Red clay-based porous ceramic with pores created by yeast-based foaming technique

Ruben L. Menchavez · Lori-Ann S. Intong

Abstract Red clay-based porous ceramic has been fabricated by using a biological foaming technique through reaction of yeast with starch in aqueous ceramic suspension. The starch plays a dual role as a growth substrate for gas bubble generation and a binder for ceramic particles. Starch-loaded ceramic slurries (55 wt% ceramic solid) were prepared, consisting of red clay, quartz, feldspar, and starch. Three types of starches were used, namely, cassava starch, corn starch, and rice flour. The rheological characterization of starch-loaded ceramic slurries showed shear thinning behavior. This resulted into a high foaming factor depending on the types of starches loaded and increased addition of yeast. Total fired porosities obtained were between 17 and 70%. These correspond to open porosities between 15% and 50%, and close porosities range from 6% to 35%. Microstructural investigation of the fired porous compacts showed irregular pore morphologies equipped with interconnecting channels that represent the open porosity.

Introduction

Porous ceramics, as the name suggests, are solid materials having a combination of an isolated and an interconnected network of open pores that are permeated by a liquid or a gas [1]. These define a porous microstructure consisting of solid struts that impart the mechanical strength to the porous compact and empty spaces usually vary in shape from irregular to spherical geometry, depending on the processing method used [1–3]. The isolated pores inside the material are pathways or channels that are not connected to the surface and not accessible to the diffusing fluid, whereas the interconnected pores are connected to the surface and allow the permeating fluid to move from one surface to another.

The variation of the pore geometry and composition of porous ceramics presents the enormous potentials of these materials in many applications [3, 4] involving high chemical, thermal or mechanical stresses where metallic or polymeric materials are unsuitable. They act as thermally insulating materials, filters, membranes, gas burners, and many others. In each of these applications, the porous ceramic matrix is controlled to render performance effective. For effective thermal insulation, it is favorable to have a high concentration of closed porosity whereas, on the other hand, filters and membranes require more open porosity to allow better fluid flow. In the bioceramics field, it is desirable to use ceramic implants possessing enough mechanical strength for support and porosity with complex structure to promote integration with biological tissues [5].

The fabrication of porous ceramic with tailored microstructure has been developed in several ways in response to the aforementioned industrial applications. Generally, three different approaches [6] can be followed: (i) replication of a sacrificial foam template; (ii) direct foaming of a liquid slurry; and (iii) burn-out of fugitive pore formers. These methods practically commence with a stable slurry that is processed to end up with a wide range of porous structures. However, these methods of producing porous ceramics have several disadvantages, such as the use of toxic polymers in water-based gel casting [3, 4], expansion and formation of ice crystals in water-based systems, contraction

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when using organic solvents in freeze forming [2], and low wet-body strength in direct coagulation casting (DCC).

To address these limitations, a new forming technique for the fabrication of porous ceramics was developed [5, 7]. It belongs to the family of direct-consolidation methods, which employs starch acting as a consolidator and a binder of ceramic particles. The presence of starch in ceramic slurry offers opportunity to synthesize porous ceramic material when the starch suspension is heated to a temperature between 55 and 80 °C. During this heating process, the intermolecular bonds holding the granules together are weakened leading to a rapid and irreversible swelling of granules by water uptake which results in an increased granule size to many times the original size. Besides the favorable gelling properties of starches, they are environmentally friendly, easy to burn out and, not least important, they are very cheap.

The synthesis of porous ceramics by swelling of starch granules presents limitations on the control of the pore size and geometry as well as on the attainment of pore concentration. It is desirable that the porous characteristics are controlled through addition of chemical foaming substances [8]. But this process requires a significant amount of chemical agent to cause foaming. This struggle has been overcome through the use of a biological foaming agent [9]. In this method, a ceramic suspension is mixed with a biological agent (e.g., yeast), a growth substrate (e.g., sugar), and a ceramic forming liquid binder (e.g., polysilazane). The biological agent is allowed to act on the growth substrate to form gas bubbles resulting into foaming of the ceramic slurry. The size of the bubbles varies depending on the viscosity of the ceramic slurry used, rate of polymerization of the binder, and other processing conditions. The biological agent can act on the growth substrate at the same time that the binder is polymerizing to stabilize the generated foam. The polymerization is triggered by heating the liquid binder until it is transformed into an oxide binder between ceramic particles. Although this process is attractive, the simultaneous additions of the growth substrate and binding agent may strongly increase the viscosity of the ceramic slurry that impedes foam growth.

Moreover, the aforementioned porous fabrications through chemical foaming and other methods have been extensively studied for pure powders such as Al_2O_3, SiC, and Si_4N_3. However, few literatures have been published using a clay-based powder mixture shaped into porous ceramics [10, 11]. Particularly, a red clay-based powder mixture primarily consists of dominant amount of red clay, and additive amounts of quartz and feldspar. The clay, containing iron impurity, imparts plasticity to the powder mix while the quartz provides filler and feldspar reduces firing temperature. This ternary ceramic mixture offers possibility to synthesize a water retention tile to counteract heat island effects

[11]. Therefore, this study aims to fabricate a red clay-based porous ceramic using biological reaction of yeast with starch in aqueous ceramic suspension. In this study, the starch acts a dual role as the growth substrate for gas bubble generation and the binder for ceramic particles.

This study focuses on the fabrication of porous materials utilizing ceramic slurry mixture consisting of red clay-based powder, starch, and a biologically active agent. Specifically, this study has threefold aims: (i) to characterize the rheological behaviors of ceramic slurry mixtures containing different starches and the ternary powder consisting of red clay, quartz, and feldspar; (ii) to determine the concentration and the foaming ability of biological agent in ceramic slurry containing different types of starches including corn, cassava, and rice starches; and (iii) to characterize the physical characteristics in terms of porosity and microstructural features of the consolidated porous ceramic bodies in the fired state.

Materials and procedure

Raw materials

The red clay was mined in lumped formed from Lamalama, Lanao del Norte, Philippines. It was dried in the laboratory oven for 4 h at a temperature of 110 °C to completely remove the moisture. The dried lumped clay was then reduced to desired sizes using a pulverizer and was sieved passing through a 100 mesh screen. The quartz and feldspar were commercially supplied by Elmars Marketing, Philippines, and screened passing through a 200 mesh screen. The average particle size (LS 100Q, Coulter Corporation) for red clay, quartz, and feldspar was 49.2, 35.1, and 27.0 μm, respectively, and their particle size distributions were shown in Fig. 1. Correspondingly, the chemical composition of the ceramic raw materials was given in Table 1. Native starches, such as corn starch and cassava starch, were also commercially provided by the mentioned supplier while the rice flour was prepared in the laboratory. To obtain the rice flour, rice grains (IR 74) were mechanically ground until the resulting powder passed through 100 mesh. The average particle size, for corn starch, cassava starch, and rice flour, was 12.1, 18.7, and 49.5 μm, respectively, and their particle size distributions were presented in Fig. 2. The biological foaming agent was an active dry yeast (*Saccharomyces cerevisiae*, Xinjiang Mauri Food Co. Ltd., China).

Preparation of ceramic slurry

To prepare the ceramic slurry, 55% solid loading of the ternary powder mixture composed of 60.7% clay, 16.6%
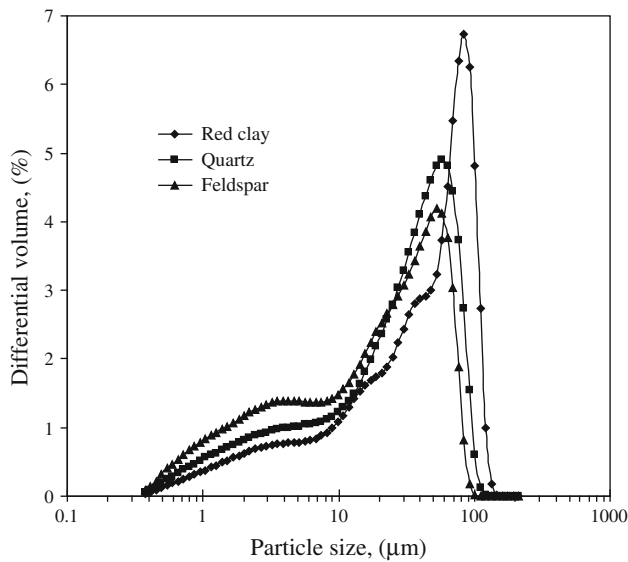
Fig. 1 Particle size distribution of the three different ceramic powders

Table 1 Chemical composition of the raw materials

Materials	Oxide contents							
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	l.o.i.
Red clay	41.6	25.2	8.2	1.1	0.5	0.5	0.5	22.4
Quartz	95.1	1.7	0.4	1.4	0.5	0.1	0.3	0.6
Feldspar	66.3	21.5	0.3	0.5	2.4	8.5	0.1	0.4
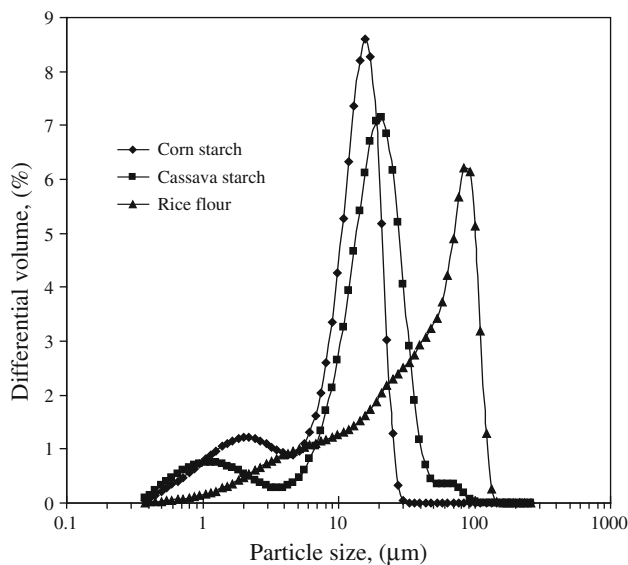
Fig. 2 Particle size distribution of the three different starches

quartz, and 22.6% of feldspar was mixed after weighing their respective amounts. This composition was formulated according to a stoneware specification. The resulting

powder mixture was dispersed with the aid of polyammonium polyacrylate (Darvan 821A, R. T. Vanderbilt Company Inc., USA). This dispersing agent was available in the form of an aqueous solution (40% active component) and added at about 0.8 wt% based on the ternary powder mixture. After thorough mixing of dispersant with water, the ternary powder was then dispersed gradually in liquid solution with regular manual stirring. Then, the predetermined weight of alumina milling balls, which is twice the weight of the solid loading, was added into the mixture to serve as a mixing media. Subsequently, the final mixture was milled for 24 h with a rotation of 55 revolutions per minute (rpm) to uniformly disperse the ceramic particles.

Preparation of the red clay-based suspension containing starch

After the milling step of the ceramic slurry, a starch-loaded ceramic slurry was prepared by adding the starch to the ceramic slurry. The amount [12] of starch was introduced at 11 and 21 wt% based on the amount of the ternary powder. Similar concentrations of starch were implemented for the three different starches. The starch-loaded ceramic slurry was then milled for 4 h with a rotation of 55 rpm. After milling, the viscosity of the starch-loaded ceramic slurry was immediately determined by using a viscometer (RVDVE 230, Brookfield Engineering Laboratories, Inc.). The viscosity was measured using Spindle 4 with varying torques at 10, 20, 30, 50, 60, and 100%.

Foaming and consolidation of starch-loaded ceramic slurry

The homogenized starch-loaded ceramic slurry was treated with yeast to generate the gaseous product for foaming. The increments of the yeast used were 8.9, 17.4, and 31.5 wt% of the amount of starch present. The respective amount of yeast was first dissolved thoroughly in a 1:1 ratio of distilled water. The resulting yeast solution was introduced to the starch-loaded ceramic slurry with manual mixing for about 3 min. The yeast-treated ceramic slurry was poured into three glass molds (250 mL beakers) to confirm the reproducibility of the process. The glass molds were equipped with a glass cover and simultaneously heated to 40 °C inside an oven with isothermal heating for 1 h at that temperature. This temperature was the desired fermentation temperature for allowing the yeast to develop effective foaming of ceramic slurry. This was followed by increasing the temperature [13] to 80 °C with holding for 2 h at this temperature to consolidate the liquid foam. The molds were covered to minimize evaporation of water before and during the solidification step. The cover was fitted snugly to the glass mold to minimize drying and

diffusion of the gas bubbles. After the consolidation step, the solidified ceramic foams were removed from the molds after 12 h of natural cooling inside the oven. Immediately after demolding, a foaming factor of the starch consolidated body was determined according to the equation:

$$F = \frac{H_f - H_i}{H_i} \times 100\%, \tag{1}$$

where F is the foaming factor after demolding the porous sample, H_f is the height after demolding, and H_i is the initial height of the original starch-loaded ceramic slurry. This determination of foaming factor was, respectively, repeated on three porous samples corresponding to every foaming condition and the average value was reported.

The demolded porous ceramic samples were placed on top of a screen for drying at room conditions. This setup allowed uniform access of natural air to the sample surface for about 1 week. After this drying step, the porous samples were dried in a conventional oven at 110 °C to remove the moisture content for 4 h. Continuous drying was implemented until a constant weight was achieved.

Binder burn-out and firing

The starting porous samples were a total of 24 pieces of rectangular blocks ($45 \times 30 \times 20$ mm^3), corresponding to the foaming conditions implemented. They were obtained by cutting the dried porous samples with a hacksaw and lightly polish to desired dimensions. This was followed by burning out of starch binder at a slow temperature increase (1 °C/min up to 700 °C. The heating schedule was taken at several holdings for 60 min at 100, 200, 400, 500, 600 °C, 120 min at 300 °C, and 180 min at 700 °C. Subsequently, the firing process was conducted in an electric furnace (Model: FB1315 M, Thermo Scientific) with a heating rate of 10 °C/min to 1100 °C. At this peak temperature, isothermal heating was implemented for 2 h.

Physical characterizations of porous samples

The as-fired porous samples were physically characterized in terms of bulk density, powder density, total porosity, open porosity (via the Archimedes method), and closed porosity. These properties of porous samples were individually determined in three replicates and the average value was reported. To determine the total porosity for both dried and fired samples, the bulk density of the porous sample was determined by measuring the lateral dimensions and their respective weights. Subsequently, the total porosity, ϕ, was calculated from the bulk density, ρ, using the formula

$$\phi = 1 - \frac{\rho}{\rho_o}, \tag{2}$$

where ρ_o is the theoretical density of an equivalent powdered material. The theoretical density of the dried porous samples was determined by pycnometer method. Since the dried samples contained varying amount of starch, the density was, respectively, determined. The theoretical density for the fired sample was determined to be about 2.63 g/cm^3. The open porosity of the samples was measured by the Archimedes displacement method [14] using distilled water according to the equation:

$$P = \frac{m_1 - m}{m_1 - m_o}, \tag{3}$$

where P is the open porosity of the sample, m is the sample weight in air after complete drying, m_o is the sample weight in distilled water, and m_1 is the sample weight measured after immersing it in boiling water for 4 h and wiping off the water on the surface. Obviously, the closed porosity is the difference between total and open porosity, i.e.,

$$\phi_{closed} = \phi - \phi_{open} \tag{4}$$

A microstructure investigation, mainly disclosing the overall pore structure formed in the fired materials, was conducted on a scanning electron microscope (JSM-6100, JEOL, Japan). The fired porous samples were fractured into small fragments for visual observation. The viewing magnifications were chosen at ×19 and ×43 to clearly reveal the pore structures.

Results and discussion

Rheology of starch-loaded ceramic slurry

The concentrated suspension of starch in water [15] is usually exhibiting higher viscosity with increasing applied shear stress, resulting in shear thickening behavior. In this case, the viscosity increases continuously as a consequence of its dependence on particle configuration accompanied by an order/disorder transition in the particle configuration [5].

When the starch was added to the concentrated ceramic suspension, in this study, the shear thickening behavior of starch suspension was transformed to shear thinning behavior. This may be due to the fact that the rheological behavior of the slurry is dominated by the properties of the ceramic particles as shown in Fig. 3. It can be observed that the viscosities for all starch-loaded ceramic slurries are decreasing with increasing shear rate. This type of concentrated stable suspensions usually exhibits the shear thinning behavior due to perturbation of the suspension

structure by shearing force [16]. It is further observed that the trend of increasing average particle sizes for the different types of starches (corn 12.1 μm, cassava 18.7 μm, and rice 49.5 μm) is consistent with increasing viscosity of the starch-loaded ceramic slurries. However, this observation contradicts with the general concept that the viscosity increases with decreasing particle size. The small particle provides a greater number of jam particles resulting to high particle interaction while the large particle requires fewer numbers of particles to interact, leading to the decrease in viscosity [17]. It is believed that this principle is practically true only for suspension made of single powder with uniform chemical composition. In the present study, this concept may not be valid anymore because the ceramic slurry is involved with the complex mixture of four different powders, each of different chemical compositions. Specifically, the corn starch-loaded ceramic slurry demonstrated the lowest viscosity despite of the fact that the corn starch has the smallest average particle size. In contrast, it is seen that the ceramic slurry loaded with rice flour exhibited the highest viscosity, which has the largest average particle size. These findings were verified as to whether the rice flour fragments were reduced into fine grains after milling for 4 h. This was tested using ceramic slurries loaded with different starches (11 wt% based on the amount of ceramic solids) as a function of increasing milling time as shown in Table 2. It is worthwhile to note that the average particle size of starch-free ceramic slurry after 24 h milling was measured to be about 1.675 μm. It can be seen that all starch-loaded ceramic slurries were reduced after 1 h of milling as indicated by average particle sizes closer to the average particle size of starch-free ceramic slurry. Moreover, it confirmed that that rice flour fragments were converted to rice starch grains. As shown in Table 2, the ceramic slurry loaded with the rice flour remained the highest average particle size among the starches, which is also higher than the mean particle size of the starch-free ceramic slurry. There is also a slight increase in mean particle size of all starch-loaded ceramic slurry, which is attributed to a possible swelling of starch grain due to absorption of available water. The possible swelling of large grain of rice flour may explain the highest observed viscosity for rice-loaded ceramic slurry. This is because of the fact that the large grain size of starch swells largely to strongly contribute to the increasing viscosity. This finding agrees with the reported study on rheology of starch suspension with increasing granule size undergoing swelling process [18].

When the starch concentration was increased, the viscosity of the ceramic slurry increased, regardless of starch types, as illustrated in Fig. 3. It can be seen that the shear thinning behavior is maintained even at a high amount of starch addition. The increase in viscosity might be due to
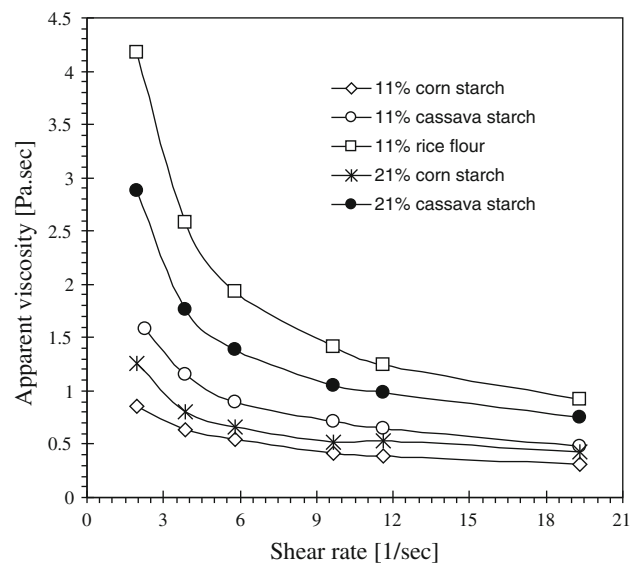
Fig. 3 Viscosity versus shear rate flow curves for the starch-loaded ceramic slurries

Table 2 Average particle size in micrometers of ceramic/starch slurries with increasing milling time

Ceramic slurry loaded with	Milling time (h)			
	1	2	3	4
Corn starch	7.873	1.651	1.659	1.671
Cassava starch	8.242	1.648	1.697	1.695
Rice flour	8.536	1.740	1.746	1.757

the fact that the increased amount of starch replaces some of the dispersing liquid medium to maintain the weight fraction of solids (55 wt%). A serious effect on viscosity was observed for ceramic slurry with 21 wt% rice flour, which precluded the inclusion of rheological data because of too high viscosity. The dramatic rise in viscosity is probably due to the aggregation of large particle clusters creating jammed particle networks [15]. Subsequently, it is worthwhile to emphasize that the slurry rheology for all the ceramic slurries studied was suitable for direct slip casting except for ceramic slurry with 21 wt% rice flour. Low viscosity of the slurry is required to achieve adequate mold filling without entrapping air but, at the same time, the viscosity should be high enough to avoid critical particle segregation during consolidation step.

Foaming behavior of starch-loaded ceramic slurry

The key to the production of a high foaming suspension is the use of appropriate amount of yeast with low viscosity ceramic slurry. This high foaming results from uniform nucleation of bubbles in ceramic slurry by reaction of yeast with starch. Hence, this study started with low viscosity

slurry using 11 wt% corn starch in ceramic slurry. It was found that there was no significant foaming observed until 8.9 wt% yeast addition as illustrated in Fig. 4a. This foaming behavior was similar to cassava-loaded ceramic slurry. A better foaming performance was only observed with addition above 17.4 wt% yeast for both cassava and corn starch-loaded ceramic slurry as shown in Fig. 4b, c. However, when the yeast addition of 8.9 wt% was tried for rice-loaded ceramic slurry, the foaming activity was strongly evident as depicted in Fig. 4d. This indicates that the rice flour is more reactive with yeast to produce sizable amount of gas foamer. Although the rice flour has the largest average particle size, it is still the most chemically reactive because the particle size of starch does not have a strong influence on the starch interaction [19]. The interaction of starch is strongly dependent on its chemical composition relating to the amount of amylose and amylopectin. It is worthwhile to note that the amylose is a linear molecule whereas the amylopectin is a branched molecule. In the present study, it is believed that the rice flour contains the highest amount amylopectin according to literature [19]. The amylopectin is preferentially attacked by the yeast during reaction [20] to produce gaseous products. This indicates that the higher the amount of such molecule in starch, the higher its chemical reactivity. On the other hand, the particle size of starch is thought to be a

contributing factor on how rapidly a starch gelatinizes and its gelatinization temperature.
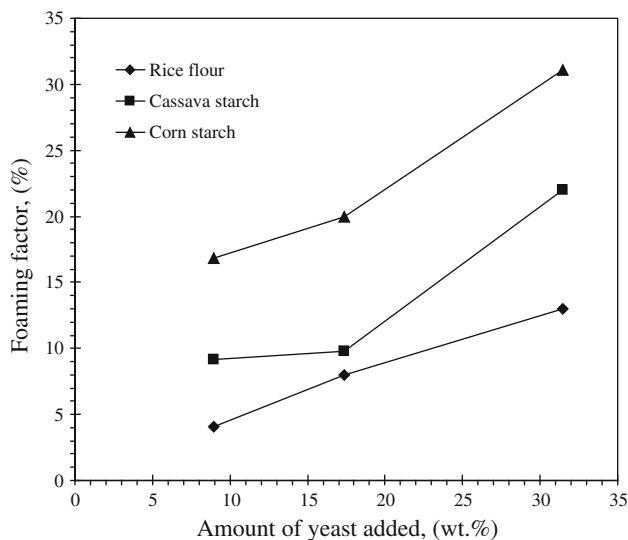
The foaming performance of yeast in different type of starch-loaded ceramic slurries was evaluated using the proposed equation in this study. The results were shown in Fig. 5 for the foaming factors of ceramic slurries containing 11 wt% starch with increasing addition of yeast. It is evident from the trend that increasing the yeast concentration increases the foaming factor for all ceramic slurries studied, regardless of starch type used. The foaming factor corroborates with the decreasing trend in viscosities of the ceramic slurries with different types of starch. Particularly, the cornstarch exhibits the highest foaming factor at any concentration studied. The cassava starch-loaded ceramic slurries demonstrated an intermediate foaming performance. The rice flour-loaded slurry exhibited the lowest foaming factor even though it developed obvious porosity. This might be attributed to a possible collapse of the foams during the consolidation step. During consolidation heating, the dissolving rice flour might not effectively stabilize the inflating gas bubbles [21, 22] despite of its high viscosity. The collapsed consolidated foam structures are clearly evident in Fig. 4d–f.

The foaming behavior was also studied at higher starch amount of about 21 wt% with 31.5 wt% yeast addition. The rice flour, cassava, and corn starches rendered foaming

Fig. 4 Porous green bodies consolidated with different forming conditions. *Upper panel* 11 wt% corn starch-loaded ceramic slurries with yeast additions of **a** 8.9 wt%, **b** 17.4 wt%, **c** 31.5 wt%. *Lower panel* 11 wt% rice flour-loaded ceramic slurries with yeast additions of **d** 8.9 wt%, **e** 17.4 wt%, **f** 31.5 wt%
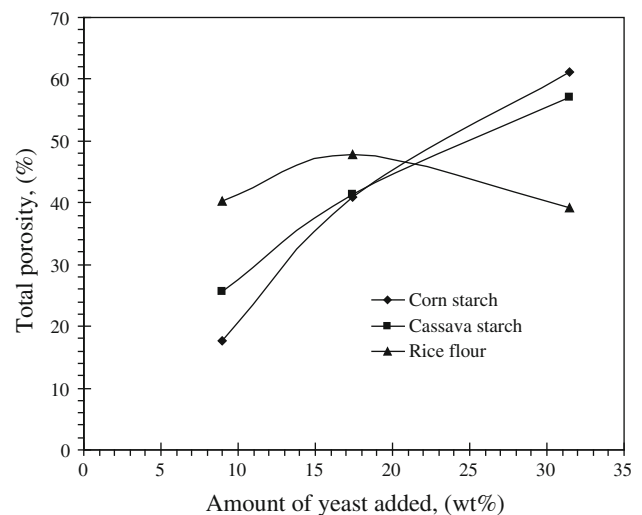
Fig. 5 Foaming rates of starch-loaded ceramic slurries with increasing amount of yeast

Fig. 6 Total porosities of dried porous samples shaped with different starch type treated with increasing amount of yeast

factors of 25.0, 36.4, and 51.0%, respectively. It is obvious that rice flour presented the lowest foaming factor, which can be traced back to its high viscosity and poor gas stabilization.

The foaming of ceramic slurry through reaction of yeast with starch is thought to be similar to the process employed in bread making [23]. In this process, the yeast is added to dough made from a starchy portion of ground grains (such as wheat or rye flour). The yeast breaks down some of the starch and sugar present in the mixture, producing carbon dioxide and alcohol. This reaction may initiate at 26 °C and ferment best [24] at 30–35 °C. The yeast dies off above 50 °C. If the solution reaches 105 °C the yeast will disintegrate. The carbon dioxide bubbles through the dough, forming many air holes that cause the bread to rise. Since oxygen is present, no alcohol is produced when the bread is rising. When the foamed mixture is baked, the yeast dies off and the air holes set to give the baked product a soft and spongy texture. When the yeast is mixed to the starch-loaded suspension, it reacts with the starch present forming carbon dioxide bubbles [24]. Thus, the gas bubbles will create permanent pores when heat treatment is employed.

Characteristics of dried and fired porous compacts

The total porosity of dried porous samples with 11 wt% of different starch types and varying yeast concentration are depicted in Fig. 6. It can be observed that the concentration of pores is increasing as the yeast concentration increases except for rice-loaded sample. The decrease in total porosity for rice-loaded sample is due to foam collapsed during consolidation step as discussed above. For corn and cassava-loaded samples, the porosity is increasing with

increasing yeast additions. This is due to the higher amount of yeast reacting with starch to form carbon dioxide bubbles as the foaming agent. This further indicates that the dissolving cassava or corn renders better gas stabilization of foams, thereby minimizing gas diffusion. Comparing these two starches, the corn starch in ceramic slurry yielded the best dried total porosity of about 61% with highest yeast addition as indicated in the Fig. 6. At lower yeast concentration, the measured total porosities were found to be the lowest between 20 and 25%. This is may be due to lower gas generation within the ceramic slurry. The dried total porosity was also determined for porous samples consolidated with 21 wt% starch and 31.5 wt yeast addition. The rice flour, cassava, and corn starches rendered total porosities of 47.2, 55.5, and 62.5%, respectively.

The well-dried porous samples were fired to determine how the dried porosity changes. Figure 7 illustrates the fired porous samples shaped with 11 wt% starch and increasing addition of yeast. The fired porous samples shaped with rice flour showed evidence of porosity at any addition of yeast (Fig. 7a–c). It is also noticeable that the corn-loaded samples rendered less porosity than rice-loaded sample at addition of 8.9 wt% yeast (Fig. 7a, d). The significant porosity concentration is only observable above 8.9 wt% yeast (Fig. 7e, f). The mechanism behind this observation was already explained above. As shown in Table 3, the fired porous sample shaped with 11 wt% starch and highest amount of yeast can reach up to a total porosity of about 70.3%. Comparing the dried and fired total porosities (Fig. 6; Table 2), there is a substantial increase in porosity attributed to the starch binder. Similar finding was observed for the fired porous samples consolidated with 21 wt% corn starch and 31.5 wt% yeast. The rice flour, cassava, and corn starches rendered total
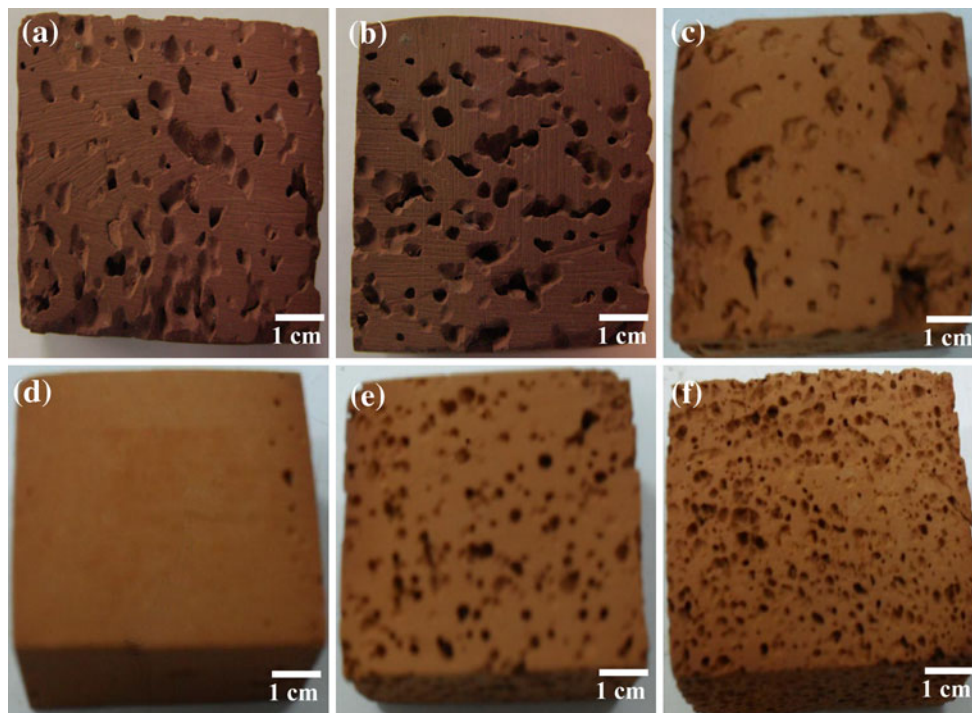
Fig. 7 Fired red clay-based porous compacts shaped with different forming conditions. *Upper panel* 11 wt% rice flour-loaded ceramic slurries with yeast additions of **a** 8.9 wt%, **b** 17.4 wt%, **c** 31.5 wt%. *Lower panel* 11 wt% corn starch-loaded ceramic slurries with yeast additions of **d** 8.9 wt%, **e** 17.4 wt%, **f** 31.5 wt%

Table 3 Porous characteristics of fired porous ceramic compacts

Starch (11 wt%)	Amount of yeast added (wt%)								
	8.9%			17.4%			31.5%		
	Total	Open	Closed	Total	Open	Closed	Total	Open	Closed
Corn	31.8	24.2	7.6	50.4	44.0	6.4	70.3	35.8	34.5
Cassava	29.3	15.3	14.0	40.5	29.0	11.5	58.1	49.8	8.4
Rice	44.2	30.0	14.2	46.2	27.6	18.6	46.2	34.8	11.4

porosities of 59.2, 60.4, and 72.3%, respectively. This observed increase in porosity could be traced back to binder burnout stage. During heat treatment, the starch binder left holes between ceramic particles which are difficult to be removed by the firing process. Thus, the solid part supporting the porous structure is porous by itself contributing to the increase in total porosity. Confirmation of such porosity in relation to the mechanical properties is deferred to a future study.

Table 3 also compares the closed and open porosity achieved after firing. At 11 wt% starch and increasing amount of yeast, the closed porosity ranges from 6.4 to 33.2%, whereas the open porosity ranges from 15.3 to 49.8%. On the other hand, at constant yeast dosage at 31.5 wt%, the porous sample with 21 wt% corn starch yields the highest closed porosity whereas the porous

sample with 11 wt% cassava starch yields the highest open porosity. As observed above, the porous ceramics prepared by biological foaming exhibit significantly higher open porosities at low starch content. This is because of the fact that the slurry with low starch content has a low viscosity allowing the bubbles generated during foaming to coalesce or join, creating pore networks. On the other hand, the closed porosities are small and more or less independent of the starch content. This indicates that highly three-dimensional interconnected pore spaces [25, 26] consisting of large pore bodies connected by small pore throats were developed. This is further observed even in the case of small starch contents. At high starch content, the difference in the final porosity becomes smaller presumably because of the higher viscosity restraining the pore growth.

Microstructures of fired porous ceramics

Figure 8 shows the micrographs of fractured surfaces of fired porous samples consolidated with different type of starches treated with 31.5 wt% yeast. These porous samples showed the highest total porosity. Microscopic investigation of the porous microstructure of the samples revealed that the porosity consisted mainly of distorted pore structures with varying sizes and intact cell struts with no indication of firing cracks. It is also observable that some pores are interconnected through pore windows defining the open porosity of the porous materials. Specifically, this is observed for porous sample with 11 wt% corn starch-loaded porous samples depicting the largest pore sizes (Fig. 8a). As the cornstarch content was increased to 21 wt%, there is a slight decrease in porosity as illustrated in Fig. 8b. Smaller and irregular pore sizes are observable for porous samples shaped with cassava starch and rice flour (Fig. 8c, d). Moreover, a substantial decrease in porosity equipped with asymmetric channels [26] is visible for 21 wt% rice flour-loaded ceramic sample as an indication of collapsed gas bubbles during consolidation.

Variation of pore sizes can also be traced back to the increasing viscosity of the slurry, which resulted from the increased addition of starch and particle sizes. A high porosity with large pores is generated for low viscosity slurry as in the case of using low amount of corn starch. This is because of the fact that the generated foams can expand easily with less strain [3]. In the case of high viscosity slurry, a low porosity with smaller size is realized due to poor foam generation and hindered foam enlargement demonstrated by slurry containing rice flour.

Conclusions

A new shaping technique for porous ceramics has been successfully developed in this study using biological foaming of ceramic slurry through reaction of yeast with starch. The flow behaviors for all the ceramic slurries loaded with three different types of starches demonstrated shear thinning behavior suitable for the fabrication of porous ceramics. The starch type and increasing addition of yeast strongly influenced the attainment of high foaming factor of ceramic slurries. Specifically, the ceramic slurry containing 11 wt% corn starch treated with 31.5% yeast rendered the highest foaming factor. This provided the fired total porosity of up to 70.3% comprising of 35.8% open porosity and 34.5% closed porosity. The microstructural investigation of the fired porous compact showed porous microstructures with irregular pore geometry equipped with interconnecting pore networks representing the open porosity.
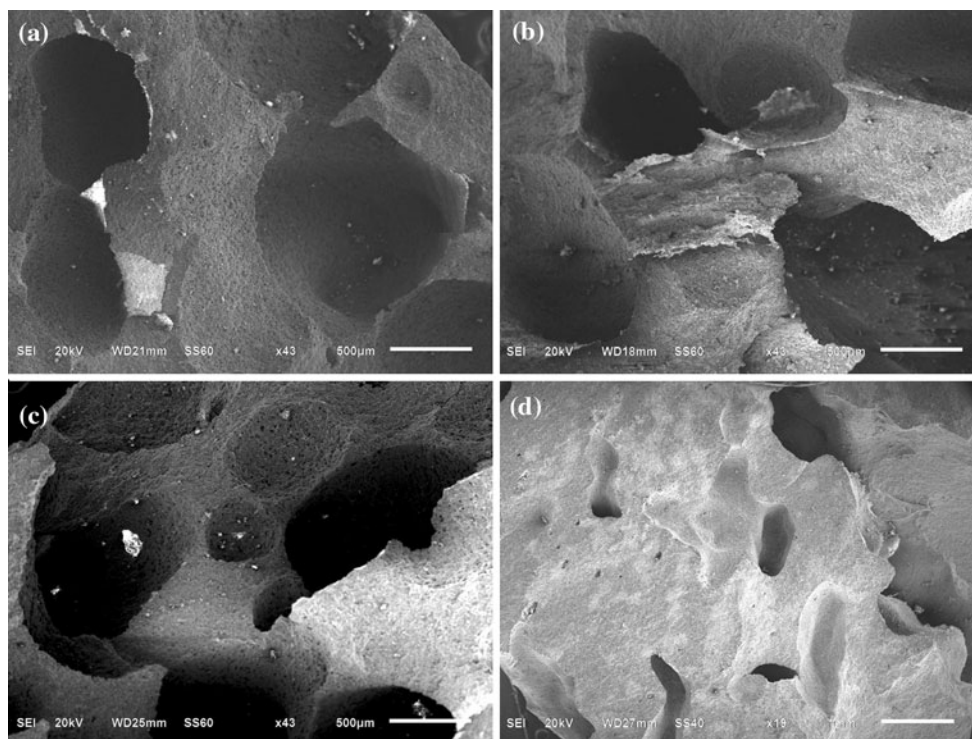
Fig. 8 Micrographs of fired samples formed with different amount and type of starch and 31.5% yeast: **a** with 11% corn starch, **b** with 21% corn starch, **c** with 11% cassava starch, and **d** with 11% rice flour

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