Influences of Starch on Ceramic-Foam Fabrication: A Short Review

N.H Yatim¹,²,a and H.A. Rahman¹,b*

¹ Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia
² Politeknik Ungku Omar Jalan Raja Musa Mahadi, 31400 Ipoh, Perak, Malaysia

E-mail: a nhamidah@puo.edu.my, * hamimah@uthm.edu.my

Abstract. Ceramic foams are high-value products with multiple functions, such as thermal insulation, acoustic insulation, fireproof and freezing tolerance. Wide-ranging ceramic-foam applications can reduce energy consumption and indoor fire hazards. The utilisation of ceramic materials in manufacturing requires appropriate methods to reduce the problems associated with these features. Ceramic foams have excellent thermal stability and structural resilience against organic solvents and chemical corrosion. They can also be used in various engineering applications. Natural additives such as starch, sucrose and yolk are used to control the pore structure of the products. These additives serve as foaming and binding agents to enhance the stability of foaming slurry. The use of starch strengthening in the ceramic fabrication is widespread because of its low cost and reduced impact on the environment. The effects of starch addition on the mechanical properties of ceramic foams include increased density, linear shrinkage and compressive strength, as well as decreased porosity and water absorption. These effects depend on the contents of starch and sintering temperature. This review focuses on the use of starch as a binding agent for ceramic-foam fabrication.

1. Introduction
Ceramic foams are inorganic materials formed from a three-dimensional ceramic fibre network. Ceramic foams have low density, high specific area, controlled permeability, thermal insulation and good acoustic as well as very strong chemical resistance. Ceramic foams with open pore structure are mostly used as carriers for catalysts, filters, bioreactors and bone substitutes, while ceramic foams with closed pore structure are used for sonic insulation and lightweight structured components. Ceramic foams are a specialised class in porous ceramics and have high structural and porosity. The spherical pores in ceramic foams are randomly arranged and closely stack together [1]. Ceramic foams with special combination properties, such as thermal conductivity and water absorption, have attracted the attention of manufacture using it as heat insulation, sound absorption and shock wave-absorbing construction [2]. Special characteristics of ceramic foams, such as great surface area, high porosity, low density, high refractoriness, good chemical resistance, long severe environment and low thermal...
conductivity, have attracted several fields for use. These features make ceramic foams be widely used in many respects, including thermal insulation, fire resistance, waterproof and chemical stability. With the excellent combination of their special characteristics, ceramic foams have been widely used in the area of construction insulation [3].

Ceramic foams have been widely utilised because of their usability in some areas of technology. Among other things, ceramic materials are used as insulation refractories, catalyst support and filters for molten metals [4]. Ceramic foams are also increasingly being used in various engineering fields as catalyst, liquid or gas filtrate, extractor, separator, thermal insulator, scaffolding for biological and special low application and gravity components for structural applications. Ceramic foams that have such characteristics as high permeability, relatively low density, high surface area and low thermal conductivity, are therefore indispensable nowadays. The usage of ceramic foams depends on the technique used in their fabrication [5].

Various methods, such as particle stacking, polymeric sponge technique, sacrificial template technique, freezing casting and direct foaming technique, are used to fabricate ceramic foams [4]. Another technique to fabricate ceramic foams such as particle organisers, replication of sacrificial template, burning out of fugitive pore formers and direct foaming of colloidal slurry [6]. Moreover, several techniques, including replicas, templating techniques and direct foaming, have been developed to produce ceramic foams [7]. Ceramic foams are ecologically porous materials with excellent characteristics, such as low density, high specific strength, good thermal insulation and chemical constancy. Current techniques used to produce ceramic foams include sol-gel, sacrificial template, addition of pore-forming agent and foaming technique of powder [8]. Foams can be defined as a spreading system based on the bubble gas of their standard phase, air, dispersed in a continuous liquid or solid matrices (solid foam), such as steel, glass and concrete foam. Drenckhan, W., et al (2010) studied foam preparation to evaluate the stability of foaming time and the control of bubble size [9]. The structure, coarsening process, drainage and dynamic properties of foams are influenced by fine particles [10]. Various methods have been established to acquire the best ceramic foams for different engineering applications. Each of the techniques used to produce ceramic foams, however, has respective weaknesses. Among the methods commonly used in fabricating ceramic foams are gel casting, freeze casting, extrusion, compaction, starch consolidation casting (SCC) sol–gel synthesis, organic foaming method and using pore-forming agent.

2. Types of methods for ceramic-foam fabrication

Many methods have been developed to fabricate ceramic foams. The preparation of ceramic foams has significantly affected the microstructure/ceramic-foam properties produced. Ceramic foams delivered by replica techniques, sacrificial templates and direct bubbling methods typically have a high porosity [11]. Ceramic foams can be formed through different methods, and the most conservative technique is the reticulated sponge method or replica technique. By this method of replication, the polymer span is coated with a ceramic slurry, dried, covered and sintered [12]. Ceramic foams have been widely used as thermal insulator, catalyst support, filter and medical implants because they affect the cellular microstructure of the ceramic foams. Several ceramic foam-processing methods, such as replica and direct foaming methods, have been developed. The direct foaming technique is an interesting technique, in which foams are made with open cells or closed cells [13]. Ceramic foams have multipurpose pore density, surface range and chemistry [14]. The actual cell shape, however, depends on some factors, including the manufacture process. Ceramic foams can also be produced via starch consolidation, uniaxial pressing, polymeric sponge replication method and foaming method.

Porous ceramics have been produced by many processing methods, such as sol–gel synthesis, freeze casting technique, organic foaming technique and pore-forming agent technique. Among the methods, the pore-forming agent method is most usually used and is an effective method; pore-forming agents, such as starch, graphite, organic particulates or saw dust, have been used usually. Nevertheless, most of these pore-forming agents only form structures with casually organised irregular pores with several sizes in the final structure caused by agglomeration and nonuniformity of pore-
forming agents in raw materials; such condition is threatening to be avoided [15]. Different methods, such as gel casting, freeze casting, extrusion, compaction and SCC, have been used to fabricate cellular ceramic techniques. In the fabrication of porous ceramics, various types of binders, such as potatoes, corn, potato, rice, wheat and poppy seeds, can be used. The use of starch take out from seeds of cereals (corn, sorghum, wheat or rice), certain roots (potato, cassava or tapioca or arrowroot) and the sago palm has been applied in the use of commercial ceramics. Starch, as an additive, is a material that has the features of easy processing, commercial availability and burning completely without residual ash. Sago starch has great potential as a binder and a pore-forming agent in the manufacture of cellular ceramics [16]. The main benefit of using starch as a consolidation agent for ceramic slurries compared with other biopolymers is that it is a liquid and secures the characteristic of being residual-free through starch burnout. This method is a technology that is eco-friendly and environmentally friendly to be implemented in the processing of ceramic materials with various applications [17].

3. Starch consolidation
The starch consolidation method for ceramic-foam characteristic produces the capability to get a porous body with complex shapes and controlled microstructures by using early suspensions with dissimilar solid loading and can be formed in multiple applications. The use of starch from various sources provides the resulting ceramic body with different porous morphologies. The most commonly used starch examples are rice, potatoes and corn. The potato starch shows the biggest and most anisometric granules, whereas rice starch is the least and more isometric. A technique that uses starch as a consolidation agent for tricapit pore-structured silica bodies adopts two consolidation methods, starch and foam [18]. The starch consolidation way for ceramic slurries, as one of the consolidation procedures, has been usually explored. In this process, starch is loaded in the aqueous slurry of the ceramic powders. Direct consolidation is a novel process based on colloidal processes. This process has the potential to form complicated ceramic bodies from minor to huge components with exact porosity, defects and density. The powder used in this technique should be fully smoothed to prevent the decline in the strength and reliability of the ceramic body produced [17].

SCC techniques are based on the capability of starch to swell and ultimately gelatinise in the water at a temperature of 60 °C–80 °C. Ceramic green samples can be formed from suspension in resistant moulds (usually metal moulds). When the granules or starch particles swell, they will also entertain as binders adding strength to the unified body, which allows it to form before drying. After burning out of the starch and sintering of the ceramic matrix, a material is gained with a porosity equivalent to the original amount, shape and size of the starch particles [19]. Starch consolidation techniques have been broadly explored to form ingredients for ceramics through the use of starch loaded in ceramic slurry. The inactivity of the starch in the ceramic slurry enables the formation of the ceramic green body through slip casting method into a nonporous mould [20]. This condition is due to the casting of starch strengthening categorized as a direct pouring method with no drainage required to form the desired ceramic.

Sopyan, I., and Fadli, A. (2012) developed a method for protein foaming and consolidation by using yolk as a pore-forming agent to fabricate porous ceramics using alumina as raw materials [21]. Alumina powder and egg yolks were stirred in a beaker with ratio of alumina of 0.65 (slurry A), 0.75 (slurry B) and 1.00 (slurry C). Magnetic powder was blended at 150 rpm for 3 h at room temperature. The slurry was put into a cylindrical open stainless steel mould and heated in an oven at 180 °C for 1 h. Castor oil was used as a lubricant to facilitate mould release. The samples were sintered in a furnace at 10 °C/min up to 600 °C to remove egg yolks and then at 2 °C/min up to 1550 °C.

The diagram of the processing scheme for porous silica ceramics using foaming and starch consolidation technique is presented in Figure 1. A slurry is ready with silica powder of 0.2wt% CMC and 10wt% of cassava starch and added with distilled water by a planetary ball mill for 30 min. Lactic acid with pH value of 3–4 was added to the mixture to complete the slurry. After consolidation and cooling, the mould is left at room temperature for 36 h and then stored at 50 °C–80 °C for 2–3 days.
Complete drying is conducted at 120 °C, and burnout is completed by heating in air at 1.0 °C min\(^{-1}\) to 500 °C, with holding time of 2 h at 300 °C to avoid violent contamination. The mould is then sintered at 1250 °C for 5 h [17].

Mao, X, et al. (2008) stated that the foaming and starch combination technique is suitable for porous ceramic fabrication [22]. Techniques that combine foaming and starch consolidation can produce extremely porous ceramics and are also economical, practical and environmentally friendly [23]. The foaming and starch consolidation method includes ceramic suspensions, foaming, consolidation, drying and sintering, as described in Figure 2.

**Figure 1.** Flow chart of the process for porous silica ceramics using foaming and starch consolidation method [22].

**Figure 2.** Flow chart of the process for preparing porous mullite ceramics by foaming and starch consolidation [23].
foam fabrication. This process uses the capability of starch to form pores and granule binders in ceramic foams. The starch can swell and calibrate at a certain temperature of 60 °C–80 °C and a sintering temperature of 1250 °C. This swelling is due to the amount of water absorbed by starch. Swelling improves the strength of the consolidated body. This technique can control the size of pores and the resulting pore distribution by altering the amount of starch used and the type of starch used. Starch is used as a pore-forming agent because of the naturally occurring chemical properties that can guarantee the absence of waste after combustion.

4. Types of starch

Lyckfeldt, O, et al. (1998) stated that starch grains are usually white, dense and unsolvable in water at room temperature and comprise a mixture of two polysaccharides, a linear amylose and a split amyllopectin [24]. Amylose gives its soil starch in aqueous suspension. The polymer chains in the starch are formed by glucose units that produce large amounts of hydrophilics which provide strength to starch granules, as shown in Figure 3. This condition produces good features, such as coagulating, stabilising, membrane-forming and gelling properties [19].

![Figure 3. Starch is a polymer consisting of condensed glucose units [19]](image)

Binders are a long chain of polymer networks that work to provide strength to the green body by building bridges among particles. In the drying process, binders are removed, leaving the holes in the frame or cell wall. The traditional binders are in the form of starches obtained from plants, such as tubers or roots and cereals. They are a major source of eco-friendly materials that are easily processed and operated, low cost, consistent and have good and biodegradable distribution of shapes and sizes. Existing biopolymers consist of condensed glucose units. The dissolution of part of glucose starch molecules causes them to undergo irreversible swelling and crystalline crystallisation called starch gelatinisation and alter from pure suspension to elastic gel [16]. Gregorova, E, et al. (2010) demonstrated that various types of binders, such as potatoes, corn, cassava, rice, wheat and poppy seeds, are used for porcelain ceramics [25]. No literature related to the use of sago (Metroxylon sagu) as a starch source and a binder to produce ceramic cells is available. Sago has the same properties as those of binders; it is available in Malaysia at a low cost and can be used as a component used in adhesive production. Sago is gelatinised because it has a low gelatinisation temperature, has high viscosity and is easily formed because of low-syneresis gel [16].

Starch is a high molecular carbohydrate comprising linear amylose and amyllopectin [17]. When in the water at a high temperature, starch experiences glutamine, followed by hydrolysis containing amylose. Amylose and amyllopectin are also known as polysaccharides with much sugar and are formed from the combination of several glucose units that form long chains. They consist of two types of macromolecules having different glucose monomers. Glucose units are arranged in an alternate arrangement. Amylose is largely linear polymer having a repeating hydroxide bond. Starch can increase viscosity, especially at low shear rates. When the shear rate is high, the polymer leads to the
flow of visible clear viscosity. The phenomenon is due to the amylopectin effect, which spreads into its structural solution, such as the tree, thereby keeping the particles in the distance to escape separation, as shown in Figure 4. Changes affect yield stress at time out but do not show a strong impact on plastic viscosity. The weight of starch molecules may show a role in the stabilisation influence, and the ratio between amylose and amylopectin may be very high [1].

![Chemical structure of amylose and amylopectin](image)

**Figure 4.** Chemical structure and performance of starch components in aqueous media: (a) chemical structure of amylose and amylopectin [17].

Starch is from several types of cereals, such as corn, rice, flour, potato and cassava. Starch is widely used in manufacturing process as a component in the field of ceramic processing and as an additive in the textile industry, paper manufacture, food processing, pharmaceuticals and building materials. Among the characteristics of starch that allow them to be widely used are the increase in viscosity, gelatin, fasteners and the ability to form. Table 1 and Figure 5 show the type and amount of the starch used in the various fabrications of ceramic foams from previous studies.

| No. | Types of starch          | Amount       | Raw material          | Reference |
|-----|--------------------------|--------------|-----------------------|-----------|
| 1.  | Wheat starch, Potato and corn | 10–50vol% | Alumina powder | [6]       |
| 2.  | Cassava                  | 10–20vol%   | Alumina oxide        | [2]       |
| 3.  | Corn                     | 3–13mass%   | Calcined alumina     | [13]      |
| 4.  | Potato                   | 10–40vol%   | HA                    | [1]       |
| 5.  | Sago and Tapioca (solid weight) | 50–70wt% | Porcelain raw powder | [12]      |
| 6.  | Cassava                  | 25wt%       | Sayong ball clay     | [24]      |
| 7.  | Corn                     | 10wt%       |                       | [5]       |
| 8.  | Cassava                  | 10wt%       | Silica                | [17]      |
| 9.  | Wheat flour              | 4 g         | HA                    | [19]      |
5. Influences of starch on the mechanical properties of ceramic foams

After the formation of ceramic foams through the drying process, several mechanical, physical and chemical tests are performed to study the characteristics of ceramic-foam fractions. Mechanical tests are conducted to evaluate the compressive strength of ceramics formed. For features, linear shrinkage, foam morphology, porosity and density are studied through physical testing. Mechanical properties are particularly emphasised in the characterisation of ceramic-foam structures. The compressive strength of ceramic foams is evaluated to test the strength of ceramic foams, which are designed to have a high porosity of more than 80%. Compressive strength affects the porosity, size, distribution and morphology of pores. The porosity of a ceramic foam utilizes a high effect on compressive strength, because it determines the solid cross-sectional load bearing of ceramic foams [6].

![Figure 5. Summary of starch used.](image)

5.1 Density and porosity

Starch content effects the apparent porosity and bulk density of porous alumina samples [19]. Archimedes water displacement procedure is used to measure the bulk density and total porosity of sintered samples [16]. Bulk density and open porosity are determined by the Archimedes method in water [20]. Table 2 presents that previous studies showed that linear shrinkage will change according to the starch composition used.
Table 2. Density and porosity of porous ceramic body.

| No. | Technique of fabrication | Starch amount | Linear shrinkage (%) | Density, g/cm³ | Porosity, % | Reference |
|-----|--------------------------|---------------|----------------------|----------------|-------------|-----------|
| 1   | Starch consolidation casting | 10–50vol% | - | 20–50 | [6] |
| 2   | Starch consolidation casting | 10–40vol% | 1.36–1.65 | 79.2–90.2 | [1] |
| 3   | Starch consolidation casting | 3–13mass% | 0.00%–9.44% | 1.4–2.05 | 46–64 | [13] |
| 4   | Alumina consolidation | 10–20vol% | 15.2%–29.6% | 0.4–0.75 | 13–15 | [2] |
| 5   | Foaming and starch consolidation | 10wt% | 18–30 | - | - | [17] |
| 6   | Sponge replica | 50–70wt% (solid weight) | 0.37–0.51 | 79–81 | [12] |
| 7   | Uniaxial pressing | 25wt% | - | - | [24] |
| 8   | Protein foaming consolidation | 4 g | 26–77vol% | - | 46–52 | [19] |
| 9   | Foaming and starch consolidation | 10wt% | - | 86–73 | [5] |

5.2 Shrinkage
Linear shrinkage occurs due to a defined sintering process as the decline or shrinkage of a percentage of the length of a ceramic sample, and it is important in the ceramic industry. Linear shrinkage tests are performed to examine the sample shrinkage rate produced by the drying process. Length and dimensions are required in several applications to determine the amount of ceramic samples produced before the formation process. Linear contraction is due to changes in particle size and sample size. Linear shrinkage is almost inversely proportional to the radius of particles.

Shrinkage is measured using a slide calliper and calculated from mould dimensions and body dimensions after firing [20]. Linear shrinkage depends on the content of starch used and the sintering temperature. The linear shrinkage of porous alumina samples sintered at different firing temperatures of 1400 °C–1700 °C is depicted in Figure 6.
Figure 6. Linear shrinkage of porous alumina samples sintered at different temperatures of 1400 °C, 1500 °C, 1600 °C and 1700 °C [13].

5.3 Compressive strength
The compressive strength test is executed to evaluate the mechanical properties of formed sintered samples using a universal testing machine. The compressive strength is calculated from the maximum point of the stress/strain graph, which occurs when the first crack performed in the samples. The average of three samples is taken as the measure of the compressive strength of the samples [17]. Gong, L, et al. (2014) studied the compressive strength of porous mullite ceramics sintered at different temperatures, as shown in Figure 7. For 62.5wt% solid loading, the compressive strength of porous mullite ceramics increases from 1.02 MPa to 13.61 MPa with increased sintering temperature; for 67.5wt% solid loading, it increases from 2.14 MPa to 22.38 MPa. Two factors could impact the mechanical strength of porous mullite ceramics prepared in this work: porosity and sintering neck. From 1200 °C to 1500 °C, the compressive strength increases slightly because the effect of porosity is dominant. After sintering at 1600 °C for 2 h, the samples display a affected improvement in compressive strength. The result is attributed to that the increased sintering temperature leads to improved densification and hence increasingly strong sintering neck, resulting in dramatically increased compressive strength [23]. Table 3 shows the obtained compressive strength in previous studies using different raw materials.
Figure 7. Compressive strength of porous mullite ceramics sintered at different temperatures [23].

On the basis of previous studies using the same technique to form foaming ceramics, the compressive strength of foaming ceramics is closely related to the amount of starch used, material porosity, material density and solid content. Compressive strength increases with decreased material porosity decreases, and material density increases with increased solid content.

Table 3. Compressive strength of porous ceramic body.

| No. | Raw material | Compressive strength, MPa | Reference |
|-----|--------------|---------------------------|-----------|
| 1   | Porcelain raw powder | 0.33–0.93 | Jamaludin A.R, et al. (2014) |
| 2   | Porcelain raw powder | 0.22–0.58 | Jamaludin A.R, et al. (2015) |
| 3   | HA           | 5.6–21.4     | Ahmed, Y. M. Z, et al. (2015) |
| 4   | Silica       | 4.17          | Mao, X, et al. (2008) |
| 5   | HA           | 0.1–6.4       | Sopyan, I., et al. (2012) |
| 6   | Mullite powder | 1–22         | Gong, L, et al. 2014 |

6. Conclusion
This study reviews the commonly used starch in the market for ceramic-foam fabrication, especially in starch consolidation techniques. From previous studies, many types of starch, such as corn, cassava, tapioca, potato, wheat flour and sago, are used in ceramic-foam fabrication. The main benefit of using starch as a consolidation agent over other biopolymers is that it is residual-free during burnout. The value of starch content affects the characteristics of fabricated ceramic foams. Ceramic foams containing the same starch content indicate increased density with increased sintering temperature,
whereas porosity and water absorption decrease. The values of linear shrinkage and compressive strength also increase with increased starch consumption. This review shows that the sintering temperature used in previous studies ranged from 1200 °C to 1700 °C. Starch is able to swell and gelatinise at temperatures of 60 °C– to 80 °C. Current swelling gives strength to the ceramic-foam body. Starch is used in ceramic-foam fabrication because of its natural properties that guarantee the environment.

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