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Subyakto · Toshimitsu Hata · Shuichi Kawai
Yuji Imamura · Isamu Ide

Anisotropic thermal properties of molded carbon phenolic spheres

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Abstract Anisotropic thermal properties of molded carbon phenolic spheres (CPS), a mixture of sugi wood charcoal powders and phenol formaldehyde resin molded with a hot press, were investigated. The effects of the carbonizing temperature, particle size of chars, and density of the CPS on thermal properties were discussed. The molded CPS specimens were measured for their thermal properties using the laser flash method in both horizontal and vertical directions. The configuration of the CPS was observed by scanning electron microscopy. Anisotropy of the thermal properties (thermal diffusivity and thermal conductivity) between horizontal and vertical directions of the molded CPS was much higher than that of the uncarbonized molded phenolic spheres. Therefore, converting wood into molded CPS is an effective way to enhance the thermal-anisotropy properties. More marked effects of the carbonizing temperature, particle size, and density were observed in the horizontal direction than in the vertical direction. Anisotropy in thermal properties of the molded CPS may be considered an advantage for developing a new fire-retardant material for wood composites.

Subyakto
R&D Centre for Applied Physics, LIPI, Puspiptek Serpong 15310, Indonesia

T. Hata (✉) · S. Kawai · Y. Imamura
Wood Research Institute, Kyoto University, Uji, Kyoto 611-0011, Japan
Tel. +81-774-38-3667; Fax +81-774-38-3678
e-mail: hata@kuwri.kyoto-u.ac.jp

I. Ide
Lignyte Co., Sakai, Osaka 592, Japan

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Key words Carbon · Wood charcoal · Phenol formaldehyde resin · Anisotropy · Thermal properties

Introduction

Among the assessment properties of wood composite of structural members in building construction, fire performance is important and getting more attention nowadays. Addition of chemicals is common practice to enhance the fire resistance of wood composites but is detrimental to the environment due to the contained toxic chemicals. The application of fire-retardant agents based on nonchemical materials, for example wood char, would be more environmentally preferable in the future. Some studies have been done using carbon materials from wood for enhancing the fire retardant property of wood composite.[1–4] Utilization of wood charcoal for carbon composites and other uses has been reviewed by Ishihara.[5]

A new composite called carbon phenolic spheres (CPS), developed in recent years,[2–4] is basically a mixture of carbon graphite and wood charcoal with a phenol formaldehyde resin. The development of this material opens the possibility of utilizing wood char as a fire protection for wood-based products. However, the thermal properties of molded CPS have not been fully clarified. The objective of this study was to examine the anisotropic thermal properties of molded CPS using a laser flash method and to determine the production conditions for enhancing thermal anisotropy. The thermal properties of molded CPS (i.e., thermal diffusivity, heat capacity, thermal conductivity) were evaluated. The effects of the carbonizing temperature, particle size of the char, and density of the molded CPS on the thermal properties were investigated. The optimum condition of anisotropy in thermal properties between horizontal and vertical directions was discussed for application of the fire-retardant materials based on self-heat diffusion. In addition, scanning electron microscopic (SEM) observations analyzed the relation between the morphological changes of char and the thermal properties.

Materials and methods

Preparation of wood char powders

Chars were prepared from wood powders of sugi (*Cryptomeria japonica* D. Don). The wood powders were carbonized at temperatures of 600°, 800°, 1000°, 1200°, and 1400°C with a heating rate of 4°C/min and then kept constant at the targeted temperature for 1 h in nitrogen gas flowing rate at 100 ml/min. The chars were then sieved with wire mesh screens of 30 (503 μm openings) and 50 (279 μm openings) to obtain a uniform size of the chars (30-pass/50-on).

The chars carbonized at 800°C were sieved with wire mesh screens of 20 (840 μm openings), 30 (503 μm openings), 50 (279 μm openings), 100 (149 μm openings), and 300 (46 μm openings) meshes resulting in three particle sizes of chars (i.e., 20-pass/30-on, 30-pass/50-on, and 100-pass/300-on) so we could discuss the effect of particle sizes of chars on the thermal properties of molded CPS. The average particle lengths (standard deviations) of chars sieved as 20-pass/30-on, 30-pass/50-on, and 100-pass/300-on were 1.32 mm (0.96 mm), 1.18 mm (0.15 mm), and 0.96 mm (0.15 mm), respectively. The average particle widths (standard deviations) of those chars were 0.57 mm (0.10 mm), 0.46 mm (0.15 mm), and 0.11 mm (0.05 mm), respectively.

Preparation of molded carbon phenolic spheres

Carbon phenolic spheres were made by mixing char powder with a phenol-formaldehyde resin that had a resin content of 25% based on dry weight of char. The mixture was stirred in a hot bath with temperatures starting at room temperature up to 85°C for 1 h and then kept constant for 3 h. The mixture was then cooled to room temperature and rinsed with water to remove the excess phenol-formaldehyde resin. It was oven-dried at 45°C for 12 h, and CPS was obtained.

The CPS was hand-formed and molded with a hot press at 160°C for 10 min at a pressure of 16–18 MPa in a pair of metal dies to make a 25 mm square (1 mm in thickness) and 10 mm in diameter (1 mm in thickness) specimens for measurement of thermal properties in horizontal and vertical directions, respectively. The amount of CPS put in the die was adjusted to meet the targeted density. To evaluate the effect of the carbonizing temperature, CPS carbonized at 600°, 800°, 1000°, 1200°, and 1400°C with a particle size of 30-pass/50-on were pressed to a targeted density of 0.6 g/cm^3. To evaluate the effect of density of molded CPS, CPS with a particle size of 30-pass/50-on powder carbonized at 800°C was pressed to targeted densities of 0.5, 0.6, 0.7, and 0.8 g/cm^3. For evaluating the effect of particle size, the 20-pass/30-on, 30-pass/50-on, and 100-pass/300-on powders carbonized at 800°C were pressed to a targeted density of 0.6 g/cm^3. All specimens were kept in a desiccator before the measurement.

Measurement of thermal properties of molded CPS

The thermal properties (i.e., thermal diffusivity, heat capacity, thermal conductivity) of molded CPS were measured using a laser flash thermal analyzer (Ulvac Shinku-Riko TC-7000, Japan) in accordance with JIS R 1611.[6] The thermal properties of specimens were measured at room temperature. The specimen was flashed by laser beam for a short period, and the temperature rise was recorded.[7] To observe the anisotropy characteristic of molded CPS, the thermal diffusivity of the specimens was measured in two directions (i.e., horizontal and vertical).

The thermal diffusivity was calculated as

$$\alpha = (0.1388 \cdot d^2)/t_{1/2} \quad (1)$$

where α is the thermal diffusivity (cm^2/s), d the thickness of test piece (cm), and $t_{1/2}$ the half time of maximum temperature rise due to laser irradiation (s).
While specific heat capacity was calculated as

$$C = Q/(d \cdot \rho \cdot \Delta T_o) \quad (2)$$

where C is the specific heat capacity (J/g/K), Q the absorbed quantity of heat (J), d the thickness of the test piece (cm), ρ the density of the test piece (g/cm^3), and ΔT_o the extrapolated temperature rise (K).
Thermal conductivity was calculated as

$$\kappa = \alpha \cdot C \cdot \rho \quad (3)$$

where κ is the thermal conductivity (W/cm/K).

Statistical analysis was performed to determine the effects of the carbonizing temperature, density, and particle size on the thermal properties, Multiple regression analyses were conducted to establish their relations.

Observation of molded CPS using scanning electron microscopy

To observe the morphological changes in wood cell structure of char due to different carbonizating temperatures, SEM (JEOL JSM 5310, Japan) observations were conducted on CPS carbonized at different temperatures and on uncarbonized phenolic spheres.

Results and discussion

Thermal properties of molded CPS

The ratios of horizontal (H) and vertical (V) measurements of thermal diffusivity and thermal conductivity and the values of specific heat capacity of molded CPS manufactured in various conditions are shown in Table 1.

Because of its inherent micro- and macrostructures of wood (i.e., the orientation of fibers and of cellulose microfibrils in cell walls and cell structures) wood has anisotropic thermal properties. For example, the thermal conductivities of many solid woods in both longitudinal and transverse directions show linear relations to the density, and the ratio of the thermal conductivity between the longitudinal and transverse directions of solid wood at a given density is estimated as about 2.3.[8] Particleboard consists of discrete pieces of particles where particles are randomly

Table 1. Ratios of horizontal and vertical measurements of thermal diffusivity and thermal conductivity; values of specific heat capacity of uncarbonized CPS and CPS at various carbonizing temperatures, densities, and particle sizes

Factors			H/V ratio of thermal diffusivity	H/V ratio of thermal conductivity	Specific heat capacity (J/g/K)
Carbonizing temperature (°C)	Density (g/cm^3)	Particle size			
Uncarbonized CPS	0.6	30-pass/50-on	9.5	9.6	0.8191
Carbonized CPS					
600	0.6	30-pass/50-on	32.4	30.4	0.6186
800	0.6	30-pass/50-on	27.4	25.8	0.6107
1000	0.6	30-pass/50-on	30.6	30.0	0.6387
1200	0.6	30-pass/50-on	28.3	27.9	0.6209
1400	0.6	30-pass/50-on	27.8	28.3	0.6200
800	0.5	30-pass/50-on	29.2	28.9	0.5708
800	0.7	30-pass/50-on	22.2	22.0	0.6066
800	0.8	30-pass/50-on	19.2	19.4	0.6299
800	0.6	100-pass/300-on	31.5	31.3	0.5986
800	0.6	20-pass/30-on	33.9	34.4	0.7235

H, horizontal; V, vertical; CPS, carbon phenolic spheres

oriented in the plane direction and have a more or less layered structure along the thickness. Therefore, the heat flows along the thickness of the particleboard basically similar to its flow across solid wood. The discontinuity of particles and existence of adhesive may cause significant resistance to the heat flow. As a result, the thermal conductivity of particleboard along the thickness is reported as somewhat lower than in the transverse direction of solid wood.[8] The thermal conductivity of particleboard in the plane (horizontal) direction can be roughly estimated to be an average value between the longitudinal and transverse directions of solid wood. Thus the anisotropic ratio in thermal conductivity of particleboard would be lower than that of the solid wood.

In uncarbonized molded phenolic spheres, the values of thermal properties in the vertical direction are similar to those of solid wood, but in the horizontal direction the values are about four times higher than those of solid wood.[9] These results produce higher horizontal/vertical direction (H/V) ratios (Table 1).

The values for thermal properties of molded CPS made at different carbonizing temperatures, densities, and particle sizes were much higher in the horizontal direction than in the vertical direction, and the H/V ratios of molded CPS were much higher than those of solid wood and uncarbonized molded phenolic spheres (Table 1).

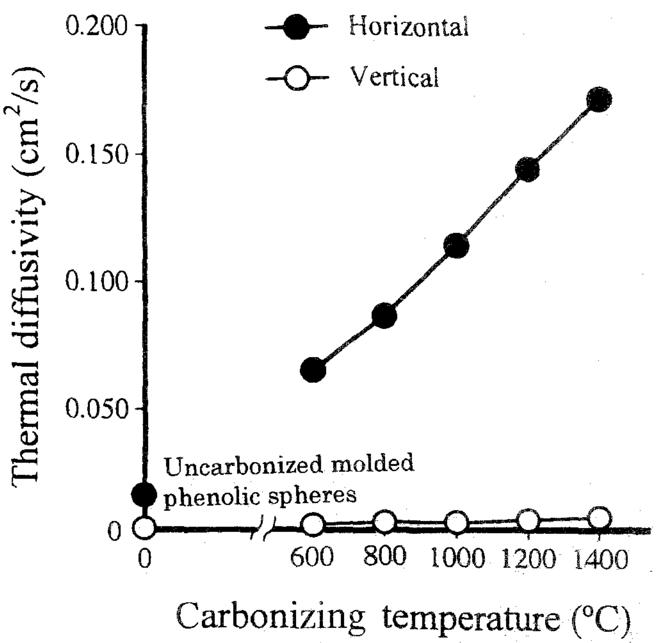

Fig. 1. Effect of carbonizing temperature on thermal diffusivity of molded carbon phenolic spheres (CPS)

Effect of treatment on the thermal diffusivity of molded CPS

Figure 1 shows the thermal diffusivity of molded CPS in relation to the carbonizing temperatures. With increasing carbonizing temperatures the thermal diffusivity of molded CPS increases linearly in both horizontal and vertical directions, but the increases were much higher in the horizontal than the vertical direction. Therefore, the H-V differences in the thermal diffusivity of molded CPS increase with increasing carbonizing temperature. Statistical analysis showed that the effect of the carbonizing temperature on thermal diffusivity is significant in both horizontal and vertical directions.

Cutter et al.[10] found that tracheid diameters of southern pine decreased whereas the lumen diameters behaved erratically with increasing carbonizing temperature. Probably the crystalline regions of the cell walls increase with carbonization and are accelerated with higher carbonizing temperatures. As a result the heat flows much faster in the fiber direction of the carbonized wood.

It is also shown in Fig. 1 that by carbonizing the wood powder the thermal diffusivity became much greater compared with that of uncarbonized wood powder in horizontal and vertical directions. The carbonizing temperature of char can be chosen as 600°C because it gave relatively a high H/V ratio. Lower carbonization temperature is preferred from the point of saving energy.

Figure 2 shows the thermal diffusivity of molded CPS in relation to the density. The thermal diffusivity of molded CPS decreases with increasing density in the horizontal direction but increases somewhat in the vertical direction. Therefore, a lower density gave a higher H/V ratio. During the process of pressing CPS, the particles are not uniformly compressed in both horizontal and vertical directions; that is, it is denser in the vertical direction. Therefore thermal diffusivity in the vertical direction increases with increasing density due to relatively highly densified particles in the thickness (vertical) direction, whereas thermal diffusivity in the horizontal direction decreases with increasing density owing to almost nondensified particles in the horizontal direction. Statistical analysis showed that the effect of density on thermal diffusivity is significant in both horizontal and vertical directions. The H/V ratio of thermal diffusivity was optimized at a density of 0.5 g/cm^3.

Figure 3 shows the thermal diffusivity of molded CPS in relation to the particle size of the chars. The thermal diffusivity of molded CPS increases with increasing particle size in the horizontal direction but remains unchanged in the vertical direction. In the horizontal direction, the discontinuity of smaller particles was observed more frequently than that of the larger particles. Consequently, the heat flows faster in larger particles than in smaller particles in the horizontal direction. Statistical analysis showed that the effect of the particle size on thermal diffusivity is significant in both horizontal and vertical directions. To observe the most dominant factors that affected the thermal diffusivity of molded CPS, multiple regression analysis was performed, with the results shown in Table 2. From the analysis, it seems that the carbonizing temperature is the most dominant factor that affects the thermal diffusivity of molded CPS.

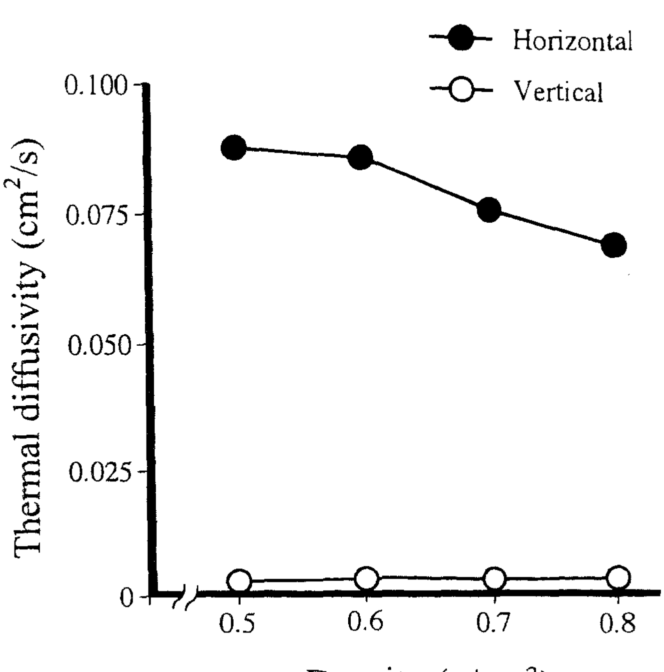

Fig. 2. Effect of density on thermal diffusivity of molded CPS

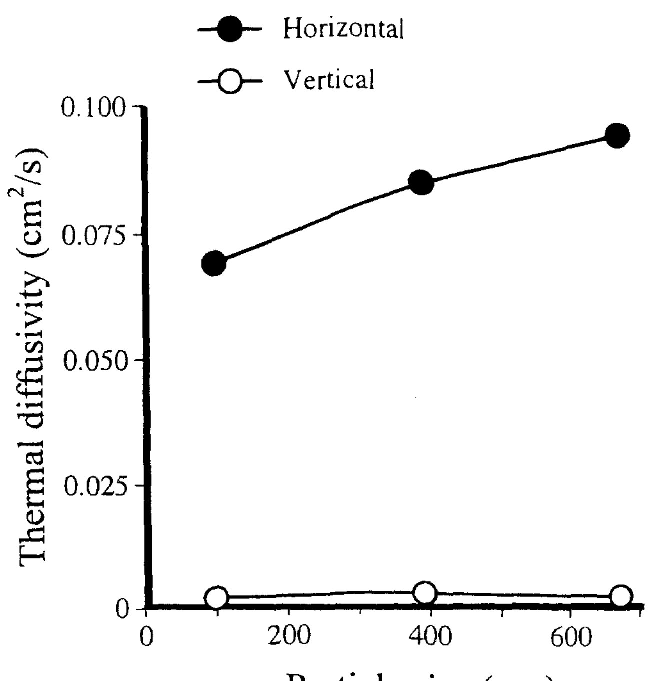

Fig. 3. Effect of particle size on thermal diffusivity of molded CPS

Table 2. Results of multiple regression analysis

Equations	r^2
$TDH = -0.0039 + (1.4299 \times 10^{-4})CT - 0.0739D + (5.0966 \times 10^{-5})PS$	0.977
$TDV = -0.0033 + (5.3415 \times 10^{-6})CT + 0.0031D$	0.909
$HC = 0.5401 + (2.1469 \times 10^{-4})PS$	0.419
$TCH = -0.038 + (5.4712 \times 10^{-5})CT + 0.0231D + (3.2223 \times 10^{-5})PS$	0.951
$TCV = -0.0029 + (2.0364 \times 10^{-6})CT + 0.0034D + (7.0058 \times 10^{-7})PS$	0.939

TDH, thermal diffusivity at horizontal direction (cm^2/s); *TDV*, thermal diffusivity at vertical direction (cm^2/s); *HC*, heat capacity (J/g/K); *TCH*, thermal conductivity at horizontal direction (W/cm/K); *TCV*, thermal conductivity at vertical direction (W/cm/K); *CT*, carbonized temperature (°C); *D*, density (g/cm^3); *PS*, particle size (μm); r^2, coefficient of determination

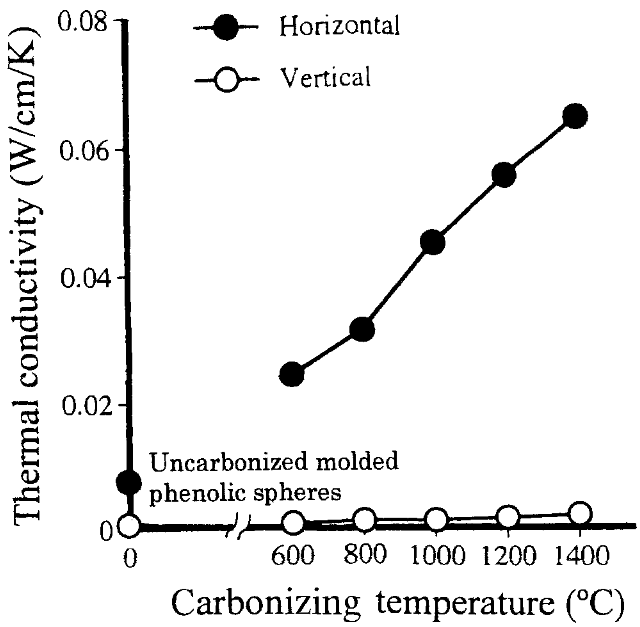

Fig. 4. Effect of carbonizing temperature on thermal conductivity of molded CPS

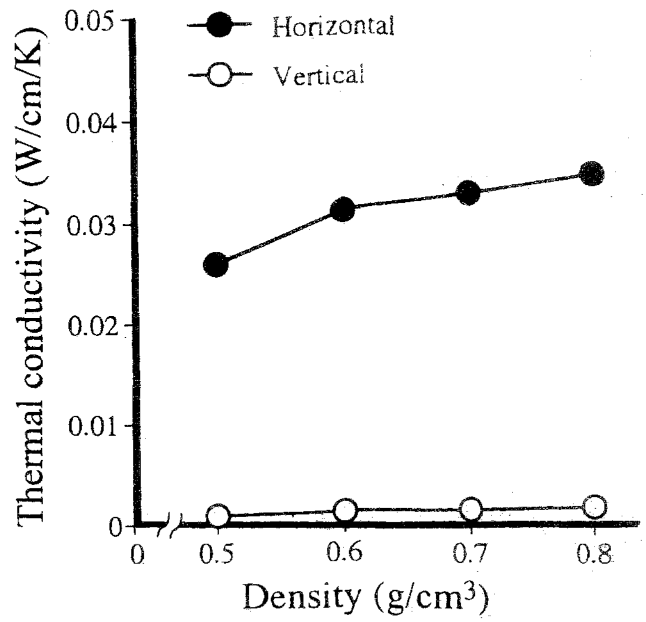

Fig. 5. Effect of density on thermal conductivity of molded CPS

Effect of treatment on specific heat capacity of molded CPS

As shown in Table 1, the heat capacity of molded CPS was not affected by the carbonizing temperature. Heat capacity is the amount of heat needed to raise the temperature of a unit mass of the substance by 1 K.[9] It was confirmed in the statistical analysis, which showed no significant effect of the carbonizing temperature on heat capacity. It was also found in this experiment that the heat capacity of uncarbonized molded phenolic spheres was higher than that of molded CPS. Similarly, Wilcox et al.[9] reported that heat capacity of wood is higher than that of charcoal.

The heat capacity of molded CPS increases slightly with increasing CPS density or particle size. The statistical analysis showed that CPS density and particle size had a significant effect on heat capacity, although the changes in heat capacity were rather small. From the multiple regression analysis, it seems that particle size is the dominant factor affecting the heat capacity of molded CPS.

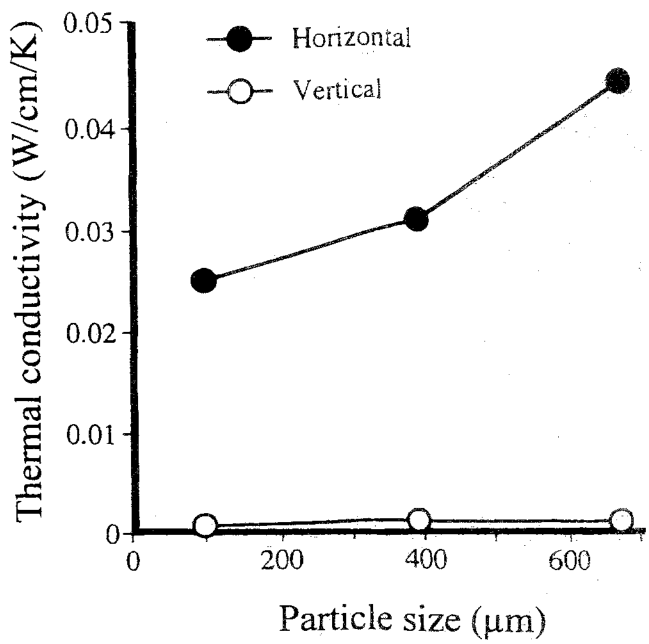

Fig. 6. Effect of particle size on thermal conductivity of molded CPS

Effect of treatments on thermal conductivity of molded CPS

Thermal conductivity was calculated as the product of thermal diffusivity, heat capacity, and density. Figure 4 shows the thermal conductivity of molded CPS in both horizontal and vertical directions in relation to the carbonized temperatures. Similar to thermal diffusivity, the thermal conductivity of molded CPS increases markedly with increasing carbonizing temperature in the horizontal direction but increases only slightly in the vertical direction. In contrast to thermal diffusivity, the thermal conductivity of molded CPS increases with increasing density in the horizontal direction but is only slightly increased in the vertical direction (Fig. 5). As shown in Fig. 6, the thermal conductivity of molded CPS increases with increasing particle size in the horizontal direction but is only slightly increased in the vertical direction. Statistical analysis showed that the effects of the carbonizing temperature, density, and particle size on thermal conductivity are significant in both horizontal and vertical directions. From the multiple regression analysis, it seems that the carbonizing temperature is the most dominant factor affecting the thermal conductivity of molded CPS.

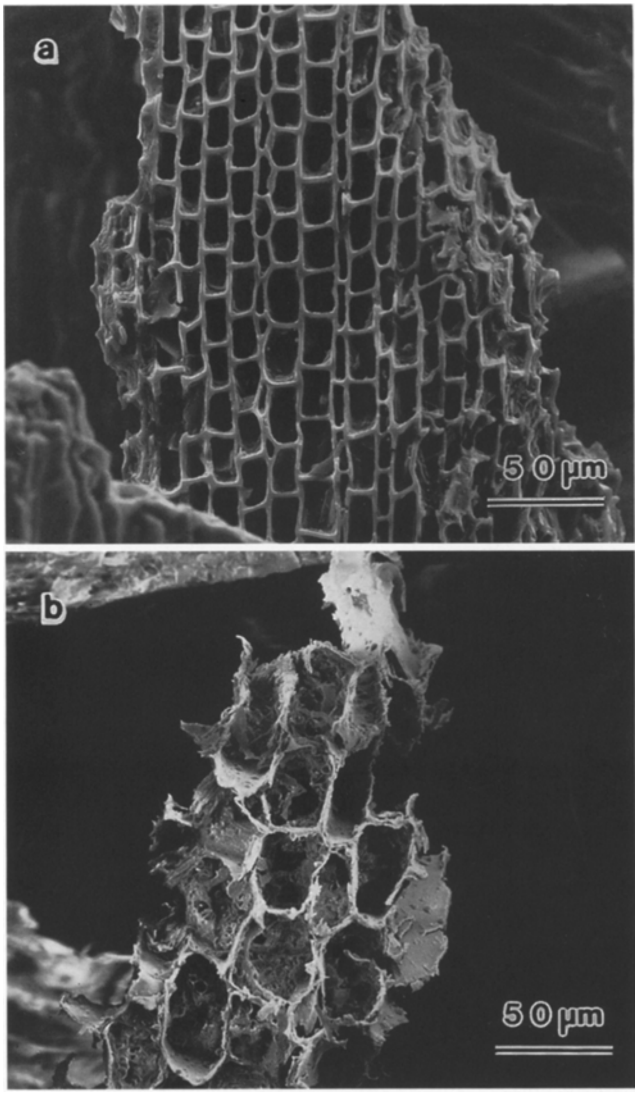

Fig. 7. a CPS particles carbonized at 600°C, showing that cell structures are maintained. **b** Uncarbonized CPS particles, showing damage to cell structures

SEM observation of CPS

As observed by others,[10,11] the wood char particles after carbonization process maintained their cell structures as in the original wood (Fig. 7A). Uncarbonized wood particles were damaged in the surfaces probably due to the acidity of phenol formaldehyde resin (pH 3.5) used during the process of coating (Fig. 7B). The damage was not observed in carbonized particles (Fig. 7A). The carbonized particles seem to be more resistant to the higher acidity.

Conclusions

The anisotropy in thermal properties was found clearly in the molded CPS. Anisotropy of the thermal properties in horizontal to vertical directions was much higher in the molded CPS than in the uncarbonized molded phenolic spheres. In the horizontal direction the thermal diffusivity of molded CPS increases with increasing carbonizing temperature and particle size, but it decreases with increasing density; in the vertical direction it remains unchanged. The heat capacity of molded CPS was not significantly affected by the carbonizing temperature, but it increases with increasing particle size and density. The thermal conductivity of molded CPS increases with increasing carbonizing temperature, density, and particle size in the horizontal direction but only slightly increases in the vertical direction.

Molded CPS with the anisotropic character in thermal properties could be used as a new fire-retardant material for wood composites. For example, thin sheets of molded CPS could reinforce the metal joints and improve the fire retardant property of a structural timber system by an overlay on the (metal) joints.

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