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Structure and properties of a moulded carbon derived from rice hull

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Rice hull was moulded into a tube (outer diameter: 54 mm; inner diameter: 17 mm, length: *c.* 170 mm) by use of an extruder and then carbonized in nitrogen atmosphere below 1000 °C. Ash content of the hull was 16 wt%, of which *c.* 94 and 4 wt% were SiO_2 and K_2O, respectively. Carbon yield and shrinkage of the mould after carbonization at 1000 °C were 42 wt%, and 43 vol%, respectively. The bulk density increased with rising of carbonization temperature to reach to 0.93 g ml^{-1} at 1000 °C via 0.82 g ml^{-1} at 500 °C. The largest compressive strength of 3.6 MPa was obtained after carbonization at 1000 °C. No micropore was developed after carbonization, and the total pore volume measured by a mercury porosimeter was 0.25–0.31 ml g^{-1} after carbonization. These data were compared with those of charcoal.

1. Introduction

Charcoal has recently been used as a soil conditioner and a water purifier for rivers or ponds. The charcoal used in these fields are usually prepared from waste wood [1, 2]. Rice hull is also a natural material which is abundantly wasted. Until now, there have been many attempts to use rice hull as an effective resource. Many of them have aimed at extracting a large amount of silicon which is included in rice hull, and preparations for this have been studied, i.e. silicon carbide [3, 4], silicon nitride [5], silicon tetrachloride [6], silicon metal [7] and so on. The preparation processes in these attempts were usually very complex, leading to high cost, and hence have never been commercialized. An important point to complete a practical application for rice hull is to develop as simple a preparation process as possible.

The present authors thought to prepare a carbon material from rice hull which could be used as a soil conditioner or a water purifier instead of charcoal. In order to be successful in this attempt, a bulky carbon like charcoal, and if possible with a similar porous structure, must be prepared. In the present work, rice hull was moulded into a tube by using an extruder and then carbonized. This paper describes the structure and some fundamental properties of the resulting rice hull-derived moulded carbon.

2. Experimental procedure

2.1. Raw materials and preparation of moulded carbon from rice hull

The hull of nonglutinous rice harvested in the Kanto region, Japan, was used in this work. A rice hull tube (inner diameter: 17 mm; outer diameter: 54 mm) was extruded continuously by use of a Grind Mill AFR-2000 (Meiji Machine Co. Ltd), and was cut into 180 mm lengths before use. The temperature and the pressure of extruding could not be measured but assumed to be several 100 °C and *c.* 200atm, respectively. Fig. 1 shows the raw rice hull and the tubes before and after carbonization at 500 °C. The tube surface changed from yellow brown to dark brown after extrusion, but the inside remained unchanged.

The rice hull tube was heated to 500 °C with a heating rate of 2.5 °C min^{-1} in nitrogen atmosphere and then kept for 30 min for carbonization. Some of the resulting tubes were further heated to prefixed temperatures below 1000 °C with a heating rate of 6–7 °C min^{-1} in nitrogen atmosphere and were kept at temperature for 30 min.

2.2. Measurements

The 500 °C-carbonized tube was burned completely at 850 °C in air, and the resulting ash was analysed quantitatively with a fluorescent X-ray analyser

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(Rigaku 3270E) and an atomic absorption spectrometer (Hitachi Z-6100). The X-ray powder method with CuK_α radiation was used to analyse the microscopic structure of the specimens. Fracture surface of the specimens was observed by scanning electron microscopy (SEM: Jeol JSM-820). Porous texture analysis was carried out by N_2 adsorption at 77 K (Autosorb 6) and a mercury porosimeter (Carlo Erba 2000). Compressive strength along the extrusion direction was measured using a Shimazu AG-5000 with a cross-head speed of $1\ \text{mm min}^{-1}$. Bulk density and bulk shrinkage were calculated by volume and weight. The data shown are the average of 3 or 4 values.

3. Results and discussion

3.1. Carbon yield, shrinkage, bulk density and compressive strength

Table I shows some properties of the specimens before and after carbonization. The carbon yield at 500 °C was 44 wt %, and a further slight decrease was observed at higher temperature up to 1000 °C. The yields are almost the same or slightly higher than those of woods [1, 8]. Volume shrinkage of the rice hull mould was 38% at 500 °C and increased to 43% at 1000 °C with sintering. The sintering caused a bulk density increase between 500 and 1000 °C, for which the values were less than $1.00\ \text{g ml}^{-1}$. The mould became relatively hard after carbonization. The compressive strength of 2.9–3.6 MPa for the moulded carbons are strong enough to be handled. The mould before carbonization was too soft to be measured.

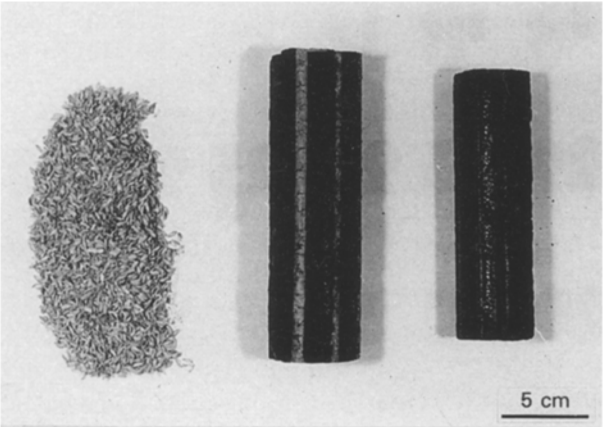

Figure 1 Photographs of raw rice hull (left) and rice hull moulds before (centre) and after carbonization at 500 °C (right).

3.2. Ash analysis and X-ray diffraction

Ash content of the 500 °C-carbonized specimen after burning at 800 °C was 16 wt %, which is far larger by several per cent of that for woods [1, 8]. One of the largest ash content in woods reported previously is 8.6 wt % of the 450 °C-carbonized Lauan wood [2]. Table II shows analytical data of the resulting ash. About 94 wt % of the ash was SiO_2. Four wt % of K_2O should be emphasized, because it acts as a favourable fertilizer.

X-ray diffraction profiles are shown in Fig. 2. It is well known that a disordered low crystalline carbon structure has (0 0 2) broad diffraction peak around 25° (2θ, CuK_α), but the peaks for the rice hull-derived carbons were situated around 20°. Peaks from crystalline SiO_2 or its related compounds were not observed.

3.3. Porous structure

The Brunauer–Emmett–Teller (BET) surface areas of the specimens are shown in Table I. Only several $\text{m}^2\,\text{g}^{-1}$ were obtained for the rice hull-derived moulded carbons, which means no formation of micropores occurred after carbonization. This small surface area makes a remarkable contrast to the surface areas of charcoals, i.e. $57–174\ \text{m}^2\,\text{g}^{-1}$ by Hirose *et al.* [8], $345–1359\ \text{m}^2\,\text{g}^{-1}$ by Hitomi *et al.* [9] and $262–300\ \text{m}^2\,\text{g}^{-1}$ by Kitagawa [2].

The pore size distribution curves and pore volumes obtained using the mercury porosimeter are shown in Fig. 3 and Table I, respectively. Fig. 3 shows a wide range of pore size distributions of the rice hull moulds both before and after carbonization. Charcoals derived from Alder Buckthorn wood and Beech wood have similar pore sizes [10]. As can be observed from their SEM photographs [10], charcoals have far larger pore volumes than the rice hull-derived carbons shown in Table I. Pore volume increased at 500 °C and then decreased at 1000 °C with sintering.

3.4. SEM photographs

Fig. 4 shows the outside and inside surfaces of a piece of rice hull carbonized at 1000 °C. These characteristic morphological structures were clearly derived from those of an original raw rice hull.

Fig. 5 shows the fracture surfaces of the moulds before and after carbonization. The characteristic morphological structure of the outside is observed in the mould before carbonization. The parts labelled by 1 and 2 show the inside and outside surfaces of the rice hull, respectively. These structures remained after carbonization at 1000 °C. The parts labelled by 3, 4 and

TABLE I Properties of rice hull moulds before and after carbonization.

	Carbon yield (wt %)	Shrinkage (vol %)	Bulk density (g ml^{-1})	Compressive strength (MPa)	BET surface area ($\text{m}^2\,\text{g}^{-1}$)	Pore volume[a] (ml g^{-1})
Raw	0	0	1.11	—	2.7	0.13
500 °C	44	38	0.82	2.9	3.4	0.31
1000 °C	42	43	0.93	3.6	3.6	0.25

[a] Measured using a mercury porosimeter (pore radius: 3.8 ~ 7500 nm).

TABLE II Ash analysis of 500 °C-rice hull mould[a]

SiO_2	93.63 wt %
Al_2O_3	0.06
Fe_2O_3	0.18
TiO_2	0.01
CaO	0.31
MgO	0.27
K_2O	4.00
Na_2O Ig. loss	0.23
H_2O	0.12
S	0.07
P	0.3
Cr	0.8
Total	99.98

[a] Burnt at 800 °C in air.

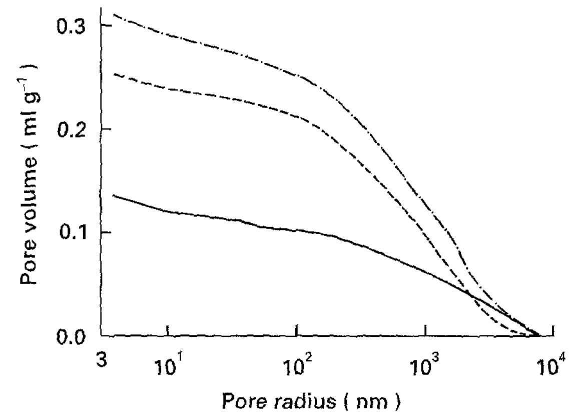

Figure 3 Pore size distribution curves of rice hull moulds before and after carbonization.

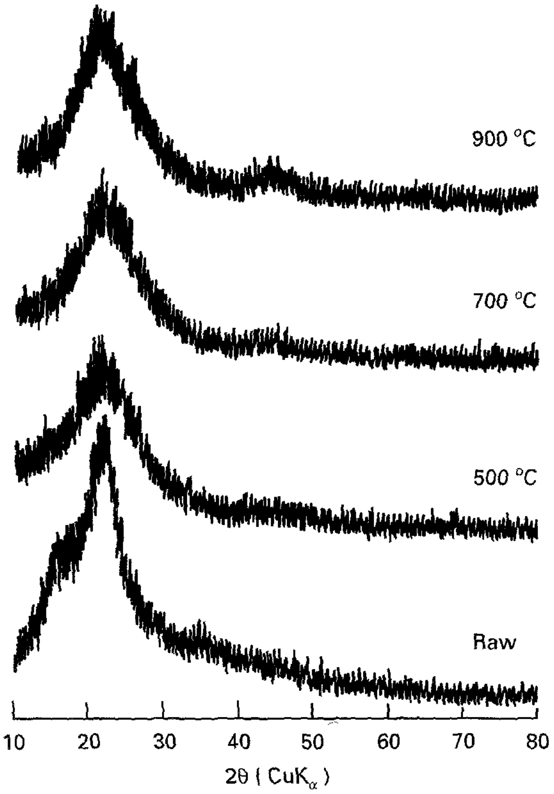

Figure 2 X-ray diffraction profiles of rice hull moulds before and after carbonization.

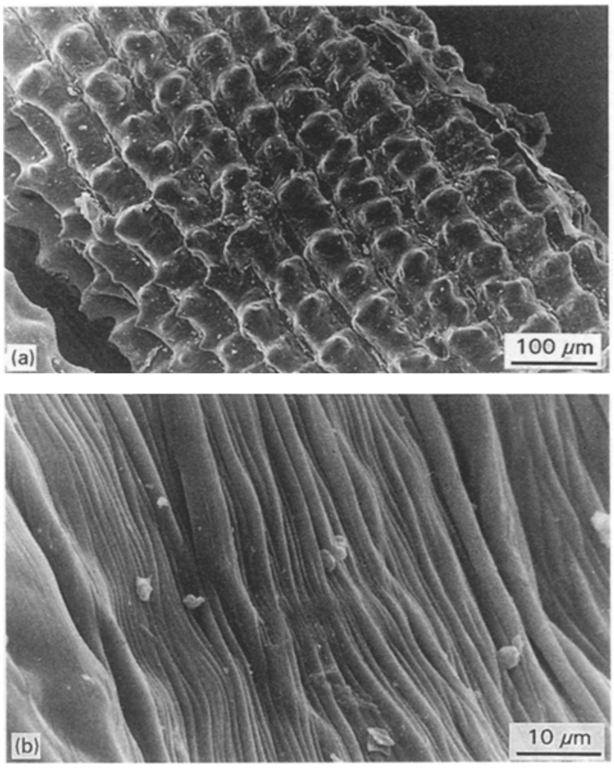

Figure 4 SEM photographs of surfaces of rice hull. (a) Outside; (b) Inside.

5 are the outside and the inside of the rice hull, respectively. The large pores 6 were rarely observed. These pores are somewhat analogous to narrow pores derived from conducting vessels in wood [10].

Through the comparison with charcoal, the rice hull-derived moulded carbon was concluded to have the following characteristics;

1. The characteristic porous structure in charcoal has narrow pores derived from conducting vessels, but such pores were not observed in the rice hull-derived moulded carbon.
2. Different from charcoal, the rice hull-derived moulded carbon does not have micropores as suggested from its small BET surface area.
3. The rice hull-derived moulded carbon contains a larger amount of ash than charcoal.

Potassium is somewhat included in addition to a large amount of silicon.

In view of applications as a soil conditioner and a water-purifier, the next step in a series of present works is to examine how to form and how to control a porous structure in the moulded carbon. Such a characteristic narrow porous structure as in charcoal can not be formed in the rice hull-derived moulded carbon by the present moulding technique, but a larger porosity could be introduced into it by controlling the pressure and temperature on extruding, which is now in progress.

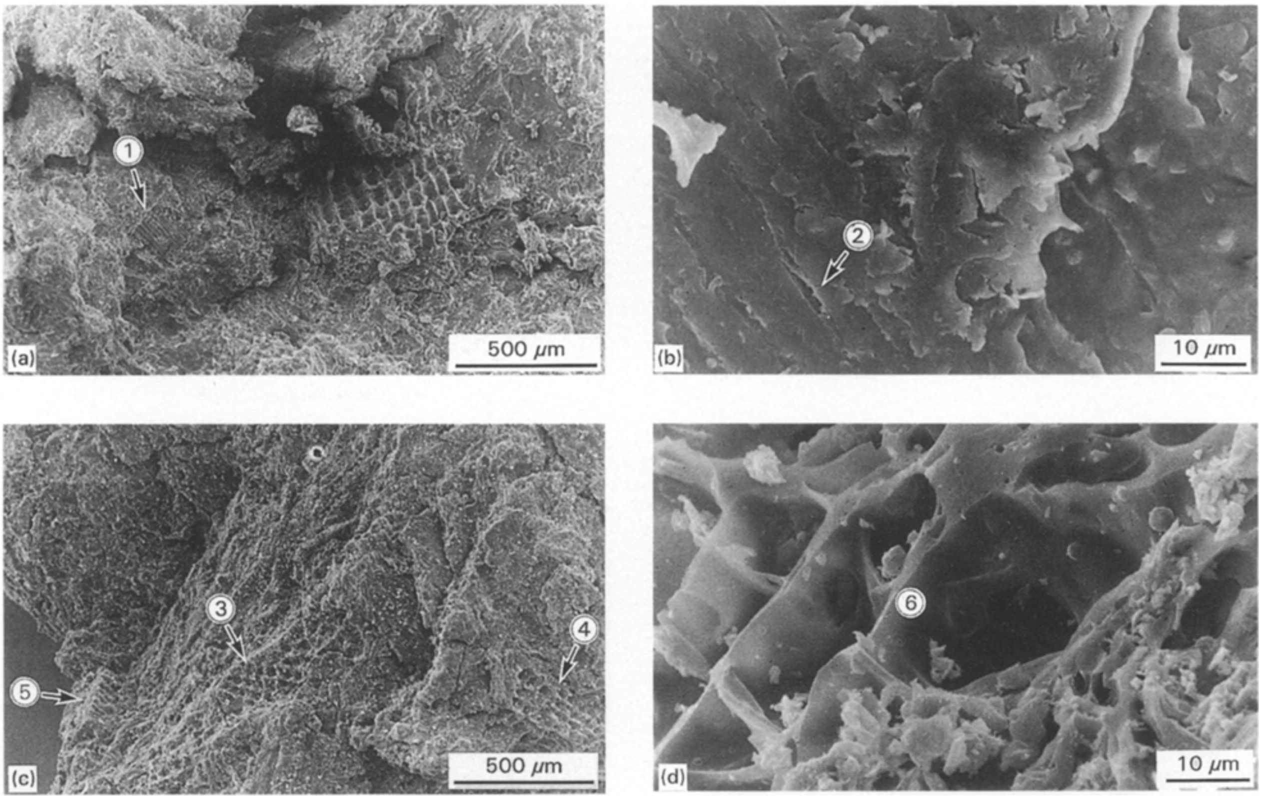

Figure 5 SEM photographs of fracture surfaces of the rice hull moulds before and after carbonization at 1000 °C. (a) Before carbonization; (b) Before carbonization; (c) Carbonized at 1000 °C; (d) Carbonized at 1000 °C.

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