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Characterization of Woodceramics Prepared from Liquefied Corncob and Poplar Powder

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A woodceramics is prepared from liquefied corncob and poplar powder. The basic property of this material is closely correlated to the carbonization temperature and liquefied corncob content. The thermogravimetric analysis indicates that the high liquefied corncob content can decrease weight loss. X-ray diffraction analysis shows that higher carbonization temperature can improve the graphitization degree of this material, but the phase composition is not mainly related to the liquified corncob content. Scanning electron microscopy confirms that the poplar powder is as a natural plant template and the pore of woodceramics partly keeps the native characteristics of the wood with size ranging from 5 to 20 μm. It is porous carbon material with three-dimensional network structure.

Key Words: Characterization, Liquefaction corncob, Poplar powder, Woodceramics.

INTRODUCTION

Woodceramics are new porous carbonic materials that can be produced using renewable resources and environmental wastes[1]. These materials have several advantages such as light-weight, high specific strength, good friction properties and excellent thermal stability and so on. Woodceramics is widely being used in the fabrication of materials[2-4], such as the wood-based high-temperature filter and catalytic carrier[5,6]. Currently, the typical method of preparing woodceramics is to impregnate a wooden material (bulk wood, medium-density fiberboard and wood powder, *etc.*) with thermosetting resin (phenol-formaldehyde or epoxy), which are subsequently carbonized at high temperature. A bamboo-based wood ceramics was prepared from bamboo powder and epoxy resin[7] and a basswood powder woodceramics was obtained through phenol-formaldehyde resin impregnation[8]. Ozao *et al.*[9] discussed the odorless woodceramics made from chicken wastes, whereas a laminated structure woodceramics had been studied by Sun *et al.*[10]. Aside from consuming a considerable amount of industrial chemicals, these methods also pollute the environment because of their free formaldehyde and volatile organic compound contents.

Corncob is a kind of agricultural residue. Many corncobs, which also serve as waste biomass resources, are discarded in the field or used as fuel in northern China. At present, there is still no report about the preparation of woodceramics from liquefied corncob (LC). In the present study, a corncob is liquefied and reused as biomass waste instead of phenol-formaldehyde resin and poplar powder is used as biomaterial to prepare woodceramics. The preparation, thermogravimetric analysis (TGA) and microstructure, as well as mechanical property, characterization of these biomaterials are discussed in the following sections.

EXPERIMENTAL

Discarded corncob is dried at 5 % moisture content and smashed into 0.5 mm granules. Liquefied corncob is obtained when a mixture of 2 parts of phenol and 1 part of the corncob powder with suitable water is stirred for 2 h at 140 ºC, using 98 % sulfuric acid as catalyst. Different amounts of poplar powder are mixed with the liquefied corncob and stirred for 3 h. The mixture is dried at 70 ºC for 24 h and then the dried material is hot-pressed into liquefied corncob-poplar powder composites under 8 MPa pressure at 160 ºC for 8 min. Finally, the composites are placed into a vacuum carbonization furnace to carbonize with 5 ºC min^{-1} heating rate from ambient temperature to the desired temperature and subsequently cooled down to ambient temperature in the furnace. Thus, liquefied corncob woodceramics are prepared and the process is shown in Fig. 1.

A thermogravimetric analyzer (Perkin-Elmer Pryis6, USA) is employed to record and analyze the weight loss of the woodceramics and the morphology is investigated with a scanning electron microscope (SEM, JSM-35C, Japan). The degree of carbonization of woodceramics is recorded and analyzed by an X-ray diffractometer (XRD; XD-2, China), scanning at the speed of 2° min^{-1}. A density tester (MDMDY-300, China) is employed to measure the density.

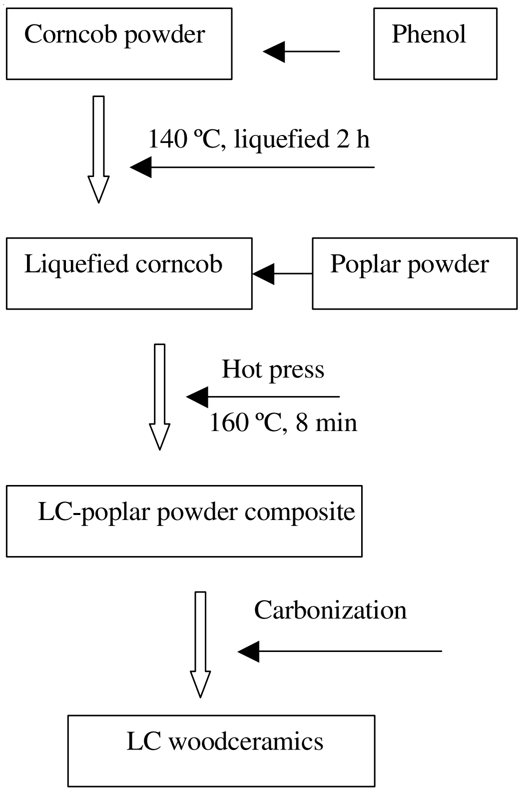

Fig. 1. Prepare process of liquefied corncob woodceramics

RESULTS AND DISCUSSION

Thermogravimetric analyzer: There are lots of physical and chemical changes during the carbonization process and the thermogravimetric analyzer (TGA) curve can describe effectively the weight loss process of the organics[11]. Fig. 2 shows the TGA curves of the three samples with different liquefied corncob contents. The TGA curves show four stages. Prior to 100 ºC (dry stage), the curves are very similar. During this stage, the free water in the composite evaporates. The thermolysis stage slowly takes place at the temperature range 100-300 ºC, where the cellulose, hemicellulose, lignin and liquefied corncob begin to dehydrate as well as decompose. Moreover, pyrolysis gases, such as H_2O and CH_4, among others, begin to escape. As the temperature rises from 300 to 550 ºC (thermal pyrolysis stage), fierce thermal pyrolysis takes place. The C-O and C-C bond in the wood and liquefied corncob are broken, the condensation reaction continues to occur between the hydroxy and methylene, to form an aromatic ring structure[12,13]. At the same time, a substantial amount of pyrolysis gases escape during carbonization, leading to weight reduction and generation of pores. Hence, there is a remarkable weight loss at this stage. Moreover, the sample with lower liquefied corncob content presents a higher weight loss. After 550 ºC, the fiercest thermolysis almost ends, but the remaining hydrogen is deprived continuously until a stable structure is formed.

Comparison of the three TGA curves (Fig. 2) shows that the TG value at 400 ºC is 52.3 % of the sample with 150 % liquefied corncob content, whereas that with 50 % liquefied corncob content had only 37.4 %. This result suggests that the liquefied corncob content is advantageous in increasing carbon yield.

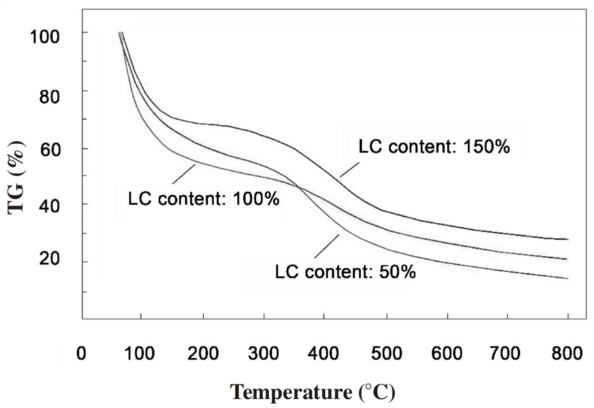

Fig. 2. Thermogravimetric curves of woodceramics with different liquefied corncob (LC) content

Phase change: Chemical and structural changes occurred during the process of carbonization, such as pyrolysis and rearrangement reactions of benzene ring, hydroxy, methylene of the liquefied corncob-poplar powder composites, as a result, the poplar powder is transformed into amorphous carbon, whereas the liquefied corncob becomes a glassy carbon[14].

Fig. 3 shows the XRD patterns of liquefied corncob woodceramics with 100 % liquefied corncob content and carbonize at different temperatures for 2 h. As carbonization temperature rises from 800 to 1600 ºC, a remarkable 002 peak changes from wider into sharper and its Bragg angle (2θ) shifts to a large angle. At the same time, 10*l* peaks appear and change sharper, indicating that the graphitization degree of liquefied corncob woodceramics has increased. However, the 002 and 10*l* diffraction peaks are broad, which suggest the phrse of liquefied corncob woodceramics has been changed, but it has amorphous state of partial graphitization with half crystalline structure.

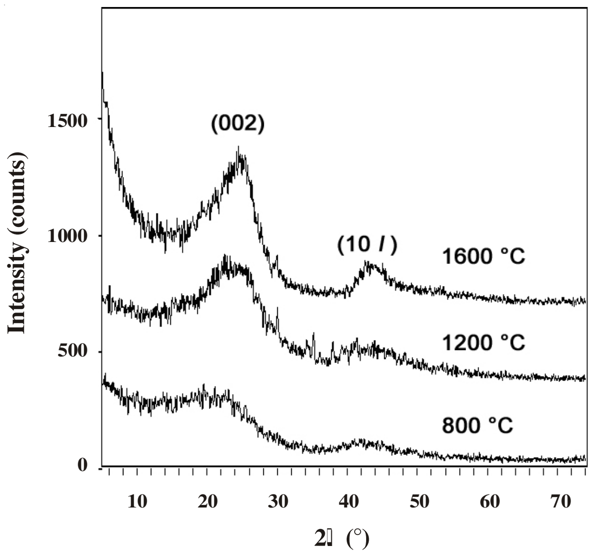

Fig. 3. XRD patterns of liquefied corncob woodceramics carbonize at different temperature

The graphitization degree can be estimated by the d_{002} value[15]. Generally, d_{002} value will reduce while the quantity of graphite crystallite increase and the coherent length of the graphite crystallite in the basal plane and the crystallite size along the *c*-axis enlarge. Fig. 4 shows the changes of d_{002} value of liquefied corncob woodceramics obtained at different carbonization temperature. As the temperature increases from 600 ºC to 1600 ºC, d_{002} value decreases from 0.3925 nm to 0.3663 nm. But the value is always bigger than the 0.3354 nm, which is a value at state of being perfectly graphitized, suggesting that liquefied corncob woodceremics is hard to be completely graphitized, even if at higher. This is because that elevation of carbonization temperature can increase the quantity of graphite crystallite, the coherent length and the crystallite layers thickness, which lead to more uniform arrangements of the crystallite layers.

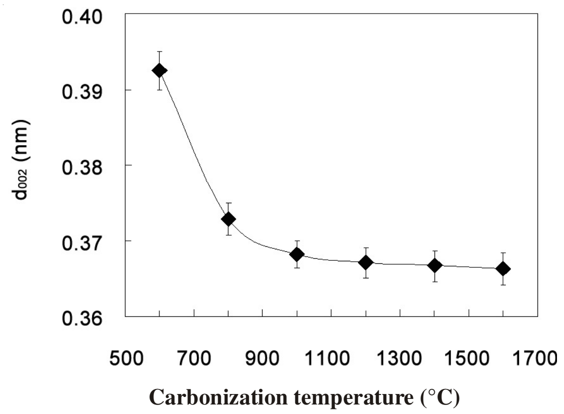

Fig. 4. Changes of d_{002} value of liquefied corncob woodceramics with different carbonization temperature

In Fig. 4, it also finds that the d_{002} value reduces rapidly as the carbonization temperature increases, until temperature reaches about 800 ºC. However, the curve of the d_{002} value become flat as temperature rise further, that because the fierce chemicla reaction has completed and the baics structure of woodceramics has completed at 800 ºC.

Fig. 5 shows the XRD patterns of liquefied corncob woodceramics carbonized at the same carbonization temperature with different liquefied corncob content, the patterns are almost similar, suggesting that phase composition of liquefied corncob woodceramics is not mainly related to the liquefied corncob content.

Microstructure: SEM is used to observe the microstructure of the woodceramics. Fig. 6a shows the micrograph obtained from the sample with 50 % liquefied corncob content and carbonization temperature of 1100 ºC. Bigger holes and cracks with irregular shapes and size, which presents three three-dimensional network are observed due to liquefied corncob-poplar composite contraction and small molecules material release during the carbonization process. A lot of pores with honeycomb shapes with sizes ranging from 5 to 20 μm are also observed in this material. The micropore structures are evidently shown in the enlarged micrograph, which partly maintains the evident pore structure of poplar. This condition convince that poplar is as a natural plant template and that the biological characteristic of wood can be inherited.

Fig. 6b shows the micrograph of the woodceramics with 150 % liquefied corncob content. The surface is covered with glassy carbon and presents a special glossy translucent state, indicating that more liquefied corncob content produces more glassy carbon, which has good agreement with the results of thermogravimetric analyzer.

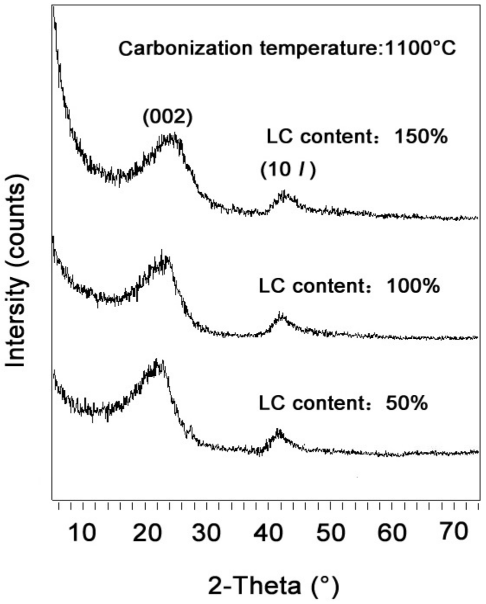

Fig. 5. XRD patterns of liquefied corncob woodceramics with different liquefied corncob content

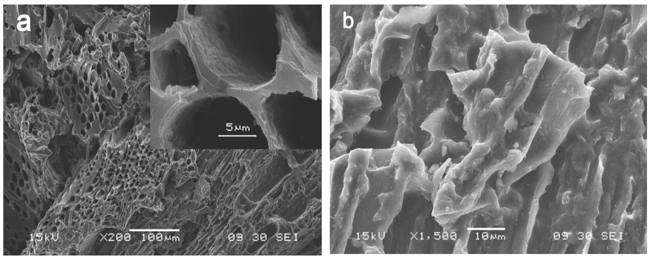

Fig. 6. Microstructure of woodceramics; a. Carbonization temperature, 1100 ºC; liquefied corncob content, 50 %; b. Carbonization temperature, 1100 ºC; liquefied corncob content, 150 %

Conclusion

Woodceramics prepared from liquefied corncob and poplar powder, which not only can reuse the biowaste, but also save the industrial chemicals. Carbonization temperature and liquefied corncob content have played important roles and have improved the basic property of this material. More liquefied corncob content lead to more carbon yield. Along with the elevation of the carbonization temperature, the phase composition has great changes and the d_{002} value decreases as well as the graphitization degree increases. Meanwhile, liquefied corncob woodceramics can partly keep the biological structures of wood and presents three-dimensional network.

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