

EFFECTS OF SINTERING CONDITIONS ON MICROSTRUCTURE CHANGES OF WOOD-CERAMICS IMPREGNATED WITH LOW-MOLECULAR-WEIGHT PHENOL-FORMALDEHYDE RESIN

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Abstract. The microstructure of a new type of wood-ceramics made from poplar fiber impregnated with low-molecular-weight phenol-formaldehyde (PF) resin under atmospheric pressure was studied under changing sintering conditions. X-ray diffraction analysis indicated that the d_{002} value was reduced with increasing sintering temperature. The wood-ceramic structure also became more uniform and orderly, but still was nongraphitic carbon. Scanning electron microscopy showed that the pore structure partially retained the microstructural characteristics of wood fiber, and a graphitic phase was formed with increased sintering temperature and longer holding time. All analyses showed PF resin molecular weight had little impact on phase composition and graphitization. The apparent specific gravity of wood-ceramics increased as sintering temperature increased to 1200°C but decreased as temperature rose further. Specific surface area and apparent porosity were increased with higher sintering temperature, greater sintering rates, and longer holding times. In addition, specific surface area was also affected by the molecular weight of PF resin and the impregnation method, in which low-molecular-weight resin increased the specific surface area.

Keywords: Wood-ceramics, low-molecular-weight PF resin, sintering conditions, microstructure change.

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INTRODUCTION

Wood-ceramics is a new porous carbonaceous material made from wood or biomaterials impregnated with a thermosetting resin or liquefied wood and sintered at high temperature (Hirose et al 2002a). Studies have shown that wood-ceramics have low mass and high specific strength, good thermal and electromagnetic properties, and excellent frictional characteristics (Izuka et al 1999; Zhang et al 2004).

Sintering conditions play an important role in forming the microstructure of wood-ceramics and determining its properties and phase composition. Currently, there are two main methods to make wood-ceramics. One is that bulk wood or medium-density fiberboard (MDF) is impregnated with ordinary phenol-formaldehyde (PF) resin or liquefied wood and sintered at high temperature (Kano et al 1997; Hirose et al 2002b); the other is that wood powder/ordinary PF resin composites are sintered (Qian et al 2004a; Tao and Liu 2006). However, the wood-ceramics made by these methods are easily distorted and ruptured during the process of sintering because of the anisotropy of bulk wood and impregnation flaws in MDF. In addition, although using wood powder and ordinary PF resin is simple, it requires a vacuum and impregnation system using ultrasonics or high pressure, which leads to the loss of the natural structure of wood because of the small particulate size of wood powder.

In this work, wood-ceramics were made by using low-molecular-weight PF resin as a maceration extract, poplar fiber as raw material, and atmospheric pressure for impregnation. The changes of wood-ceramics phase composition and microstructure under different sintering conditions were studied and the effect of molecular weight determined.

MATERIALS AND METHODS

Material Preparation

Poplar fibers 3 mm or longer (*Populus euramericana* cv. 1-214) were dried to 5% MC and impregnated with low-molecular-weight PF res-

in in a vessel under atmospheric pressure for 24 h. The molecular weight of PF resin was 400 – 500. The mixture of poplar fibers and PF resin was filtrated and dried to 8% MC at 60°C and hot-pressed into the poplar fiber/low-molecular-weight PF resin composites (also termed “fiberboard composites” in this study) under 12 MPa at 160°C for 8 min. Finally, the fiberboard composites were sintered in a high-temperature vacuum sintering furnace with different heating rates from ambient to the desired temperature (e.g., 800, 1200, 1700°C) and cooled to ambient temperature in the furnace.

Characterization

The degree of carbonization of wood-ceramics was measured by using an X-ray diffractometer (XD-2) with a Cu K α radiation source at 35 kV and 20 mA and scanning speed of 2°min⁻¹. The interplanar spacing of crystallite d002 was calculated by using the Bragg equation (Fujimoto 2003).

The morphology of the wood-ceramics was recorded and analyzed by scanning electron microscopy (SEM; JSM-35C) operated at 20 kV and 20 mA. The specific surface area of wood-ceramics was measured by using an automatic apparatus (Quanta Chrome Monosorb-1). The 40- μ m sample powder was outgassed at 250°C for 1 h followed by N₂ adsorption at 77.35 K. Apparent specific gravity of wood-ceramics was tested with a liquid-based method in which mass was measured with an electronic balance (BS124S).

RESULTS AND DISCUSSION

Effect of Sintering Temperature on Phase Composition

It is well known that chemical and structural changes occur in sintering of fiberboard composites such as caused by pyrolysis and rearrangement reactions of cellulose, hemicelluloses, lignin, and PF resin. As a result, poplar fibers are transformed into amorphous carbon, whereas PF resin becomes a glassy carbon (Akagaki et al 1999). X-ray diffractometer (XRD) patterns

describe the graphitization degrees of carbon. Figure 1 showed XRD patterns of wood-ceramics that were made from poplar fiberboard composites with a PF resin content of 86% and sintered at different temperatures for 3 h.

It was clearly observed that the sintering temperature had significant effects on the phase composition of wood-ceramics. As the sintering temperature rose to 1700°C, the distinctive (002) peak changed from a wide to sharper peak, although it was still wide but not as sharp as at 800°C. At the same time, the Bragg angle (2θ) increased, and the (101) peak appeared and also became sharper. The degree of graphitization can be estimated by the value of d_{002} and full-width-at-half-maximum. Usually, with the increase of quantity of graphite crystallite, the coherent length of the graphite crystallite in the basal plane and the crystallite size along the c-axis can reduce the value of d_{002} . Figure 2 shows the relationship between sintering temperature and the value of d_{002} , which suggests the value of d_{002} is negatively related to sintering temperature according to XRD patterns. Its value decreased from 0.3979 to 0.3783 nm as the sintering temperature increased 700–1600°C. However, the value of d_{002} was always larger than 0.3354 nm, which is a value at the state of perfect graphitization, suggesting that wood-ceramics is difficult to completely graphitize, even at 1600°C, but the arrangement of the crystallites became more orderly at higher temperatures.

In Fig 2, the value of d_{002} decreased rapidly with an increase of sintering temperature until about 800°C. As the temperature rose further, the d_{002} value became flat. This was because carbonic structure of wood-ceramics had been basically shaped at 800°C (Kercher and Nagle 2003), which has good agreement with the results from the wood powder impregnated with ordinary PF resin in a high-pressure impregnation system (Qian et al 2004b). It suggests that the phase composition of wood-ceramics is primarily related to sintering temperature.

As shown in Fig 1, some sharp peaks appeared in patterns at lower temperatures but disap-

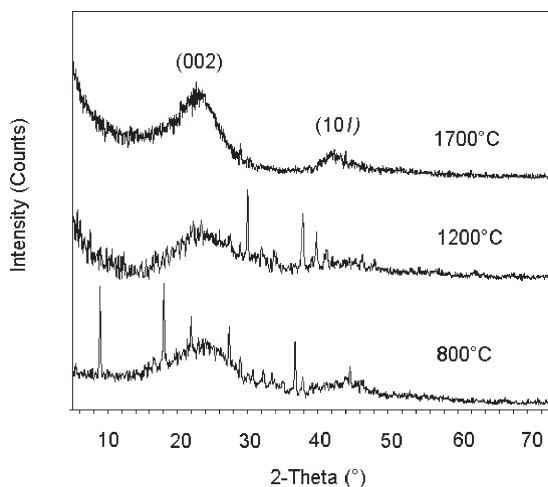


Figure 1. X-ray diffraction patterns of wood-ceramics sintered at different temperatures.

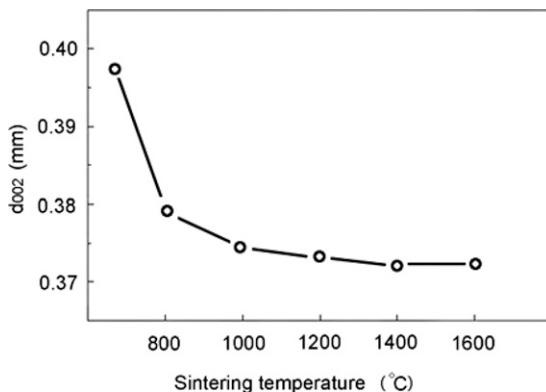


Figure 2. Relationship between sintering temperature and d_{002} value.

peared as the temperature approached 1700°C. The sharp peaks, which disappeared when inorganic compounds were gasified at higher temperature, were characteristic of some inorganic compounds from poplar fiber and PF resin. This also indicated that higher sintering temperature could make wood-ceramics purer.

SEM micrographs of wood-ceramics in Fig 3 were obtained at different sintering temperatures with PF resin content of 78% and holding time of 2 h. From the micrograph of the tested sample sintered at 1500°C in Fig 3a, some particles were observed to separate from the surface of glassy carbon, which was considered as

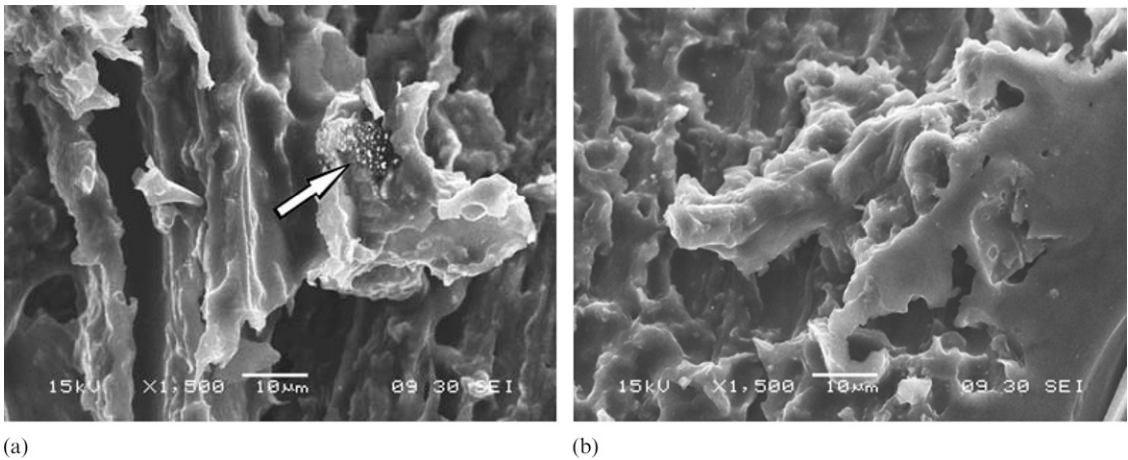


Figure 3. Scanning electron micrographs of wood-ceramics with the same phenol-formaldehyde resin contents at different sintering temperatures: (a) 1500°C, (b) 650°C.

a symbol of the precipitation phase of graphite (Qian et al 2004c). Figure 3b showed that neither the surface of amorphous carbon nor the glassy carbon had particles at a sintering temperature of 650°C, which further confirmed that higher sintering temperatures could improve the phase composition and also aid in graphitization. It also indicated that low-molecular-weight PF resin could be effectively absorbed by poplar fiber without pressure equipment.

This information suggested that the increase of sintering temperature could reduce the value of d_{002} ; increase the quantity of graphite crystallite, the coherent length, and the crystallite layer thickness; and could result in more uniform arrangements of the hexagonal network crystallite layers in wood-ceramics. However, the graphitic peak was not observed in the study, indicating that wood-ceramics was only a carbonic material consisting of graphite crystallites in disorder with turbostratic structures, which was nongraphitic carbon. The molecule size of PF resin has little effect on the phase composition of wood-ceramics.

Effect of Holding Time on Phase Composition

Holding time is another important factor in the sintering process of wood-ceramics (Hou et al 2007). The SEM micrograph of wood-ceramics

in Fig 4 was obtained at 1500°C with a holding time of 10 h. It is noteworthy that fine precipitation phases during sintering were observed (compared with Fig 3a, in which the holding time was 2 h), which suggested that its increasing holding time was beneficial to improve the phase composition of wood-ceramics.

Microstructure of Pores

The pore structure in wood-ceramics consists of macropores, micropores, and nanopores (Zhang et al 2002). SEM micrographs in Fig 5 were taken at a PF resin content of 112%, sintering temperature of 1200°C, and holding time of 3 h. Larger holes and cracks (see arrow A) with irregular shapes and sizes ranging from 10 to 100 μm were observed in Fig 5a because of fiberboard composite contraction and small molecular material releases (see arrow B). Micropore structures were found in Fig 5b showing that the cross-section morphologies were circular or elliptic ranging 1–10 μm . Also, the poplar biological structure was partially retained. All of those were related to the shape, structure, size, and distribution of poplar fibers. (Nanopores in wood-ceramics cannot be observed by SEM, so it is not discussed in this study.)

As investigated with SEM micrographs of wood-ceramics at different temperatures, the pore

structures were found to be inconspicuous at sintering temperatures below 300°C but became clearer with increasing temperature. This can be explained by aggressive pyrolysis of poplar fibers and PF resin, eg dehydrogenation, deoxidization, and condensation to the aromatic polynuclear structure. These reactions take place at 300 – 800°C. As a result, a ring-like carbon is generated (Hirose et al 2002c; Kim et al 2004; Li and Li 2007) and becomes stabilized during this process. This indicates that increased sintering temperature probably increased the number and size of graphite crystallites and reduced the interplanar spacing of the crystalline regions (as shown in

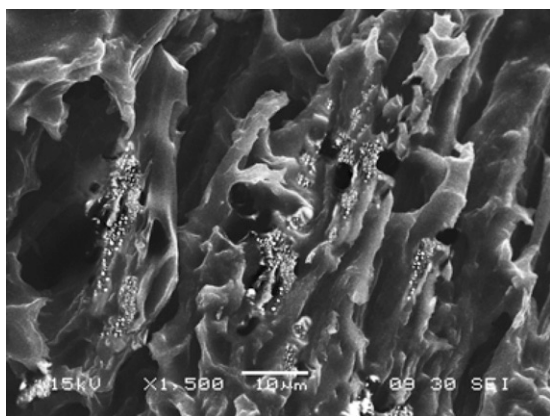
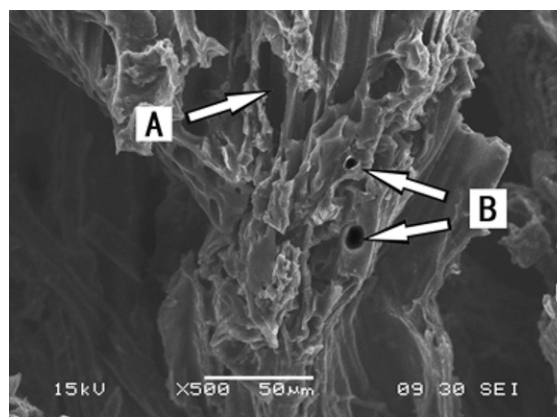


Figure 4. Scanning electron micrograph of wood-ceramics sintered at 1500°C with holding time of 10 h.



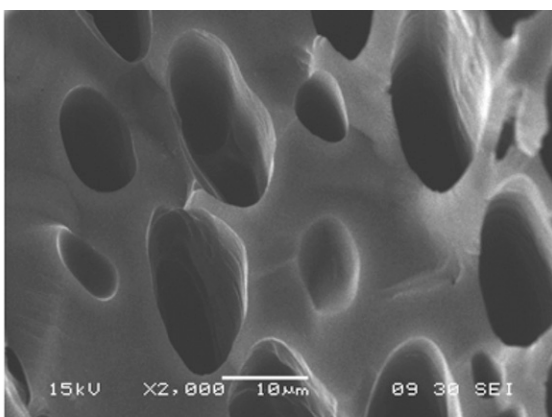
(a)

Fig 2). In addition, the interface between glassy and amorphous carbon disappeared gradually, and the volume shrank and gasification increased at the same time.

Apparent Porosity and Apparent Specific Gravity

Figure 6 shows the relationship among sintering temperature, apparent porosity, and apparent specific gravity with 112% PF resin content, 2-h holding time, and 2°C/min⁻¹ sintering rate. As seen in Fig 6, increasing sintering temperature remarkably improved apparent porosity. However, apparent specific gravity increased initially and then decreased gradually with increasing sintering temperature.

Generally, apparent specific gravity has a negative effect on apparent porosity. However, in this study, it first increased (over 750 – 1200°C) and then gradually decreased, probably because the transformation of microcrystalline structure occurred. With the increase of the quantity of graphite crystallites and the decrease of interplanar spacing of the crystalline regions, the interface of two types of carbon disappeared gradually and joined together, the volume of wood-ceramics shrank, and the compactness increased, causing an increase of apparent specific gravity. However, during the temperature-rising



(b)

Figure 5. Microstructure of wood-ceramics.

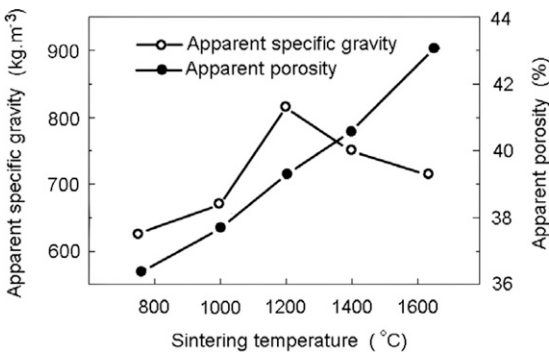


Figure 6. Relationship among sintering temperature, apparent specific gravity, and apparent porosity.

period, small molecules escaped and gasification increased also, which had a more significant impact when the temperature exceeded 1200°C and caused apparent specific gravity to decrease.

As shown in Fig 7 on the relationship among sintering rate, apparent specific gravity, and apparent porosity, apparent specific gravity reduced and apparent porosity increased as sintering rate increased, which was probably because the higher sintering rate caused more radical chemical changes.

Specific Surface Area

As shown in Fig 8, specific surface area tended to increase with increasing sintering temperature. It rose 374 – 658 m²/g⁻¹ with 50% PF resin and sintering temperatures at 600 – 1600°C (sintering rate was 2°C/min⁻¹). It suggested that the higher sintering temperature significantly enlarged pore space and enhanced gasification of carbon. In other aspects, because of the effect of PF resin in occluding interior residual holes when the sample shrank, the closed hole became an opened pore as the sintering temperature increased.

The specific surface area of wood-ceramics impregnated with low-molecular-weight PF resin was larger compared with other studies (Kim et al 2004), which was probably caused by changes in molecular sizes of PF resin and impregnating methods, although further research is needed to confirm this. This suggests that low-

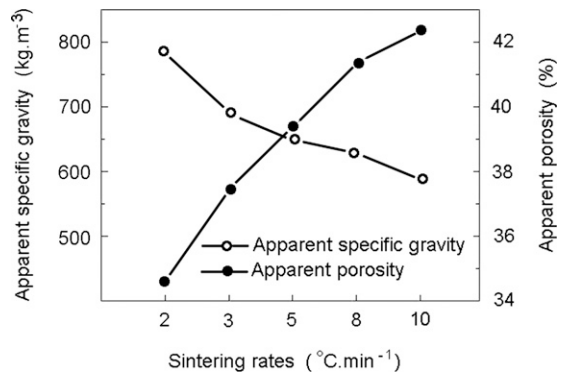


Figure 7. Relationship among sintering rate, apparent specific gravity, and apparent porosity.

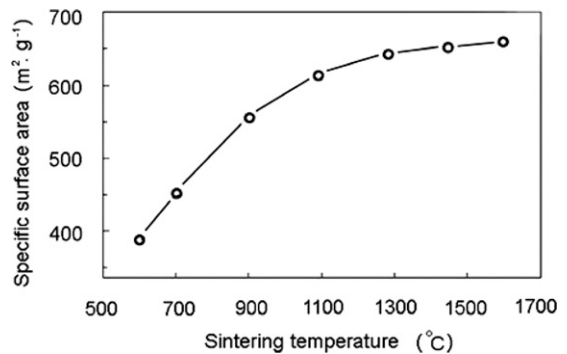


Figure 8. Effects of sintering temperature on specific surface area.

molecular-weight PF resin played an important role in generating a large surface area.

Sintering rate also had a significant effect on the specific surface area of wood-ceramics (Hirose et al 2002a). Figure 9 shows that elevated sintering rate caused an increase of specific surface area of the wood-ceramics (sintering temperature, 900°C; sintering rate, 2°C/min⁻¹). The higher sintering rate resulted in more robust chemical changes, and more small molecules escaped as well. It suggested that higher sintering rates could increase the surface area of wood-ceramics.

CONCLUSIONS

In fabricating a new type of wood-ceramics from poplar fiber impregnated with low-molecular-

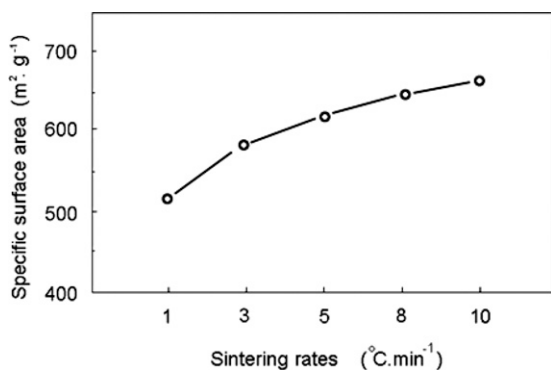


Figure 9. Relationship between sintering rate and specific surface area.

weight PF resin under atmospheric pressure, the following conclusions were reached.

The phase composition of wood-ceramics depended primarily on sintering temperature and not molecular weight of PF resin. The (002) interplanar spacing of the crystalline regions decreased with increasing sintering temperature, which favors graphitization, but it is nongraphitic carbon.

Wood-ceramics can partially retain the microstructure of wood, which is determined by shape, structure, size, distribution of wood fibers, and sintering conditions. Increasing sintering temperature, higher sintering rates, and longer holding times increases apparent porosity and decreases apparent specific gravity.

Low-molecular-weight PF resin can infiltrate into poplar fiber effectively at atmospheric pressure and results in a larger specific surface area.

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