Fabrication of porous SiO$_2$/C composite from rice husks

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Abstract

Porous SiO$_2$/carbon composites were fabricated by heating pellets composed of rice husk (RH) powders in small ($<$74 μm), medium(74–175 μm) and large(150–300 μm) sizes. The contents of the small RH were fixed at 30 mass% and the RH pellets molded at 10, 15, and 30 MPa were heated at 800–1150 °C in an inert atmosphere. The weight loss due to the thermal decomposition of the organic materials in the pellet peaked at 1000 °C, whereas the specimen heated at 1000 °C showed the lowest carbon content and density, 29 mass% and 0.40 g cm^{-3}, respectively. The SiO$_2$ phase of the specimens were amorphous at 800 and 1150 °C, but a cristobalite phase was visible at 1000 °C. The specimen fire at 1000 °C showed a higher compressive strength than the others, and the large RH particles were seen to increase the strength of the product while an increase in molding pressure decreased the medium pore size, from 17 to 7 μm, and increased the strength, from 0.25 to 3.52 MPa. The specific surface area (SSA) of the specimen peaked at 450 m^2 g^{-1}, at 1000 °C and finally, the mesopore size of the specimens was similar throughout, at $\sim$2 nm.
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1. Introduction

The rice husk (RH) used, normally a discarded agriculture by-product, consisted of organic materials (e.g. cellulose, hemicellulose and lignin) (61–77 wt.%), ash (mainly amorphous SiO$_2$) (13–29 wt.%) and water.[1] These components converted to the following useful materials in the course of each treatment. By burning out the organics, a porous SiO$_2$ with a high specific surface area could be obtained.[2] Moreover, the SiO$_2$ thus obtained from RH is particularly active and has thus been used as a raw material for the preparation of zeolite[3] and cordierite[4], respectively. Furthermore, SiC whiskers were fabricated based on the reaction between the organic materials and SiO$_2$ in the RH at a temperature of 1100–1400 °C.[1] On the other hand, porous carbons were formed by heating the RH within an inert atmosphere.[5,6] The molded RH powder tube was changed to porous carbon with a specific surface area (SSA) of 3.4 m^2 g^{-1}. The RH compact was heated under H$_2$O gas, with an SSA value of 240 m^2 g^{-1}. Furthermore, the RH compact mixed with ZnCl$_2$ compound

was heated within a CO$_2$ atmosphere and the resulting carbon showed high SSA value of 480 m^2 g^{-1}. In spite of these complicated processes, a fresh attempt to simplify the process was recently investigated.[7]

This project also aimed to obtain a porous form of carbon with a high surface area through a simple process using rice husk powder compacts. The powder compacts formed by mixing the RH powders with different particle sizes were carbonized to form a porous SiO$_2$/carbon composite. In this paper, the effects of the molding pressure and treatment temperature on the features of the product were described.

2. Experimental

Three commercial RH powders (S-RH ($<$74 μm), M-RH (74–175 μm), and L-RH (150–300 μm) from Daiso Trading Co. Ltd.) were used. Since the rice husk has a shell shape, the commercial large L-RH powder mainly consisted of anisotropic plate-like particles and the S-RH powder was homogeneously mixed with M- or L-RH powders according to a ratio; S/(S + M (or L)) = 0.3 in weight according to the previous work.[8] In order to avoid any change in the size

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and structure of the raw RH particles during the mixing process, a special mixer ("Hybrid Mixer", Keyence Co. Ltd.) was used. The mixed powder was pressed into a pellet (Ø 10 mm × 5 mm) under a pressure of 10, 20, or 30 MPa and then placed into an alumina crucible with an alumina cover. This crucible was placed into a larger alumina crucible and covered with graphite powder. The outer crucible was covered with an alumina cover again in order to avoid any combustion of the graphite powder in air. The crucible set was heated at 800–1150 °C for 2 h in air and the rate at which the temperature increased to the treatment temperature was 20 °C/min.

The thermal behavior of the products was evaluated using thermogravimetry (TG) and differential thermal analyses (DTA) in the air flow. The density and shrinkage of the pellet, meanwhile, were calculated using its dimension and weight. The microstructures were observed with a scanning electron microscope (SEM) and the SSA value was measured through the N_2 gas adsorption (BET) method at 77 K. The pore size distribution of the product was measured with a mercury porosimeter (MP) and also calculated using the N_2 gas desorption behavior using the BJH method.

3. Results and Discussion

3.1. RH Powder Compact

The density of the RH pellet increased with the molding pressure as shown in Fig. 1; 0.95–0.97 g cm^{-3} (10 MPa), 1.02–1.04 g cm^{-3} (15 MPa) and 1.06–1.10 g cm^{-3} (30 MPa). The increase in density between 10 and 15 MPa was larger than that between 15 and 30 MPa. The specimen from the (S + L) mixture powder showed a lower density than that from the (S + M), due to the anisotropic structure of the L-RH particles, which disturb the particle packing during molding. This difference in density changed the pore structure of the pellet and thus the decomposition procedure of the organic compounds in the RH pellet was also inevitably subject to change. This process also led to change in the characteristics of the SiO_2/C products as described below.
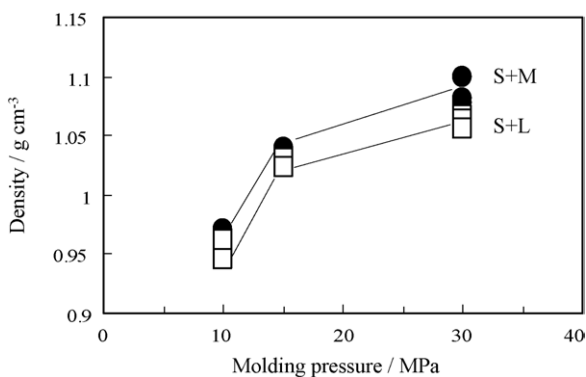

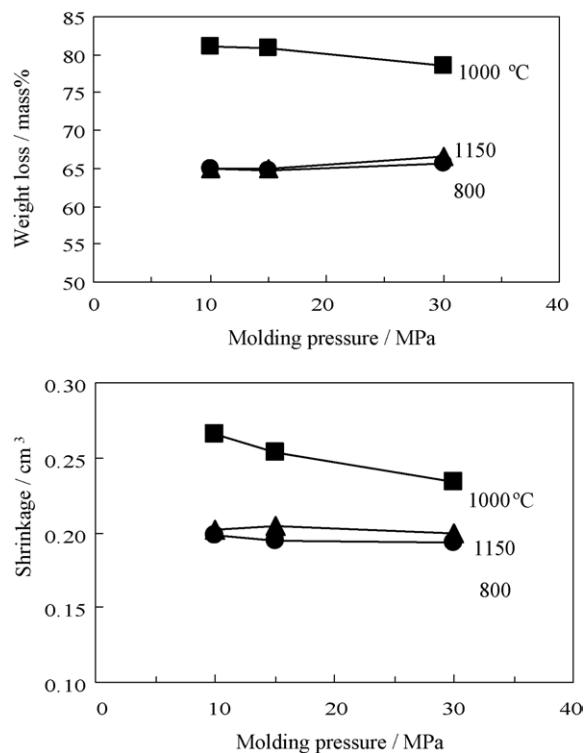Fig. 1. Dependence of pellet density on molding pressure and raw powders.

Fig. 2. Dependence of weight loss and shrinkage of (S + M) pellets on molding pressure and treatment temperature.

3.2. Formation of the SiO_2/C composite

The organic compounds decompose when heated in an inert atmosphere and partly change to H_2O, CO, CO_2, and volatile compounds,[9] remaining carbon and SiO_2. This volatilization decreases the weight of the RH pellet following heat-treatment. The change in the weight loss and the shrinkage of the (S + M) pellet with the molding pressure and the treatment temperature are depicted in Fig. 2. The weight losses at 800 and 1150 °C took place almost independently of the pressure, ∼65 mass%, but that at 1000 °C slightly decreased with the molding pressure, from 81 to 78 mass%. According to the previous project,[8] the weight loss became almost constant at 600 °C, ∼60 mass%, with a value is similar to those recorded at 800 and 1150 °C. However, the weight loss and shrinkage of the pellet at 1000 °C were far higher than those recorded at 800 and 1150 °C. Also the (S + L) pellets showed similar behavior to those in Fig. 2. In this project, the products at a temperature of 1000 °C showed different characteristics compared to those prepared at other temperatures and this behavior will be further discussed later.

The porous SiO_2/C composites were fabricated by heating the (S + M) or (S + L) pellets within an inert atmosphere. The density of the resulting pellets varied from 0.40 to 0.67 g cm^{-3} as shown in Fig. 3. In this project, the density increased with increasing molding pressure, but the heat-treatment temperature was more effective. The pellets heated
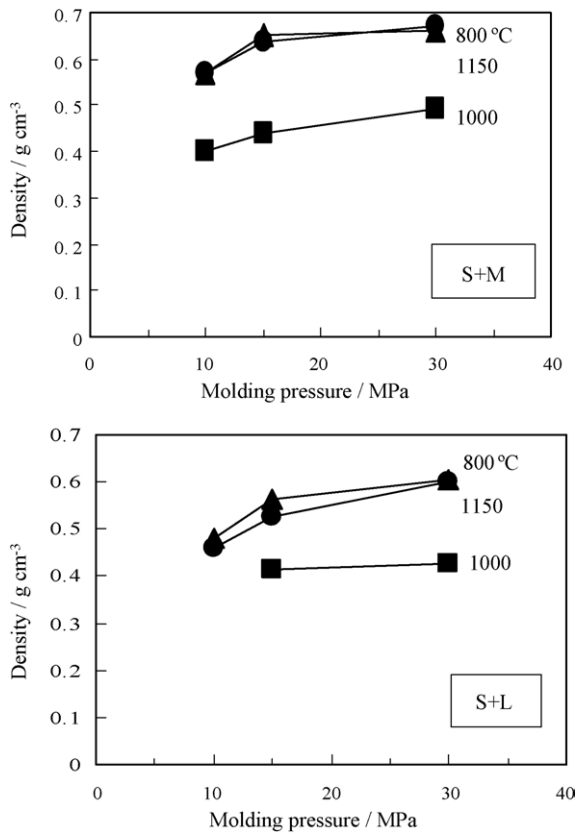
Fig. 3. Dependence of density of SiO_2/C pellets on molding pressure, treatment temperature and raw powders.

at $1000\,^{\circ}C$ showed a relatively low density, the large weight loss in this specimen being one of the reasons. The SiO_2/C prepared from the $(S+L)$ mixture showed a lower density compared to that of the $(S+M)$ one. This is due to the lower density of the original $(S+L)$ pellet (Fig. 1).

3.3. Characteristics of the SiO_2/C composite

The thermal behaviors (TG and DTA) of the specimen prepared at $800\,^{\circ}C$ were shown in Fig. 4. Three kinds of
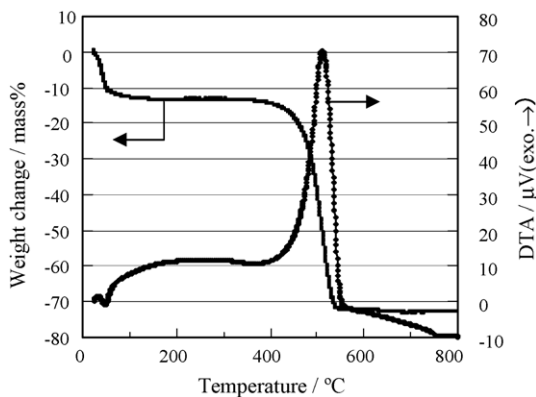

Fig. 4. Weight and thermal changes of SiO_2/C pellets $(S+M, 800\,^{\circ}C)$ on heating in air.

Table 1
Weight losses and carbon contents of SiO_2/C pellets prepared at $800–1150\,^{\circ}C$

	$800\,^{\circ}C$	$1000\,^{\circ}C$	$1150\,^{\circ}C$
Weight loss (second stage) (mass%)	59	26	41
Carbon content (mass%)	68	29	46

weight loss were observed in the TG curve. The first was due to the evaporation of the adsorbed water and the second one corresponded to the oxidation of the carbon in the specimen, which started at $\sim400\,^{\circ}C$ and ended at $\sim530\,^{\circ}C$. This was accompanied by a large exothermic peak. The starting temperature for the oxidation of the carbon prepared at 1000 and $1150\,^{\circ}C$ rose higher. From this oxidation weight loss, the carbon contents, $C/(SiO_2+C)$, of the specimens were calculated and the results listed in Table 1. The carbon content was $68\,mass\%$ at $800\,^{\circ}C$ and this value is higher than that at $1150\,^{\circ}C$, even though the weight losses of these specimens are similar as shown in Fig. 2. Furthermore, the carbon content at $1000\,^{\circ}C$ showed the lowest value, $29\,mass\%$. This low carbon content may see the crystallization of amorphous SiO_2 to cristobalite phase occur only in this specimen, although the other specimens displayed the presence of amorphous SiO_2. Inoue et al. reported that the rice husk ash crystallized to cristobalite in excess of $800\,^{\circ}C$.[10] Therefore, in the present work, the crystallization of SiO_2 in the pellet at 800 and $1150\,^{\circ}C$ was depressed by the coexisting carbon. As discussed above, the porosity of the specimen peaked at $1000\,^{\circ}C$ as shown in Fig. 5. Although it is very difficult to explain the reasons why, the carbon content in each specimen must be related to these characteristics.

The compressive strength of the specimen increased with density as shown in Fig. 6, which is reasonable behavior. The usage of the larger L-RH particle also leads to higher strength, which may be due to the anisotropic particle skeleton of L-RH remaining in the SiO_2/C specimen. Meanwhile, the specimens prepared at $1000\,^{\circ}C$ have a relatively higher strength due to the higher SiO_2 content.

The effect of the heat-treatment temperature on the microstructures of the specimens is shown in Fig. 7. The
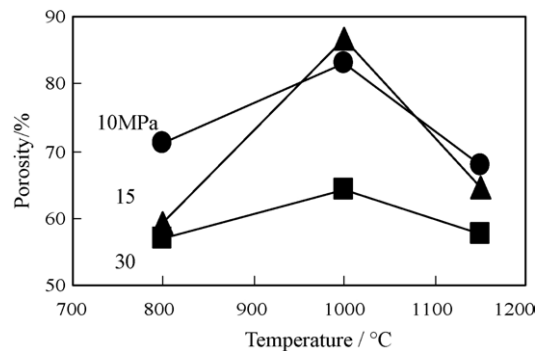

Fig. 5. Dependence of porosity of SiO_2/C pellets $(S+M)$ on treatment temperature and molding pressure.
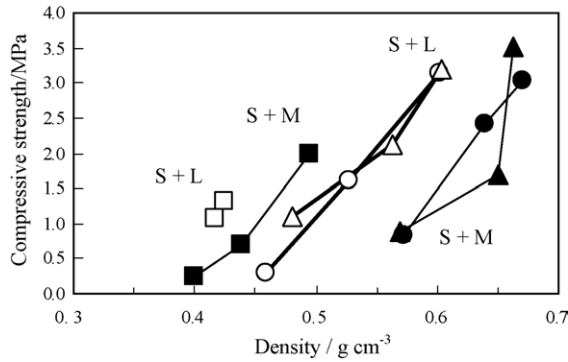
Fig. 6. Dependence of strength of SiO_2/C pellets on density and raw powders (($\bigcirc$,$\bullet$) 800 °C, ($\square$,$\blacksquare$) 1000 °C, ($\triangle$,$\blacktriangle$) 1150 °C).

specimen at 800 °C consisted of porous particles with a wide area of distribution. This structure developed by the decomposition of the organic materials into a viscous tar, which connected each particle, and finally to carbon through the evolving of H_2O, CO and CO_2 gases during the treatment process. Despite the formation of the viscous material, the coexisting SiO_2 skeleton was seen to depress the deformation of the pellet. The specimen at 1000 °C had many large pores of 10–30 μm, leading to easy evaporation and thus a relatively low density of this specimen (Fig. 3). This structure was developed due to the loss of the carbon materials. The original RH particle, meanwhile, shows a nodule-like outer shell and this structure is observed in the specimen at 1000 °C. This means that the SiO_2 skeleton rarely changed at 1000 °C even though the SiO_2 crystallization occurred. In the specimen at 1150 °C, however, the particle shape changed to a fibrous structure and became densely packed, a structural change that increased the density of the specimen. Fig. 8 shows the effect of the RH-particle size on the microstructures of the specimens. In the (S + L) specimen, large plates were observed and this increased the strength of the specimen as mentioned in Fig. 6.
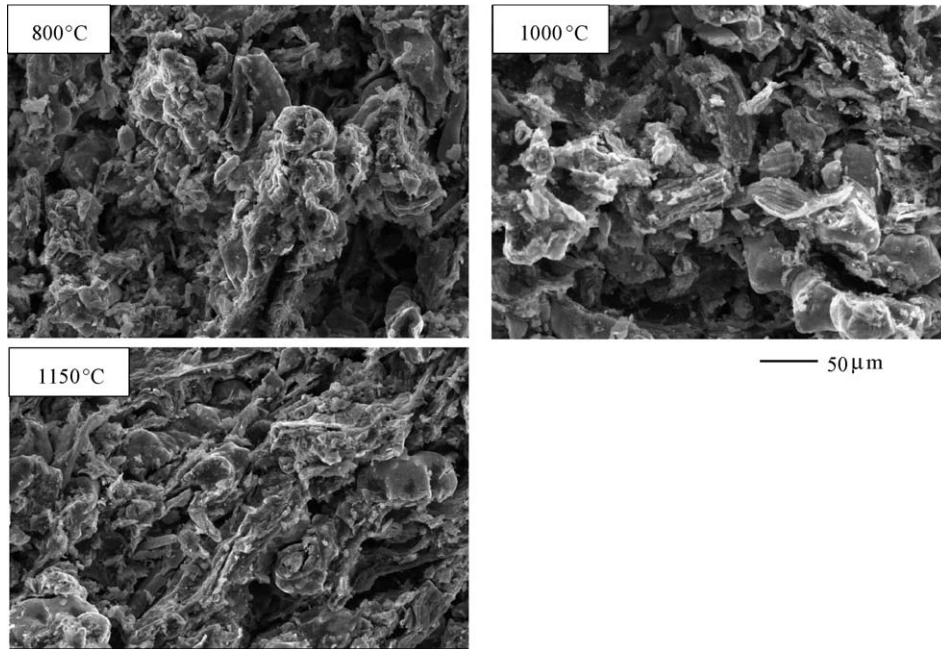

Fig. 7. Microstructures of SiO_2/C pellets (S + M) prepared at 800–1150 °C.
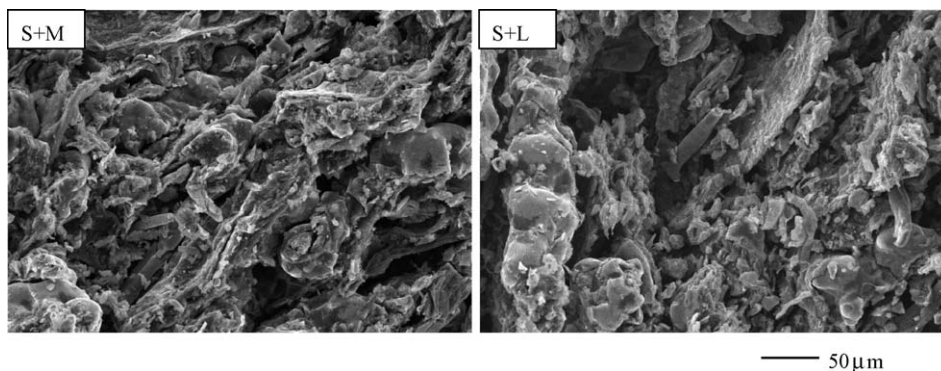

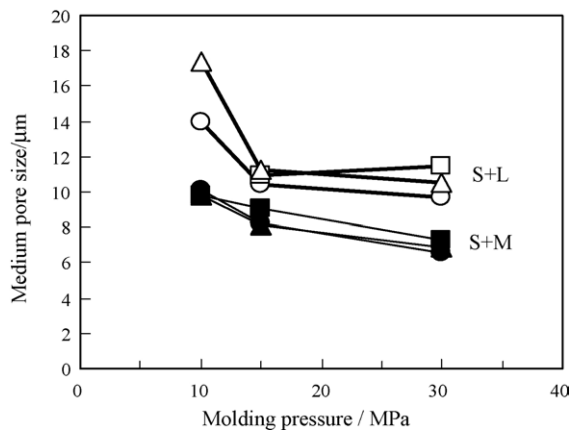Fig. 8. Dependence of microstructure of SiO_2/C pellets (1150 °C) on raw powders.

Fig. 9. Dependence of pore size of SiO_2/C pellets on molding pressure and raw powders ($(\bigcirc, \bullet)$ 800 °C, $(\square, \blacksquare)$ 1000 °C, $(\triangle, \blacktriangle)$ 1150 °C).
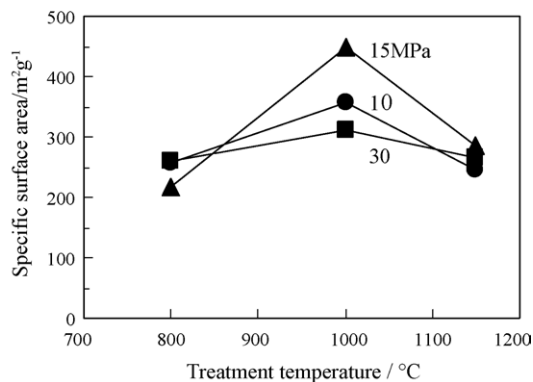

Fig. 10. Dependence of specific surface area of SiO_2/C pellets (S + M) on treatment temperature and molding pressure.

The effects of the molding pressure, treatment temperature and raw particles on the medium pore size are shown in Fig. 9. Although the pore size was unaffected by the treatment temperature, it decreased with the molding pressure, 10 μm (10 MPa)–6.8 μm (30 MPa) (for (S + M) mixture) and 17 μm (10 MPa)–10 μm (30 MPa) (for (S + L) mixture). This behavior reflected the specific packing densities in Fig. 1.

The specific surface areas of the specimens from the (S + M) mixture are shown in Fig. 10. The SSA values of the pellet at 800 °C ranged from 220 to 260 $m^2\,g^{-1}$. These values increased up to 310–450 $m^2\,g^{-1}$ at 1000 °C, but decreased to 245–290 $m^2\,g^{-1}$ at 1150 °C. The mesopore size of the specimens were all similar, at ~2 nm.

As aforementioned, it is not clear that the specimen prepared at 1000 °C showed such distinct characteristics. Further investigation should be performed in this project.

4. Conclusion

Porous SiO_2/C composite with a high surface area was able to be fabricated through a simple one-step firing process. The pore characteristics of the products could be controlled by changing the molding pressure, raw RH particle size, and heat-treatment temperature, respectively. The (S + M) pellet heated at 1000 °C displayed the optimal properties, 450 $m^2\,g^{-1}$ (SSA) and 87% (porosity). Using large RH particles increased the strength of the product. The mesopore size of the specimens were all similar, at ~2 nm.

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