LAMINATED WOOD–CERAMICS PREPARED FROM BEECH VENEER AND PHENOL FORMALDEHYDE RESIN

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Abstract. Laminated wood–ceramics were created from beech veneer by impregnation with phenol formaldehyde resin and airtight sintering. The resulting laminated biocarbon material exhibited a clearly layered structure and partially preserved microstructural characteristics of normal wood. Laminated structure and airtight sintering techniques significantly affected basic material properties. Carbon yield can increase and sintering cost can decrease through these methods. The material treatments used generate porosity, density, and volumetric shrinkage properties that are different from composites that are vacuum-sintered. Its layered structure is associated with the stacking of veneers. The fracture toughness increases to 0.6-1.2 $MPa{\cdot}m^{1/2}$ because of the laminated structure, and the material exhibits a progressive failure behavior.

Keywords: Laminated wood–ceramics, airtight sintering technology, basic structure, fracture toughness.

INTRODUCTION

Wood–ceramics, a novel porous carbon material, have previously been prepared from wood and other biomass materials impregnated with thermosetting resin and sintered at high temperature under vacuum or inert gas (Hirose et al 2002; Treusch et al 2004). It has been shown to possess many positive properties such as thermal resistance, corrosion resistance, oxidation resistance, and shielding ability against electromagnetic waves. Therefore, potential products include heat-insulating materials, light structural ceramics, machinable ceramics, and electromagnetic wave shielding materials (Kasai et al 1997; Akagaki et al 1999; Suda et al 1999; Zhang et al 2002a).

At present, there are two main types of wood–ceramics:1) bulk wood-based (Zhang et al 2004b) and 2) medium-density fiberboard (MDF)- or wood powder-based (Akagaki et al 1999; Treusch et al 2004; Li and Li 2006). However, bulk wood-based wood–ceramics easily deform and break because of the anisotropy of wood, while MDF-based and wood powder-based wood–ceramics

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lose almost all the original structure of the biomass material. A vacuum or protective-atmosphere furnace is necessary for this sintering process as well as substantial amounts of energy and shielding gases.

The new laminated wood–ceramics (LWC) reported were prepared by methods that are different from those traditionally used. It is fabricated from beech veneer and phenol–formaldehyde (PF) resin through a bionic design and an airtight sintering process. The objective is to improve the properties and basic structure of the composite while partly retaining the inherent characteristics of wood but without deformation or cracking. Sample preparation is very simple because it does not require a vacuum furnace or continuous inert gas protection. The preparation process, structural evolution, microstructural characteristics, and fracture toughness were also investigated.

MATERIALS AND METHOD

Experimental Procedure

Sliced beech veneer, 200 × 200 × 0.5 mm, was used as the base material and PF resin with 52% solid content as the dipping solution. The veneer was dried to a 5% MC and placed in a container at 0.8 MPa for 1 h. PF resin was injected, and impregnation was performed for 1 h at 1.5 MPa. The veneer was removed from the dipping tank and dried to 8% MC at 60°C. Subsequently, more than 50 layers of veneer were hot-pressed into a veneer/PF resin composite and stacked in parallel-laminated and cross-laminated layers (Fig 1) at 12 MPa and 160°C for 10 min.

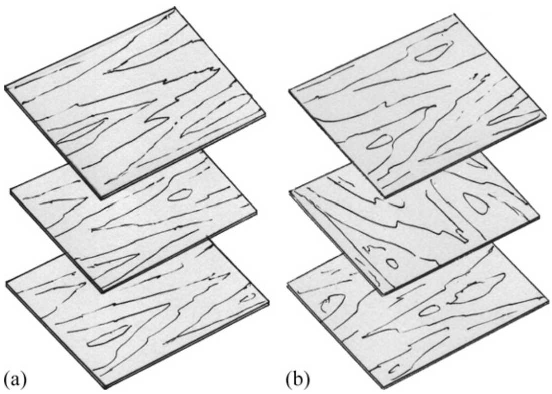


Figure 1. Stacking forms of veneer. (a) Parallel-laminated stacking. (b) Cross-laminated stacking.

A common charcoal-making technique was adopted. The structure of the sintering furnace is shown in Fig 2. This method is not significantly different from an ordinary sintering furnace, except for the two high-temperature refractory ceramic tubes with valves at the top and bottom, both of which are interlinked with the hearth (airtight furnace).

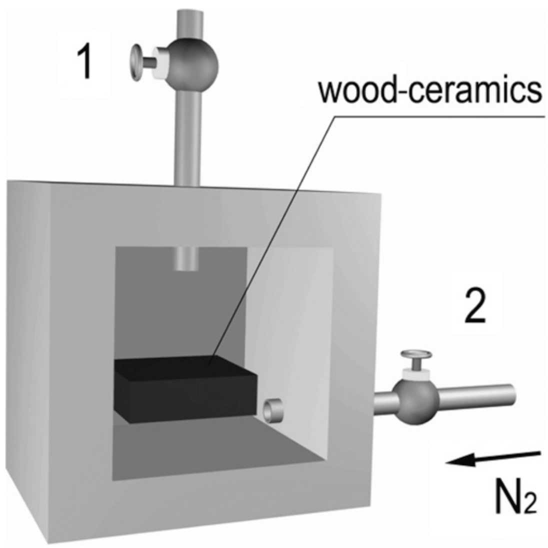


Figure 2. Schematic of an airtight sintering furnace.

The veneer/PF resin composites were placed into the furnace, and the door was closed and sealed. Valves 1 and 2 were opened, and N_2 or other shielding gases were introduced from Tube 2 at 400 mL·min^{-1} for at least 10 min. Then, Valve 2 was closed and Valve 1 opened 20%. Sintering began at 2°C·min^{-1} to 750°C and then at 5°C·min^{-1} to the desired temperature (eg 800, 1200, or 1600°C) and held 2 h. Finally, the resulting wood–ceramics were cooled to ambient temperature in the furnace at a 4°C·min^{-1} rate.

During cooling, Valve 1 was closed and Tube 2 was opened to introduce a shielding gas. This was done to balance the pressure in the hearth, which was slightly higher because of the thermal decomposition gases (such as CO_2, CO, CH_4, water vapor, etc) exiting from Tube 1 during the sintering process. However, the gas volume in the hearth shrank as the temperature decreased. Opening Valve 2 balanced the pressure between the inside and the outside of the sintering furnace, preventing air intrusion.

Characterization Methods

A scanning electron microscope (FEI QUANTA 200) operating at 20 kV and 20 mA was used to analyze the microstructure. Fracture toughness was determined with a mechanical testing machine (Instron 8802) using a single-edge notched beam method with a specimen size of 10 × 12 × 60 mm. Apparent density and apparent porosity were measured with a density tester (MDMDY-300) and Archimedes' measurements, while volumetric shrinkage was measured with an electronic digital caliper (MILAN, 0-150).

RESULTS AND DISCUSSION

Carbon Yield, Shrinkage Ratio, and Density

The carbon yield of the LWC is shown in Fig 3. All samples had the same sintering temperature and rate but different sintering environment. As sintering temperature increased 600-1600°C, carbon yield decreased, but the sample sintered in a vacuum furnace had lower carbon yield than that from an airtight furnace. This suggests that carbon yield is significantly different for the condition of negative pressure that can promote faster release of the thermal decomposition gas, promoting carbon gasification.

Figure 4 shows the volumetric shrinkage ratios of parallel- and cross-laminated samples with the same sintering process in an airtight furnace. The volumetric shrinkage ratios are different with the parallel-laminated samples having larger ratios than the cross-laminated samples. The cross-laminated shrinkage is less because of the mutual restraint that occurs similarly in plywood.

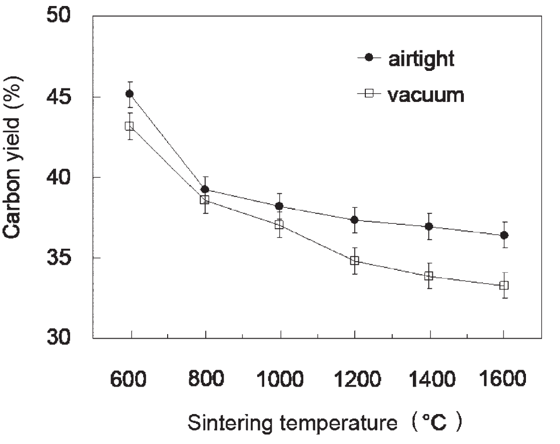


Figure 3. Effects of sintering temperature and technology on laminated wood–ceramics carbon yield. (The sample is cross-laminated.)

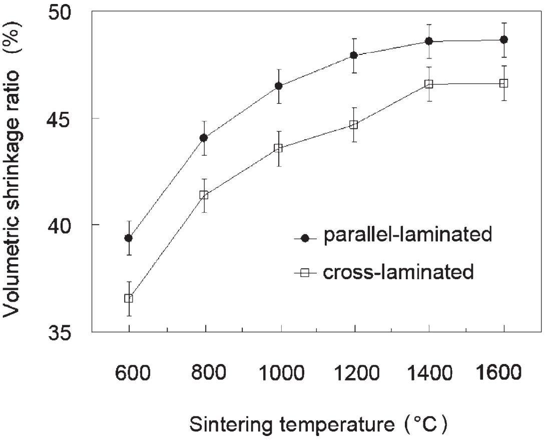


Figure 4. Effects of sintering temperature and stacking orientation on the volumetric shrinking ratios of laminated wood–ceramics in an airtight furnace.

Porosity and density are basic characteristics of porous materials that are closely related to the mechanical properties (Zhao et al 2002; Qian et al 2004a). Figure 5 shows the relationships among sintering temperature, apparent porosity, and apparent density of LWC. Increasing sintering temperature remarkably increases the apparent porosity of the material and affects the apparent density in various ways. As the sintering temperature rises 400-1600°C, the apparent porosity of the parallel-laminated

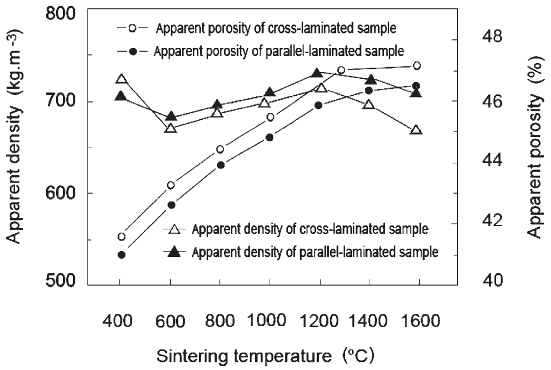


Figure 5. Effects of sintering temperature and stacking orientation on the apparent porosity and density of laminated wood–ceramics.

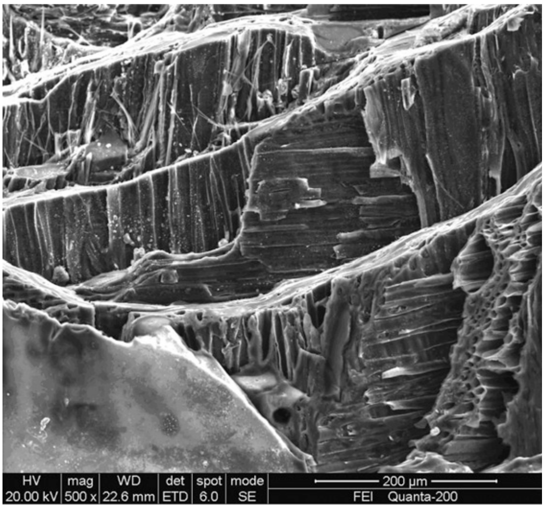


Figure 6. Micrograph of a cross-laminated sample.

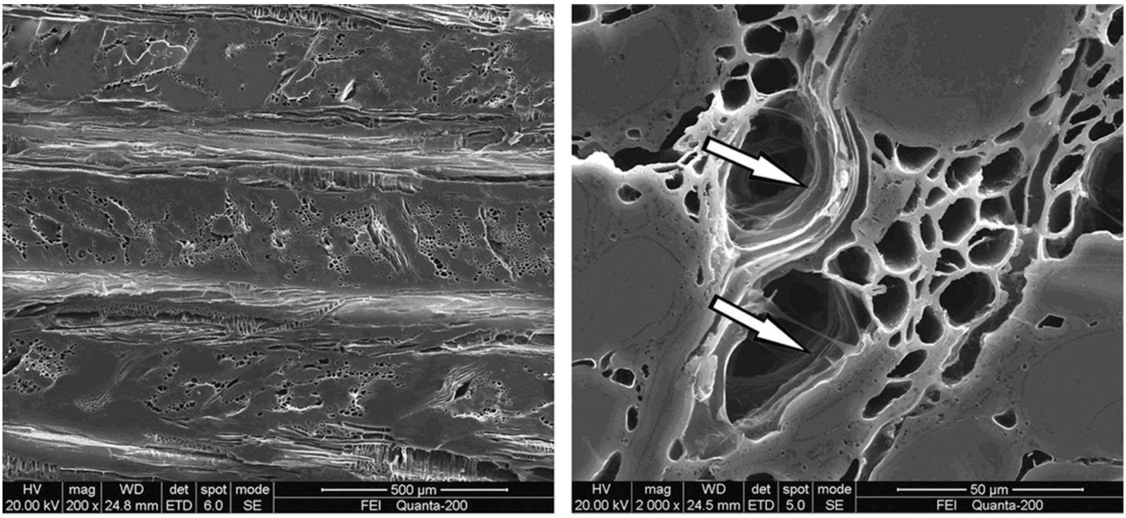
sample increases gradually 41.6-47.3%. In contrast, the apparent density first decreases before 600°C and then increases to 1200°C before decreasing again. The cross-laminated sample exhibits the same characteristics probably because of the transformation of a microcrystalline structure (Sun et al 2009) and gasification.

The apparent porosity and density are different for the horizontal- and the cross-laminated sample, although their PF resin contents and veneer layers were equal before sintering (Fig 5). For example, the apparent porosity of the cross-laminated sample is almost 3.6% greater than the parallel-laminated sample at 1400°C, but its apparent density is smaller from the restraint of perpendicular veneer. These results correspond to the results on carbon yield, but these are different from the bulk wood-based, MDF-based, and wood powder-based wood–ceramics sintered with a protective atmosphere (Li 2001; Tao 2006).

Laminated Features and Microstructure

An important objective was to make a type of wood–ceramics that not only had a laminated structure but also preserved the biological characteristics of wood. The surface of beech veneer was covered with PF resin, which acts both as the dipping solution as well as an adhesive for the veneer layers, creating a thin film of adhesive between the veneers. During the sintering process, the PF resin becomes a glassy carbon, while beech veneers become amorphous carbon. A thin film of glassy carbon exists between amorphous carbon and their density, hardness, and pore structure are different (Qian et al 2004b) in the resulting laminated structure. Figure 6 is the micrograph of the cross-laminated sample showing that the original appearance of beech is preserved and the texture of the fiber is very clear despite sample shrinkage.

Figure 7 is the cross-sectional micrograph of LWC. The white layers in Fig 7a are glassy carbon and the gray layers amorphous carbon, both of which are superposed in an alternating manner to form a laminated structure. Micropore structures of LWC can be observed clearly in Fig 7b. Many pores appear circular and elliptic with sizes ranging 1-10 µm, which is related to the beech structure and indicates that the organic structure of the wood is partially retained. The glassy carbon with special luster is found in the vessels of beech (shown by arrows), indicating that PF resin can infuse into the interior of the wood. Because PF resin is a thermosetting resin that does not soften during the sintering process, it can increase the strength of wood fibers, reducing deformation and breakage, thus, a larger size of LWC can be obtained.



(a) (b)

Figure 7. (a) Laminated structure of laminated wood–ceramics (LWC). (b) Microspore structure of LWC.

Fracture Toughness

One of the main features of laminated ceramics is its higher fracture toughness (Clegg et al 1990; Greil et al 2002; Yang et al 2008). Figure 8 shows a load-displacement curve for LWC. A progressive failure behavior is presented in which crack growth occurs in the flaws, pores, and weak interfaces. These permit the load to continue rising. Pseudoplastic deformation is capable of absorbing large amounts of energy, and failure of the second layer (or layer group) gives rise to the first load drop. This process is repeated until all layers are cracked, resulting in a step-like load-displacement response.

Figure 9 shows the LWC fractography, which can be used to estimate fracture characteristics (Li et al 2004). The surface is jagged, sharp, and uneven. Some layers are pulled out, unlike the general pattern of breakage. This suggests that layer-by-layer (or group layer) fractures of LWC prevent sudden breakage. In this study, the fracture toughness of LWC was 0.6-1.2 MPa·m$^{1/2}$, which is higher than that of other wood-based wood–ceramics (0.15-0.6 MPa·m$^{1/2}$) (Iizzuka et al 1999) but is still much lower compared with SiC ceramics. This is caused by the poor mechanical properties of amorphous and glassy carbons as well as numerous pores and cracks, which may be improved with inorganic and oxide infiltration.

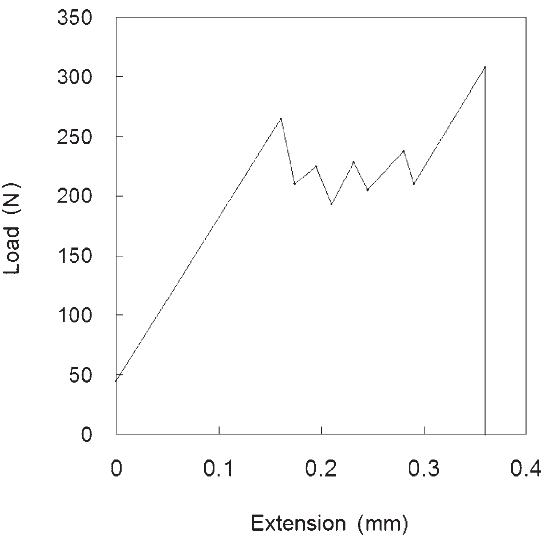


Figure 8. Example of load-displacement curves for laminated wood–ceramics.

CONCLUSIONS

LWC prepared from beech veneer/PF resin composite not only has a clearly laminated structure,

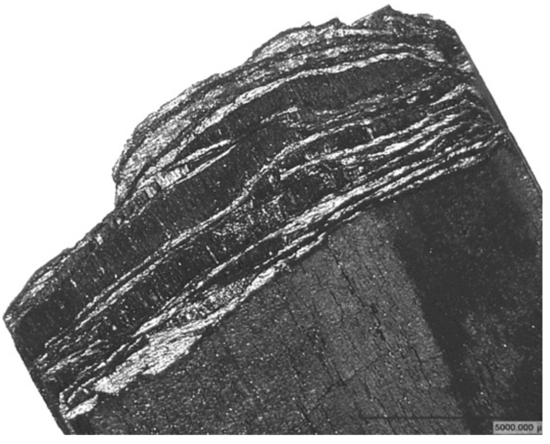


Figure 9. Fractography of laminated wood–ceramics.

but can also preserve the original microstructure of wood. The laminated structure is greatly different from tradition products, qualifying it as a biological carbon material. An airtight sintering process can replace vacuum and gas-protected sintering and produce a higher carbon yield. Sintering temperature and stacking orientation play important roles in determining the material properties. The apparent porosity increases gradually, while apparent density decreases as sintering temperature increases, and the volumetric shrinkage of the cross-laminated sample is obviously lower than the parallel-laminated sample. The laminated structure greatly improves fracture toughness because of crack deviation and progressive failure behavior, which can prevent sudden breakage.

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