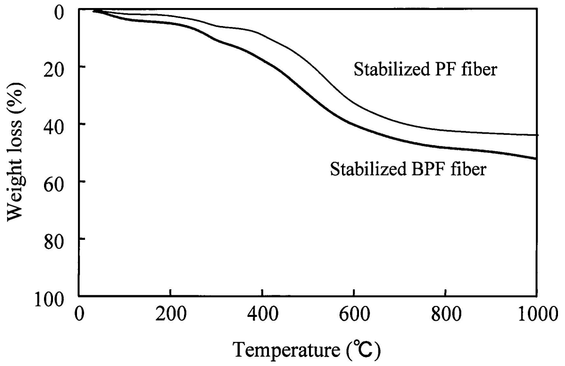

Figure 3 TG curves of stabilized PF and BPF fibers.

is appearance of two absorptions assignedto ν_sC—O—C and ν_{as}C—C—O with the BPF-fiber which did not appear the PF fiber. Both absorptions are attributable to glycoside structure introduced from cornstarch and, therefore, BPF resin is supposed to have a structure in which the compounds shown in Fig. 1 were cross-linked with formaldehyde in the same manner as in the conventional phenol-formaldehyde resin [5]. Both absorptions became weak at 200°C and almost disappeared at 300°C.

3.2. TG measurement

As shown in Fig. 3, both stabilized fibers showed similar TG curves. A small and a large weight loss were observed below 250°C and at 250–700°C, respectively. The stabilized BPF-fiber showed slightly larger weight losses around 100 and 250–400°C than the PF-fiber. Weight loss at 1000°C was 43 and 51% for the stabilized PF- and BPF-fibers, respectively.

3.3. SEM observation

Fig. 4 shows SEM photographs of BPF-1000 and PF-1000. The BPF fibers were thicker and varied more widely in the diameter. This resulted from a poor spinnability of the BPF resin. BPF resin must have included some infusible fine particles as suggested from irregular sites observed in BPF-1000.

Fig. 5 shows SEM photographs of the fiber surface (a) and cross section (b) of PF-1000. The fiber surface was smooth, and a conchoidal pattern characteristic for an amorphous structure was observed in the cross-section. SEM photographs of fiber surface and cross section of BPF-1000 are shown in Fig. 6. As can be seen from Fig. 6a, the surface was not smooth because of included infusible particles. Both sites marked by arrows must include relatively large infusible particles. The cross section shown in Fig. 6b showed a conchoidal pattern as indicated by an arrow, though not so clear as in PF-1000. It should be emphasized that many fine pores are observed in the cross section, mainly around the center of the cross-section.

Fig. 7 shows SEM photographs of the cross sections of BPF fibers before and after stabilization. The former showed a smooth cross section, but many pores were developed after stabilization. It is clear, therefore, that the macropores developed during the stabilization process.

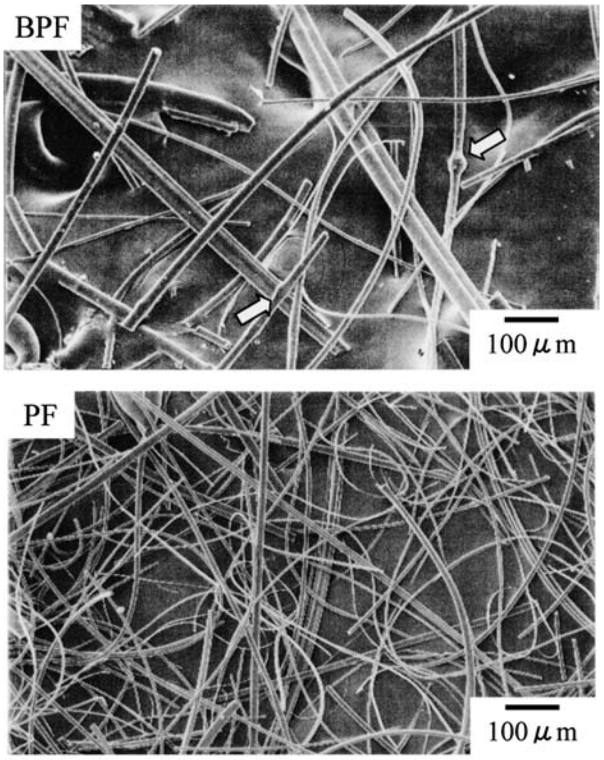

Figure 4 SEM photographs of BPF-900 and PF-900.

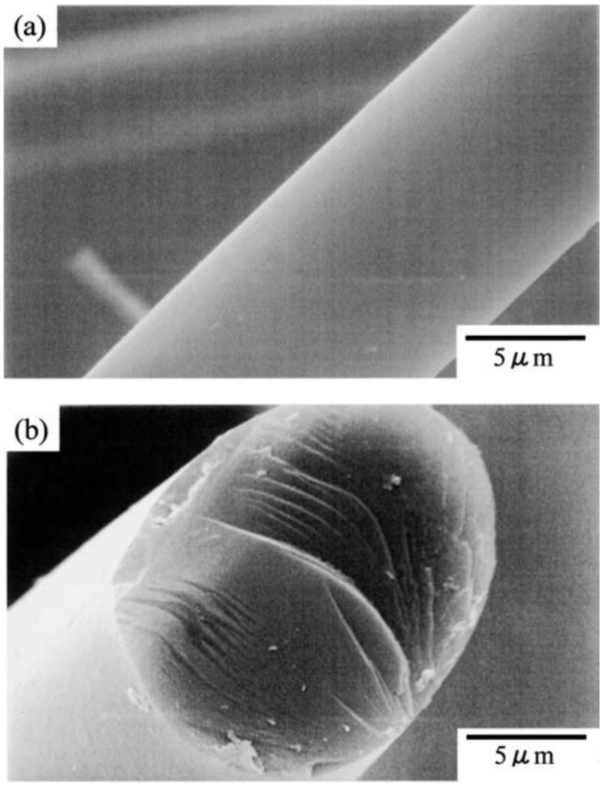

Figure 5 SEM photographs of PF-900: (a) side surface and (b) cross-section.

3.4. XRD

Fig. 8 shows XRD profiles of the BPF and the PF carbon fibers after heat-treatment. Both fibers heated at the same temperature showed similar profiles each other, except for the appearance of weak peaks from MgO in BPF-900. It is clear from the composite (002) XRD

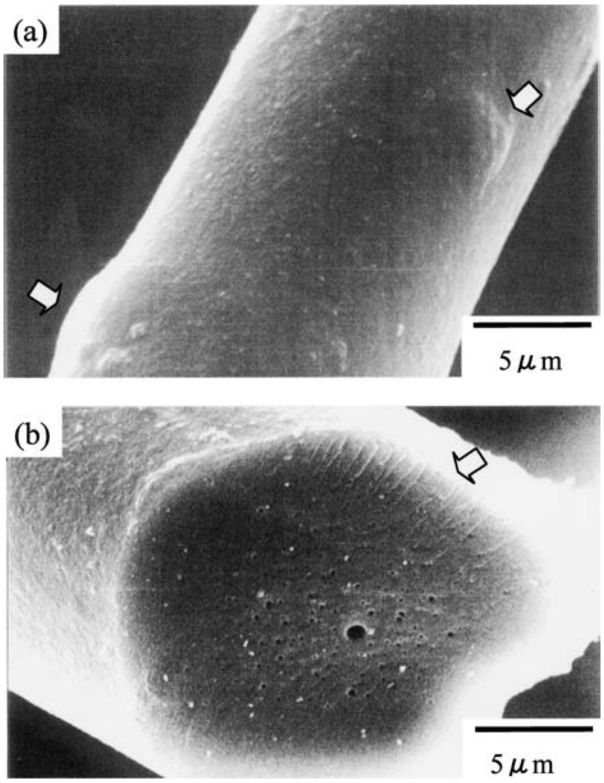

Figure 6 SEM photographs of BPF-900: (a) side surface and (b) cross-section.

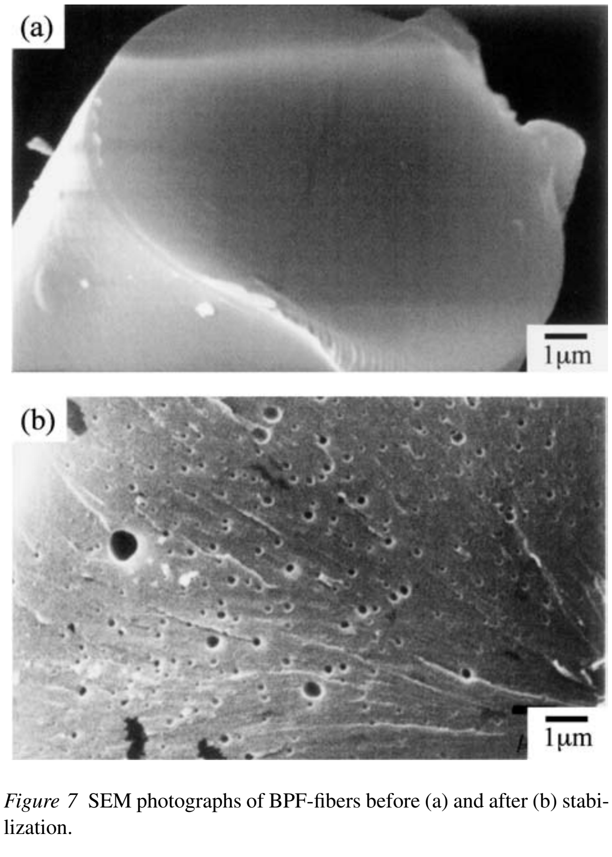

Figure 7 SEM photographs of BPF-fibers before (a) and after (b) stabilization.

profiles of both fibers after heating at 3000°C that both BPF and PF resins result in a typical non-graphitizing carbon.

3.5. N_2 isotherms

Fig. 9 shows N_2 isotherms for both BPF and PF fibers after heating at 900°C. Both fibers showed similar isotherms (type I) implying inclusion of micropores. The BET surface areas of the fibers from PF and BPF resins were 645 and 619 m^2/g, respectively.

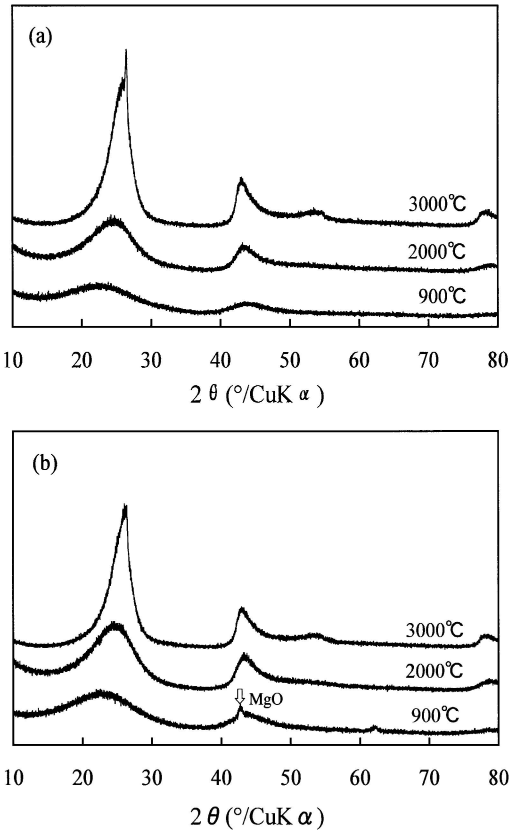

Figure 8 X-ray diffraction profiles of PF (a) and BPF (b).

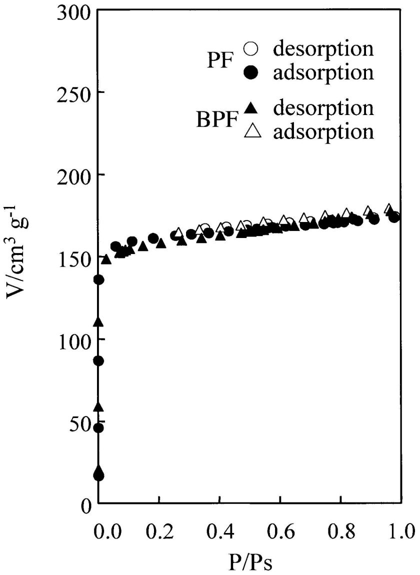

Figure 9 N_2 adsorption isotherms of PF-900 and BPF-900.

3.6. Tensile strength

The obtained data showed a relatively wide scatter. PF-900 showed a mean tensile strength of 134 MPa, with 30 and 234 MPa as the minimum and the maximum values. The tensile strength of BPF-900 ranged from 10 to 139 MPa and the mean value was 60 MPa.

4. Discussion

Carbon fibers were successfully derived from the phenol-starch-formaldehyde resin prepared by replacing one third of the phenol by cornstarch. Our target is to develop advanced carbon materials by using waste biomass, particularly waste wood, as a raw material. The present work gave a good guidance to complete the target. Two objectives remained before us for subsequent work: how to prepare a spinnable phenolic resin incorporating as large an amount of cornstarch as possible and how to prepare a spinnable phenolic resin incorporating waste wood instead of cornstarch.

As stated above, both resins exhibited somewhat different thermal behavior and the resulting carbon fibers also showed differences in structure and mechanical properties. A difference in the thermal behavior is a slightly lower carbon yield of BPF resin compared to PF resin as shown by the TG curves in Fig. 3. This will be reasonably explained by the removal of glycoside structure introduced from cornstarch as evidenced by the IR spectra in Fig. 2. BPF resin, nevertheless, gave a microscopic structure quite similar to that from PF resin as clearly shown by the X-ray diffraction profiles (Fig. 8) and N_2 adsorption isotherms (Fig. 9).

From a practical point of view, BPF resin exhibited some disadvantages compared to PF resin. The first disadvantage is that the carbon fibers derived from BPF resin were somewhat thicker and had an irregular surface as seen in Fig. 4. These phenomena certainly result from the poor spinnability of BPF resin. Two causes may be responsible for the poor spinnability. One is a specific chemical structure of the BPF resin and another one is the inclusion of infusible particles. The existence of the former is not clear presently and we suppose the latter must be more likely. The latter assumption is supported by the irregular surface morphology as shown in Fig. 6. A part of the infusible particles must be MgO, because a peak from MgO was observed by X-ray diffraction of BPF-900.

The next disadvantage is the formation of macroscopic pores in the BPF resin-derived carbon fibers, leading to a poor mechanical strength. We suppose now that MgO particles were removed in the stabilization process to result in the macroscopic pores, but it remained unsolved why the pores formed around the center of the fiber.

As stated above, the presence of MgO particles brought about various problems to the spinning of the fiber and the structure and properties of the carbon fiber. We are now preparing MgO-free BPF resin by using a filtration technique or by changing the neutralization method. The results will be reported soon.

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