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Starch consolidation of porous fused silica ceramics

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Abstract

Starch consolidation is a forming technique, in which ceramic suspension is consolidated by gelatinization of starch under suitable temperature. This technique is promising for fabricating porous ceramics because starch can act as a binder as well as a pore former. In this study, porous fused silica ceramics were prepared by starch consolidation using glutinous rice flour as a gelling agent. The 29 vol% solid loading of fused silica slurries with the addition of glutinous rice flour were prepared. After mixing the slurries were poured into a plastic mold and kept in an oven at 75ºC for an hour. The green samples were dried and sintered at a temperature range of 900-1300ºC for an hour. Bulk density and compressive strength of the fused silica ceramics with 7 wt% glutinous rice flour sintered at 1150ºC were 1.26 g/cm^3 and 13.33 MPa, respectively. The phase of the sintered specimens remained amorphous with very low thermal expansion coefficient of 0.58 x 10^{-6}ºC^{-1}.

1. Introduction

Porous ceramics have found broad applications including absorbent, catalyst support, filters and refractory due to their unique properties such as low density, high porosity, low thermal conductivity, high specific surface area and high permeability [1-3]. In all these applications, fused silica is a promising material in many industries because it possesses interesting properties such as low thermal expansion (0.5×10^{-6}ºC^{-1}), excellent thermal shock resistance, high refractoriness, and chemical inertness [4,5].

Numerous processing routes were developed to prepare porous ceramics including sacrificial template [6], direct foaming [7], freeze-casting [8], and more recently gelcasting [2]. Gelcasting is a near net shape method for fabricating complex shape products and has rapidly developed in the past few decades. The original report on gelcasting used acrylamide as a monomer and gelation was obtained by polymerization assisted with a cross-linker. However, the acrylamide monomer is a neurotoxin, which limits the application of acrylamide system [9,10]. Therefore, developing new gel systems without toxicity has become an area of intense interest in the field for many years.

Starch is a polymer of condensed glucose monomers consisting of two polysaccharides, a linear type (amylose) and a branched type (amylopectin). When starch granules are heated in the presence of water, the granules undergo a process of irreversible swelling, amylose leaching, the disruption of crystalline structure, and the realignment and formation of new intermolecular and intramolecular bond, called gelatinization. Starch gelatinization process increases the suspension viscosity and then induces the formation of gel [1,11,12].

Typically, starch is widely used as a pore-forming agent in classic ceramic forming techniques. However, the gelling capability of starch granules in hot water constitutes the basis of the new forming technique, called starch consolidation. In this technique, ceramic slurry is obtained by mixing ceramic powder, starch, and water together. Then, the slurry is poured into a nonporous mold followed by heating up to a temperature range of 55-80ºC. In this case, the starch granules swell due to water uptake to promote starch gelatinization. Then, the amount of water available for flowing gradually decreases, leading to the formation of rigid structure [13]. At the same time, starch serves as a gelling agent as well as a pore-forming agent by burnout at high temperature. Consequently, this technique is appropriate for preparing porous ceramics. Previously, many ceramic products were successfully fabricated

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by starch consolidation using various starch, such as potato starch [1], tapioca starch [14], and corn starch [15].

In this study, porous fused silica ceramics were prepared from industrial fused silica crucible waste by starch consolidation using glutinous rice flour as a gelling agent. The effects of glutinous rice flour addition and sintering temperature on properties of porous fused silica ceramics were investigated. The porous fused silica ceramics are potentially used as a mold for forming a curved glass in glass slumping process at high temperature which requires a product with low thermal expansion coefficient, high thermal shock resistance, low heat storage and stable at high temperature with suitable mechanical strength.

2. Experimental

2.1 Raw Materials

Industrial fused silica crucible waste (Italian-Thai Ceramic Refractory Co., Ltd, Thailand) was used as a raw material. The fused silica crucible waste was ground and sieved to pass through 325-mesh to obtain fused silica powder with average particle size of 4.71 µm. Chemical composition and morphology of the fused silica powder are shown in Table 1 and Figure 1(a), respectively. XRD pattern of the fused silica powder is shown in Figure 1(b). The broad peak indicates amorphous structure of fused silica. Quartz and albite are also detected as minor phases. Glutinous rice flour (food grade) was used as a gelling agent.

2.2 Preparation and Characterization

To prepare porous fused silica ceramics with high porosity, the slurries should be prepared at the lowest solid loading as possible without segregation. In this work, fused silica slurries with solid loading of 29 vol% were prepared by mixing fused silica powder, glutinous rice flour (1-9 wt% of fused silica powder), and reverse osmosis water in a plastic container. Rheological behavior of the slurries was characterized by Brookfield viscometer (Model RVDVE, 230 PV-E) at room temperature. After mixing the slurries were poured into a plastic mold and kept in an oven at 75ºC for 1 h to promote starch gelatinization. The green samples were demolded and dried at 110ºC. The dried samples were sintered at 900-1300ºC for 1 h. The photograph of the sintered sample is shown in Figure 2. The thermal behavior of glutinous rice flour characterized by simultaneous thermal analysis (NETZSCH, STA 449F3). The phase and microstructure of the sintered samples were analyzed using a X-ray diffractometer (Bruker, D8 Advanced) and a scanning electron microscope (JEOL, JSM-6480LV), respectively. Bulk density and apparent porosity were determined by Archimedes method. Coefficient of thermal expansion (CTE) were determined using a dilatometer (NETZSCH, DIL 402PC). Cold crushing strength and modulus of rupture determined by Instron testing machine with sample dimension of 50 mm × 50 mm × 50 mm and 25 mm × 25 mm × 150 mm, respectively.

Table 1. Chemical composition of fused silica powders.

	SiO_2	Al_2O_3	Na_2O	K_2O
Composition (wt%)	97.90	1.29	0.39	0.20

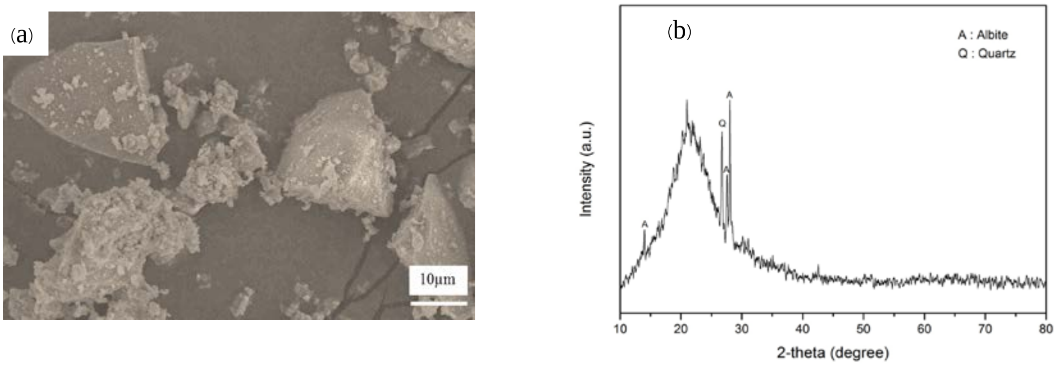

Figure 1. (a) SEM image, and (b) XRD pattern of the fused silica powder.

Figure 2. Photograph of fused silica ceramics sintered at 1150ºC.

3. Results and discussion

3.1 Rheological behavior

The effect of glutinous rice flour addition on rheological behavior of the fused silica slurries is shown in Figure 3. It can be observed that viscosity at room temperature of all slurries decreases with increasing shear rate which is a shear-thinning behavior. In term of shear-thinning behavior, apparent viscosity is relatively high when measured under low shear conditions in which large flocs are flowing. Apparent viscosity is relatively low when measured under high shear conditions in which small flocs or individual particles are flowing [16]. Moreover, the viscosity of the fused silica slurries increases with increasing amount of glutinous rice flour and leaps up when the addition is 9 wt%.

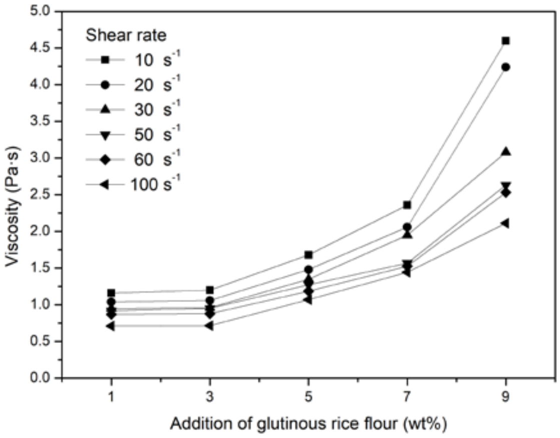

Figure 3. Rheological behavior of the fused silica slurries with different amounts of glutinous rice flour at room temperature.

3.2 Property of green samples

The effect of glutinous rice flour addition on modulus of rupture of the fused silica green samples is shown in Figure 4. It reveals that modulus of rupture of the fused silica green samples increases with increasing amount of glutinous rice flour and then slightly decreases with the addition of 9 wt% glutinous rice flour due to high viscosity slurries causing gas entrapment in the slurries which create defects in the green samples after casting. Consequently, in the present work, the fused silica green samples with 7 wt% glutinous rice flour addition exhibits the highest green strength.

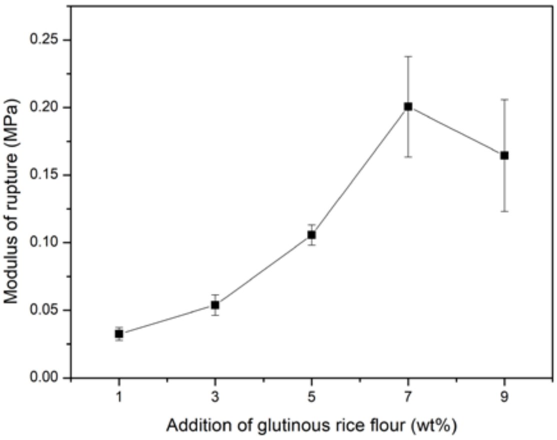

Figure 4. Modulus of rupture of the fused silica green samples with various glutinous rice flour addition.

3.3 Properties of sintered samples

Glutinous rice flour is organic matter. Therefore, it can thermally decompose during sintering process. Thermal decomposition of the glutinous rice flour is shown in Figure 5. It can be seen that glutinous rice flour is completely decomposed at a temperature about 600ºC. The amount of residue ash was less than 0.54% and should not significantly affect further sintering process.

Effect of sintering temperature on properties of the sintered samples was studied by sintering the green samples with 7 wt% glutinous rice flour at temperature of 900-1300ºC. However, the samples sintered at temperature below 1100ºC were weak and unable to handle.

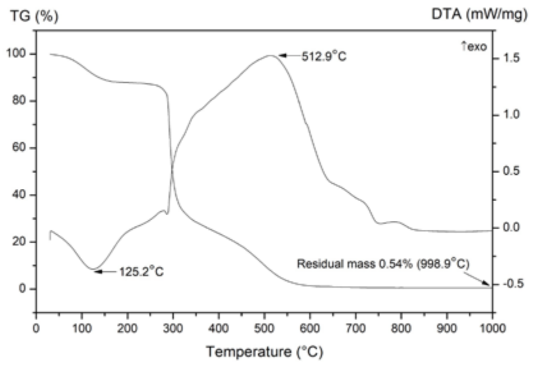

Figure 5. TG and DTA curves of glutinous rice flour.

Effect of sintering temperature on bulk density and apparent porosity of the porous fused silica ceramics with 7 wt% glutinous rice flour is shown in Figure 6(a). With increasing sintering temperature from 1100ºC to 1300ºC, bulk density of the fused silica ceramics increases, on the other hand, apparent porosity decreases. Cold crushing strength of the fused silica ceramics sintered at different temperature is shown in Figure 6(b). It can be observed that cold crushing strength slightly increases with increasing sintering temperature from 900ºC to 1100ºC and increases rapidly as sintering temperature up to 1200ºC. However, cold crushing strength slightly decreases as sintering temperature over 1200ºC. Figure 7 showed SEM images of the fused silica ceramics sintered at (a) 1100ºC, (b) 1150ºC, (c) 1200ºC and (d) 1300ºC. The particles of fused silica are connected gradually as increasing the sintering temperature leading to an increase in bulk density and cold crushing strength.

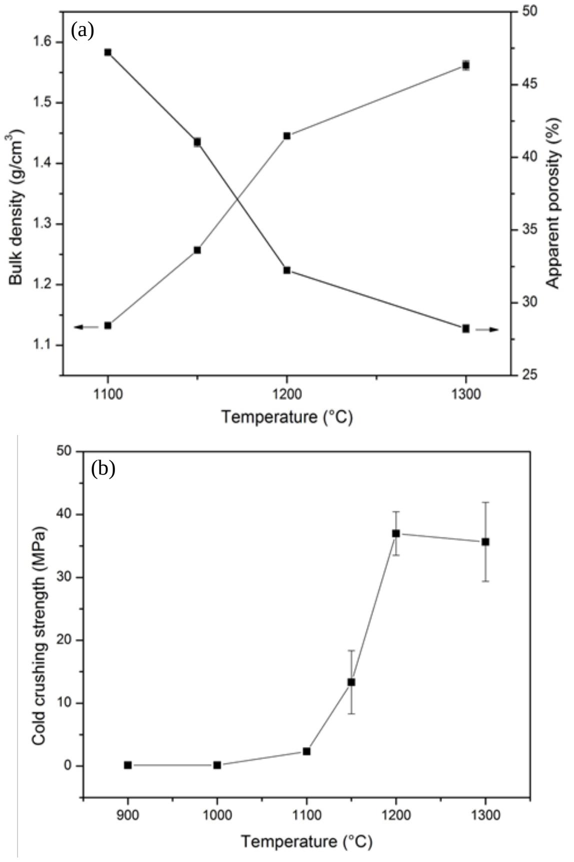

Figure 6. (a) Bulk density and apparent porosity and (b) cold crushing strength of the fused silica ceramics sintered at different temperatures.

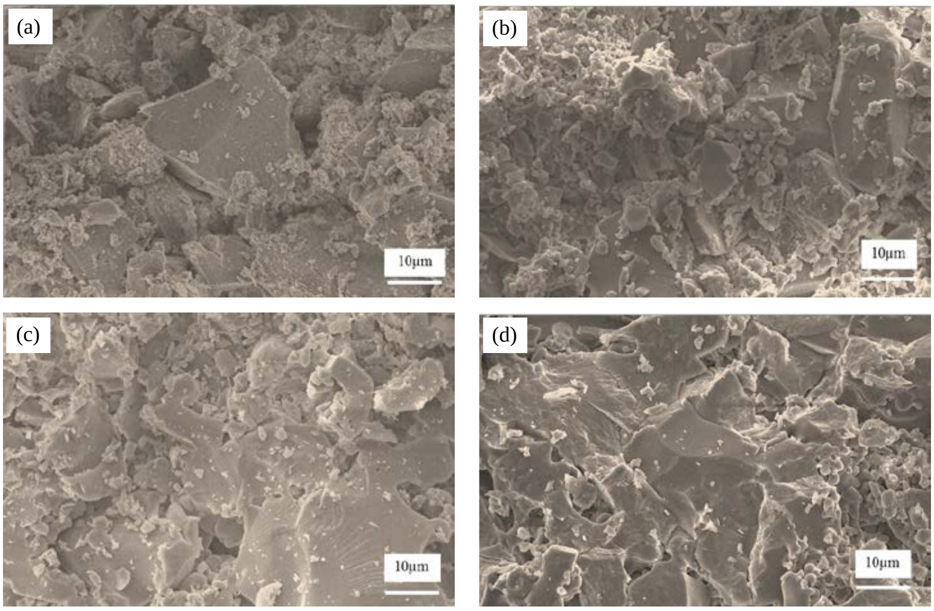

Figure 7. SEM images of the fused silica ceramics sintered at (a) 1100ºC, (b) 1150ºC, (c) 1200ºC and (d) 1300ºC.

Effect of sintering temperatures on phase transformation and thermal expansion of the porous fused silica ceramics with 7 wt% glutinous rice flour are shown Figure 8(a) and (b). The XRD patterns of the fused silica ceramics sintered at elevated temperature are shown in Figure 8(a). As sintering temperatures increase up to 1150ºC, phase of the porous fused silica ceramics remains amorphous. Cristobalite begins to appear at 1200ºC with small amount of amorphous phase. Finally, strong diffraction peaks of cristobalite is observed in the porous fused silica ceramics sintered at 1300ºC. The dilatometric curves of the porous fused silica ceramics sintered at different temperatures are shown in Figure 8(b). Thermal expansion coefficient in range 25-1000ºC of the ceramics sintered at 1100ºC, 1150ºC, 1200ºC and 1300ºC are 0.44×10^{-6}ºC^{-1}, 0.58×10^{-6}ºC^{-1}, 1.29×10^{-6}ºC^{-1} and 10.75×10^{-6}ºC^{-1}, respectively. The thermal expansion coefficient of the ceramic sintered at 1300ºC increases drastically at temperature of 200- 270ºC due to a phase transformation from β-cristobalite to α-cristobalite. Upon cooling, this large volume change leads to the formation of microcracks that will lower the strength of the porous fused silica as shown in Figure 5(b).

Effect of the glutinous rice flour addition on bulk density, apparent porosity, cold crushing strength and modulus of rupture of the porous fused silica ceramics was studied by sintering the green samples at 1150ºC as shown in Figure 9(a) and (b). Bulk density decreases with increasing amount of glutinous rice flour and apparent porosity increases with increasing amount of glutinous rice flour as shown in Figure 9(a). Increasing the amount of glutinous rice flour addition will promote pores in microstructure when glutinous rice flour is burnt out. Consequently, cold crushing strength and modulus of rupture decrease with increasing amount of glutinous rice flour as shown in Figure 9(b).

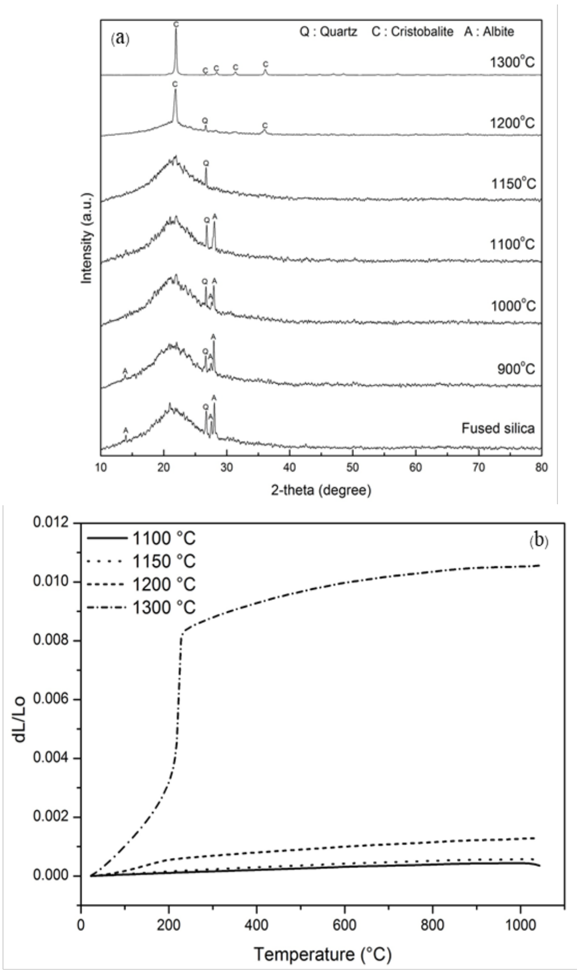

Figure 8. (a) XRD patterns, and (b) dilatometric curves of the fused silica ceramics sintered at different temperatures.

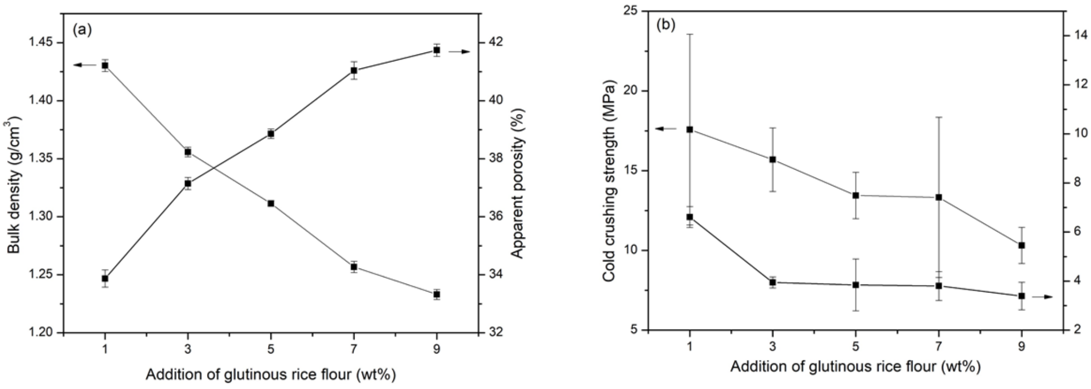

Figure 9. (a) Bulk density and apparent porosity and (b) cold crushing strength and modulus of rupture of the porous fused silica ceramics with glutinous rice flour addition sintered at 1150ºC.

4. Conclusions

Porous fused silica ceramics were successfully fabricated from fused silica crucible waste by starch consolidation technique using glutinous rice flour as a gelling agent. Slurries containing 29 vol% fused silica powder and 1-9 wt% glutinous rice flour were cast into the plastic mold and heated at 75ºC for 1 h to promote starch gelatinization, followed by drying at 110ºC to produce the rigid green body. The green sample with the maximum flexural strength can be fabricated from the slurry containing 7 wt% glutinous rice flour. The sample with maximum compressive strength of 13.33 MPa was obtained by sintering the green sample at 1150 ºC for 1 h. The sintered samples had extremely low thermal expansion coefficient of 0.58 x 10^{-6}ºC^{-1} because phase of the sintering samples remained amorphous. Increasing sintering temperature further led to crystallization of cristobalite causing an increase in thermal expansion coefficient of the sintered samples.

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