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Short communication

Porous ceramics prepared using poppy seed as a pore-forming agent

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Abstract

It is shown that poppy (*Papaver rhoeas* L.) seed is a potentially interesting and unique pore-forming agent (PFA) for use in ceramic technology, due to its large size (around 1 mm), narrow size distribution, constant shape (kidney-like), appropriate density and easy availability. Porous alumina ceramics have been produced using commercially available poppy seed in combination with a new ceramic shaping technique called starch consolidation casting. After shaping and drying the ceramic green bodies were fired at 1570 °C with a heating rate of 2 °C/min, resulting in porous alumina bodies with a bulk density of 2.50 ± 0.03 g/cm^3, a total porosity of 37.6 ± 0.8% (open porosity 32.4 ± 0.9%, closed porosity 5.2 ± 0.3%) and a linear shrinkage of 14.1 ± 0.2%. As expected, the pore size exhibits a bimodal distribution, corresponding closely to the original size of the pore-forming agents.

Keywords: A. Slip casting; B. Porosity; B. Microstructure-final; D. Al_2O_3; Poppy seed

Porous ceramics have a wide range of applications at all length scales, ranging from filtration membranes and catalyst supports to biomaterials (scaffolds for bone ingrowth) and thermally or acoustically insulating bulk materials or coating layers. Therefore, the preparation of porous ceramics with controlled microstructure (porosity, pore size and pore space topology) has been a subject of constant interest during the last decades and common processing techniques include sol–gel techniques (for pores in the nanometer size range and extremely high porosity), the use of polymeric foam templates (for large pores and extremely high porosity), biomimetic processing (using, e.g. pyrolized wood templates), ceramic hollow spheres (e.g. alumina microballons) and sacrificial (pyrolyzable) pore-forming agents (PFA), i.e. synthetic organics or natural biopolymers which burn out during firing [1–3]. Although a great number of various PFA has been proposed and used in ceramic technology, e.g. carbon [4–6], poly-vinyl-chloride [7], polystyrene [8], poly-methyl-metacrylate [9–11], polyethylene [12], wood flour (saw dust) and crushed nut shells [1–3], it seems that starch, a natural biopolymer consisting of amylose and amylopectin, has attained a prominent position as a PFA today [11–20], including its recent application as a combined pore-forming and body-forming agent in starch consolidation casting [21–31]. Among the main reasons for the success of starch as a PFA in ceramics are the lack of hygiene and ecological concerns, easy handling and processing (including defect-free burnout), the easy commercial availability in arbitrary amounts, at low cost and with constant, controlled quality, the rounded shape with well-defined aspect ratio (usually close to unity, without large scatter) and the well-defined size distribution for each starch type [32]. Moreover, as mentioned before, apart from its universal function as a PFA, starch can serve additionally as a body-forming agent in starch consolidation casting, due to its ability to swell in water at elevated temperatures, thus enabling ceramic green bodies to be fabricated by slip casting of suspensions with starch into non-porous molds (e.g. metal molds).

Unfortunately, the pore size range attainable by applying different starch types as PFA covers only approximately one order of magnitude in the range below 100 μm (median sizes between 5 and 50 μm for rice and potato starch, respectively [32]). It has to be noted that this pore size range (which is very closely connected to the original size of the starch granules) refers to the pore diameter proper, determinable, e.g. by 3D tomography or microscopic image analysis. In contrast, the pore size determined, e.g. via mercury intrusion refers to the

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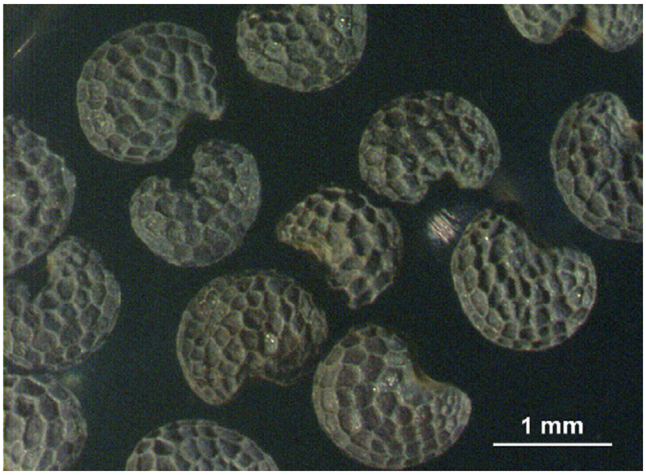

Fig. 1. Optical micrograph of poppy seed; note the kidney-like shape and the fine polygonal network texture on the surface.

pore throat size, i.e. the size of the interconnections between (open) pores and is usually much smaller (order of magnitude 1–10 μm, say). It is clear that for many purposes, e.g. for thermally or acoustically insulating materials, for large-scale lightweight ceramics or for the ingrowth of bone tissue into bioceramic implant materials, larger pore sizes are desirable (in the latter case of course connected with a high degree of interconnectivity). Blue poppy (*Papaver rhoeas* L.) seed, a natural product of biological origin and a well-known raw material in the food industry, might be a promising PFA for ceramics in this respect. Surprisingly, however, there is not a single report on this so far in the literature and thus it appears that poppy seed has not been tested for this application. In this paper we report the first results on the use of poppy seed to prepare porous ceramics. More specifically, we have chosen poppy seed (as a PFA) in combination with starch (as a PFA and body-forming agent) to prepare porous alumina ceramics via the starch consolidation casting technique.

Fig. 1 shows an optical micrograph of poppy seed (blue poppy seed, produced by RH natur s.r.o., Uherčice, Czech Republic) with its typical rounded kidney-like shape and the fine polygonal network texture on the surface. The size distribution is rather narrow. Microscopic image analysis revealed values of 1265 ± 78 μm for the maximum Feret diameter, 1038 ± 68 μm for the minimum Feret diameter and 1.22 ± 0.07 for the aspect ratio, cf. Table 1. These values indicate that the deviation from spherical shape is statistically significant but not large, i.e. not too far away from unity. It seems that the density of poppy seed is not available in the literature. Therefore, for the present work it was determined by floating in a sugar solution (saccharose), i.e. sugar was added to the water in which poppy seed had settled down until the poppy seed exhibited buoyancy; according to this measurement the density is 1.10 ± 0.05 g/cm^3. The knowledge of this value is necessary to control the volume concentration of PFA in the system, cf. Table 2.

Table 1
Size and shape characteristics of poppy seed (Feret diameters and aspect ratios determined by image analysis)

Feature	Arithmetic mean value and standard deviation
Maximum Feret diameter (μm)	1265 ± 78
Minimum Feret diameter (μm)	1038 ± 68
Aspect ratio	1.22 ± 0.07

Table 2
Densities of the ingredients used

Ingredient	Density [g/cm^3]
Distilled water	1.0
Poppy seed	1.1
Potato starch	1.5
Alumina	4.0

Alumina suspensions with 80 wt.% of submicron alumina with a median size of 0.6–0.8 μm (CT3000 SG, Almatis GmbH, Ludwigshafen, Germany) were prepared in a standard way by mixing the alumina powder with distilled water, adding 1 wt.% (related to alumina powder) of a commercial deflocculant (Dolapix CE64, Zschimmer & Schwarz GmbH, Lahnstein, Germany) and potato starch (Solamyl, Naturamyl a.s., Havlíčkův Brod, Czech Republic), followed by 2 h homogenization in a polyethylene bottle with alumina balls on a vibrating table. Finally poppy seed was added and the mixture homogenized for further 10 min. Potato starch and poppy seed was added to 100 g of the as-prepared alumina suspension in amounts of 7.5 and 5 g, respectively. According to the density values in Table 2, this corresponds to a total PFA volume of 32.3% (related to the alumina powder) after mixing. The suspensions were cast into metal molds and heated in a laboratory drier for 1 h at 80 °C to obtain cylindrical specimens of diameter 6 mm (7 mm in the green state) and length approximately 80 mm. After demolding and drying at 105 °C to constant weight the bodies were fired according to a standard schedule (heating rate 2 °C/min, 2 h dwell at 1570 °C), resulting in bodies without visible cracks, neither from drying nor from firing, see Fig. 2 and Table 3. We emphasize that it was not necessary to use a special firing schedule for the burnout of the poppy seed.

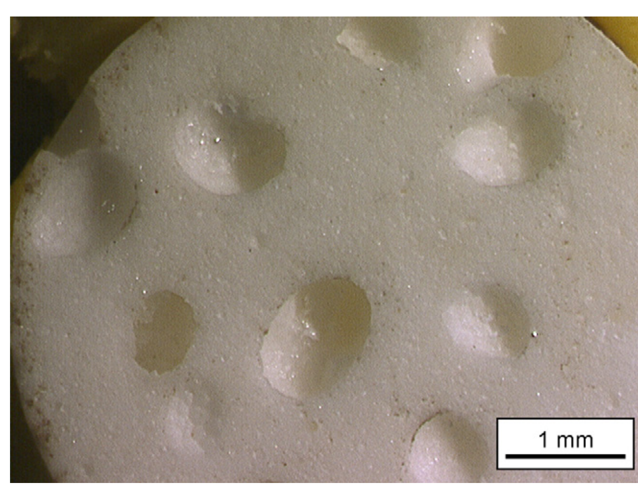

Fig. 2. Porous alumina ceramic after firing (diamond-cut cross section).

Table 3
Microstructural characteristics of as-fired porous alumina ceramics with hierarchical porosity (small and large pores caused by burnout of starch and poppy seed, respectively)

Feature	Arithmetic mean value and standard deviation
Bulk density (g/cm^3)	2.498 ± 0.032
Apparent density (g/cm^3)	3.693 ± 0.016
Open porosity (%)	32.4 ± 0.9
Total porosity (%)	37.6 ± 0.8
Closed porosity (%)	5.2 ± 0.3
Linear shrinkage (%)	14.1 ± 0.2

If the starch would not swell during heating in water to 80 °C and the pores would not shrink during firing the total porosity should correspond to the aforementioned content of PFA related to alumina, i.e. 32.3%. Since the experimentally determined total porosity (ϕ) is 37.6% (determined via the formula $\phi = 1-\rho/\rho_0$, where ρ is the bulk density of the ceramic samples, measured via the Archimedes method, i.e. by weighing water-saturated bodies in air and in water, and ρ_0 is the theoretical density of alumina, i.e. 4.0 g/cm^3) it must be concluded that this value (higher than the PFA content by 5%) is a result of starch swelling during heating in water. The pores due to poppy seed are approximately 1000 μm in size, the pores due to starch are in the range 30–60 μm and form part of the matrix around the large poppy-generated pores (see Figs. 3 and 4). Note that the alumina matrix is fully sintered, since the linear shrinkage is 14.1%, i.e. assuming isotropy the volumetric shrinkage is 36.6%, which corresponds very well to the excess volume fraction of voids in a random close packed sphere packing with a packing fraction of approximately 64%. The latter corresponds to the state of the submicron alumina matrix in the as-shaped body. It is known that pores with tens of micrometer and larger in a submicron-grain matrix do not contribute to shrinkage during firing and sintering of the matrix [33].

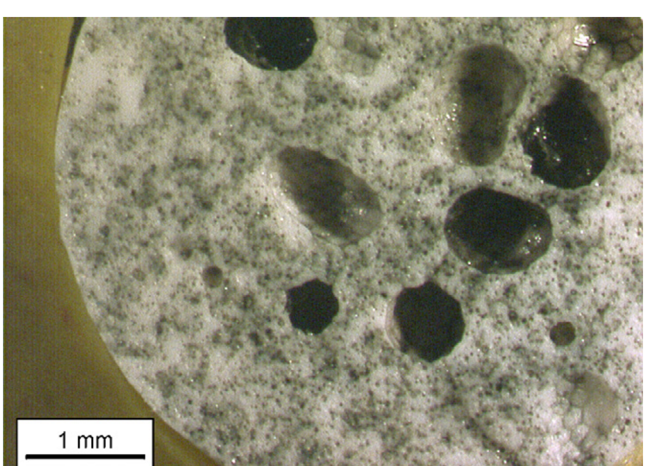

Fig. 3. Porous alumina, stained with black ink to reveal the small pores due to starch and the fine polygonal network drawing on the inner wall of the large pores coined by the poppy seed surface.

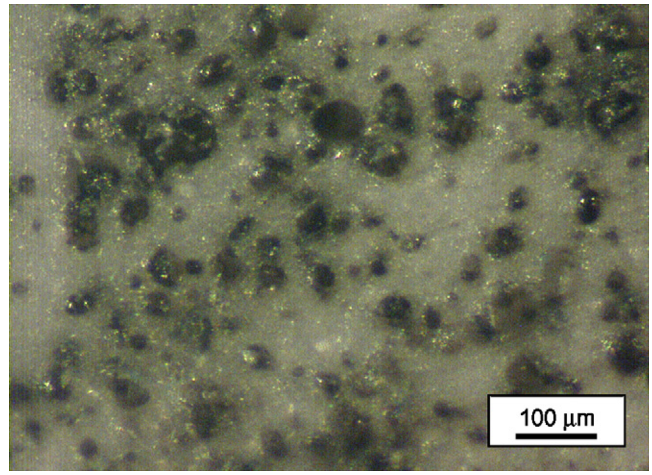

Fig. 4. Micrograph of the small pores due to starch, stained with black ink.

In concluding, it has been shown that poppy seed is a promising pore-forming agent for ceramics. In the concentration used here, defect-free burnout was possible using a conventional firing schedule (without the need to use a special heating schedule for burning out the organics). The most interesting points in using poppy seed are its relatively large size (around 1 mm) and the fact that its density is close to but slightly higher than that of water. Therefore, suspensions with poppy seed can be prepared quite easily, whereas many other PFA with lower density (many synthetic polymers and ceramic microballoons) would exhibit strong buoyancy effects at this size. In combination with the potato starch as a PFA, which is more than one order of magnitude smaller, a hierarchical pore structure results.

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