Alumina ceramics prepared with new pore-forming agents

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Abstract

Porous ceramics have a wide range of applications at all length scales, ranging from filtration membranes and catalyst supports to biomaterials (scaffolds for bone ingrowths) and thermally or acoustically insulating bulk materials or coating layers. Organic pore-forming agents (PFAs) of biological origin can be used to control porosity, pore size and pore shape. This work concerns the characterization and testing of several less common pore-forming agents (lycopodium, coffee, flour and semolina, poppy seed), which are of potential interest from the viewpoint of size, shape or availability. The performance of these new PFAs is compared to that of starch, which has become a rather popular PFA for ceramics during the last decade. The PFAs investigated in this work are in the size range from 5 μm (rice starch) to approximately 1 mm (poppy seed), all with more or less isometric shape. The burnout behavior of PFAs is studied by thermal analysis, i.e. thermogravimetry and differential thermal analysis. For the preparation of porous alumina ceramics from alumina suspensions containing PFAs traditional slip casting (into plaster molds) and starch consolidation casting (using metal molds) are used in this work. The resulting microstructures are investigated using optical microscopy, combined with image analysis, as well as other methods (Archimedes method of double-weighing in water, mercury intrusion porosimetry).

Keywords: porous ceramics, biopolymer pore-forming agents, slip casting, microstructure

I. Introduction

One of the basic methods to produce porous ceramics, apart from bonding hollow spheres (ceramic microballoons), replica methods (using synthetic polymer foams, e.g. polyurethane or carbon or natural structures, e.g. coral or wood) and direct foaming (using surfactant-stabilized or particle-stabilized suspensions), is by using pore-forming agents (PFAs) [1–5]. Among them, biopolymeric pore-forming agents have a long tradition in ceramic technology because of the fact that their burnout is usually harmless from the ecological and hygiene point of view. In particular, they are free of chlorine- and fluorine-containing hydrocarbons, while their content of ash-producing inorganic salts is mostly low enough to be neglected with respect to the ceramic composition. Depending on the biological source and the shaping technique employed, PFAs can be used to control porosity, pore size and pore shape.

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A wide variety of natural (i.e. biogenic) and carbon-based pore-forming agents (also called sacrificial templates or fugitive materials) have been tested or used so far, including saw dust (wood flour) [1,6], crushed nut shells [2], carbon fibers [7], cotton [8], peas and seeds [9], including poppy seed [10], lycopodium [11], starch [9–27] and, recently, wheat flour [28,29].

In this paper we report on the characterization of several biopolymeric PFAs, their density, particle size and shape and burnout behavior. One group of these PFAs consists of three different starch types, which can be used as pore-forming and at the same time body-forming agents in a shaping method called starch consolidation casting (SCC) [14,15]. The second group includes less common PFAs (lycopodium, coffee, fine flour, semolina and poppy seed), which might be useful in ceramic technology, because of their specific size, commercial availability and / or low price. Alumina ceramics are prepared with these pore-forming agents and the resulting microstructures are investigated and discussed.

II. Experimental

The ingredients used for sample preparation were alumina, distilled water, deflocculant, and pore-forming agents. Aqueous suspensions have been prepared with submicron alumina (α-Al_2O_3 grade *CT 3000 SG, Almatis GmbH, Germany*, median particle size 0.7 μm) in the range 65–80 wt.%, 1 wt.% (based on alumina) deflocculant *(Dolapix CE 64, Zschimmer & Schwarz, Germany)* and pore-forming agents with contents in the range 5–50 vol% (with respect to alumina).

Several kinds of natural biopolymers were used as pore-forming agents (PFAs) in this work, among them different types of starch (rice starch – Remy FG, Remy Industries NV, Belgium; waxy corn starch – Amioca TF, National Starch & Chemical, UK; and potato starch – Solamyl, Natura a.s., Czech Republic) as well as other, less common, pore-forming agents such as lycopodium (supplied by H. Klenk GmbH, Germany), coffee (commercially milled, Tchibo Exclusive, Czech Republic), fine (smooth) wheat flour (commercially milled, pšeničná mouka hladká, mlýny J. Voženílek s.r.o, Czech Republic), semolina (commercially milled, Zátkova jemná krupička, bratři Zátkové a.s., Czech Republic) and poppy seed (type modrý mák, RH natur s.r.o., Czech Republic). All PFAs were used as delivered (except for coffee which has been leached in hot water before use), calculating the concentrations via the densities 1.5 g/cm^3 for starch, 1.3 g/cm^3 for coffee, 1.2 g/cm^3 for lycopodium and 1.1 g/cm^3 for poppy seed (the first taken from the literature, and the latter three determined by neutral floating in a saccharose sugar solution).

Two methods were used for the preparation of porous alumina ceramic bodies: traditional slip casting (TSC) into plaster molds (cylindrical rods, diameter 5 mm) and starch consolidation casting (SCC) using metal molds (cylindrical rods, diameter 7 mm). After homogenization (2 h in polyethylene bottles on laboratory shaker, using alumina balls) the suspensions were cast into molds. In the SCC process the metal molds were subsequently heated for 2 h at 80°C to allow the starch to swell. After demolding the green bodies were dried and subsequently fired at 1570°C (heating rate 2 °C/min, hold time 2 h).

Size and shape of the PFAs were characterized by microscopic image analysis (Lucia G, Laboratory Imaging s.r.o., Czech Republic) and laser diffraction (Analysette 22 NanoTec, Fritsch GmbH, Germany), while the thermal decomposition behavior of the PFAs was studied by thermal analysis, i.e. thermogravimetry (TG) and differential thermal analysis (DTA) with a heating rate of 10 °C/min (Setsys Evolution 1750, Setaram, France). The resulting microstructures were investigated using the Archimedes method of double-weighing in water, microscopy image analysis, and mercury intrusion porosimetry (AutoPore IV 9500, Micromeritcs, USA).

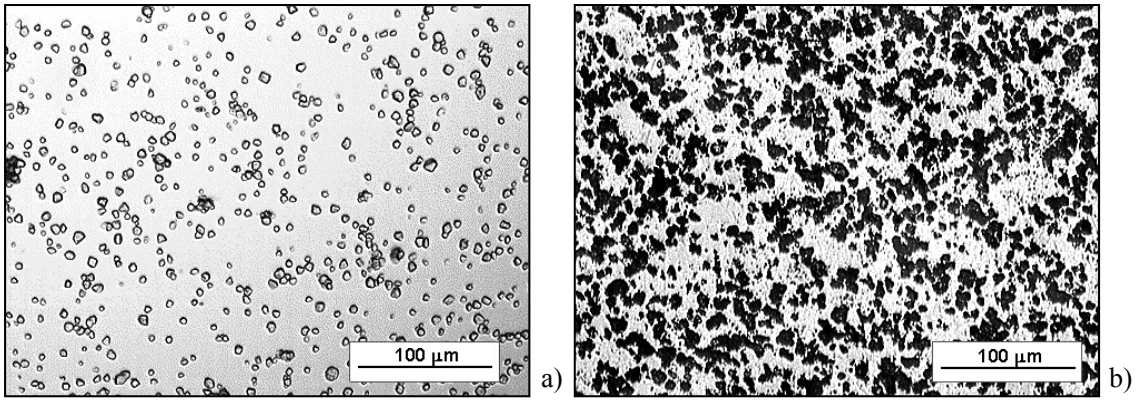
III. Results and Discussion

The left-hand-side figures, Figs. 1a–8a show optical micrographs of the PFAs. It is evident that the three starch types, as well as lycopodium and poppy seed, are well-rounded, while the milled products (coffee, flour and semolina) exhibit grains of highly irregular shape (the latter two being essentially irregularly shaped agglomerates of wheat starch). However, the aspect ratio never exceeds a value of 2, and thus all PFAs used in this work can be considered as more or less isometric.

Table 1. Density and characteristic size values (median or mode, arithmetic mean) of the PFAs; MIA – microscopic image analysis, LD – laser diffraction

	Density [g/cm^3]	Characteristic diameter [μm]	Type of characteristic diameter
Rice starch	1.5	4.8 ^{MIA} 4.4 ^{LD}	Median
Corn starch	1.5	12.9 ^{MIA} 14.2 ^{LD}	Median
Potato starch	1.5	46.3 ^{MIA} 49.0 ^{LD}	Median
Lycopodium	1.2	33.1 ^{MIA} 30.6 ^{LD}	Median
Poppy seed	1.1	265 $^{MIA\ (max.Feret)}$ 1038 $^{MIA\ (min.Feret)}$	Arithmetic mean
Coffee	1.3	405 ^{LD}	Modus
Fine flour	1.5	32.7 ^{LD}	Modus
Semolina	1.5	25.5 ^{LD} 561 ^{LD}	Modus

Due to the rather isometric shape, the particle size distributions of PFAs measured via laser diffraction and microscopy image analysis showed generally good agreement. Median diameters are approx. 4.6 μm for rice starch, approx. 13.6 μm for corn starch, approx. 47.7 μm for potato starch, and approx. 32 μm for lycopodium (very narrow distribution), cf. Table 1 and also [11,13]. In the case of wheat flour the particle size distribution is broader than for wheat starch itself, cf. [13], and exhibits a mode size shifted to higher values (32.7 μm versus 22.6 μm). In the case of semolina, which also consists of wheat starch granules, the distribution measured by laser diffraction is strongly bimodal (modes 25.5 μm and 561 μm). Similarly, for coffee the mode value is 405 μm. The large-size mode values of these PFAs are of course a direct consequence of the degree of commercial milling, in contrast to poppy seed, where both the shape (kidney-like) and the size (approx. 1000 μm) are the result of natural growth and drying processes.



a) b)

Figure 1. Optical micrograph of rice starch (left) and microstructure of porous alumina ceramics prepared via SCC with 10 vol% rice starch (polished section, right)

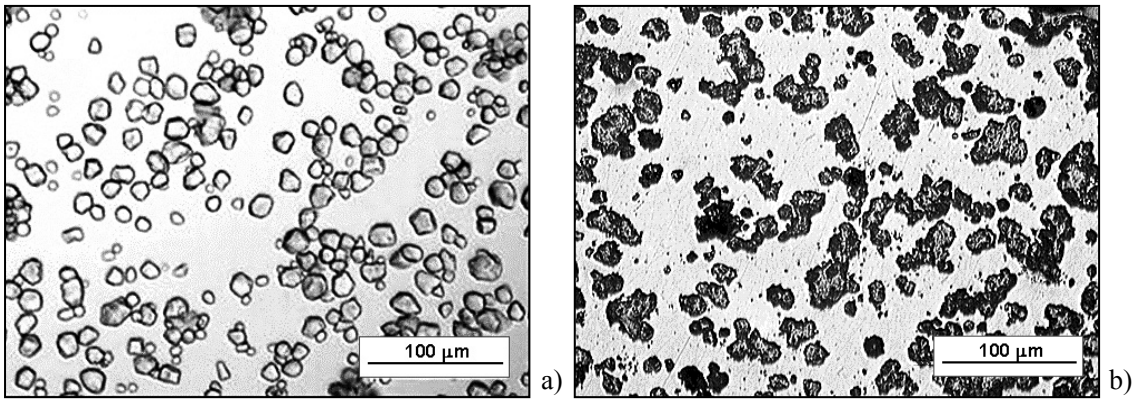


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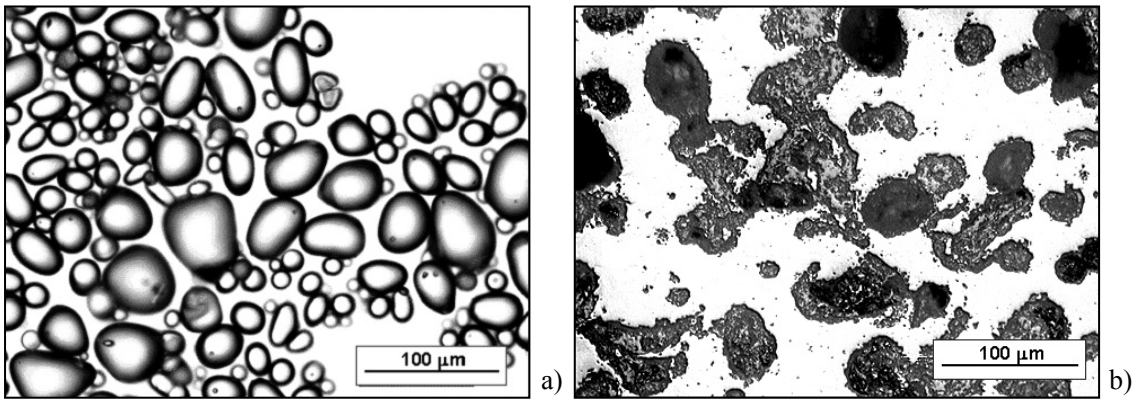
Figure 2. Optical micrograph of corn starch (left) and microstructure of porous alumina ceramics prepared via SCC with 10 vol% corn starch (polished section, right)



a) b)

Figure 3. Optical micrograph of potato starch (left) and microstructure of porous alumina ceramics prepared via SCC with 10 vol% potato starch (polished section, right)

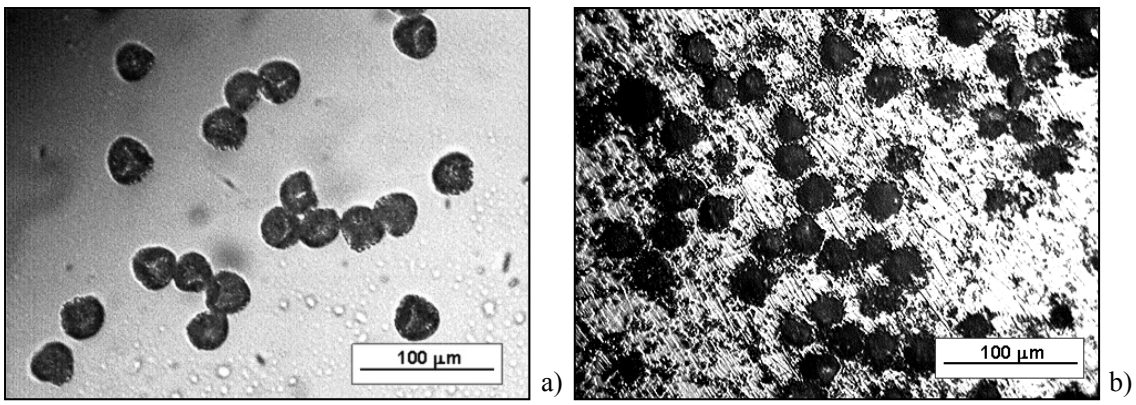


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Figure 4. Optical micrograph of lycopodium (left) and microstructure of porous alumina ceramics prepared with 10 vol% lycopodium (polished section, right)

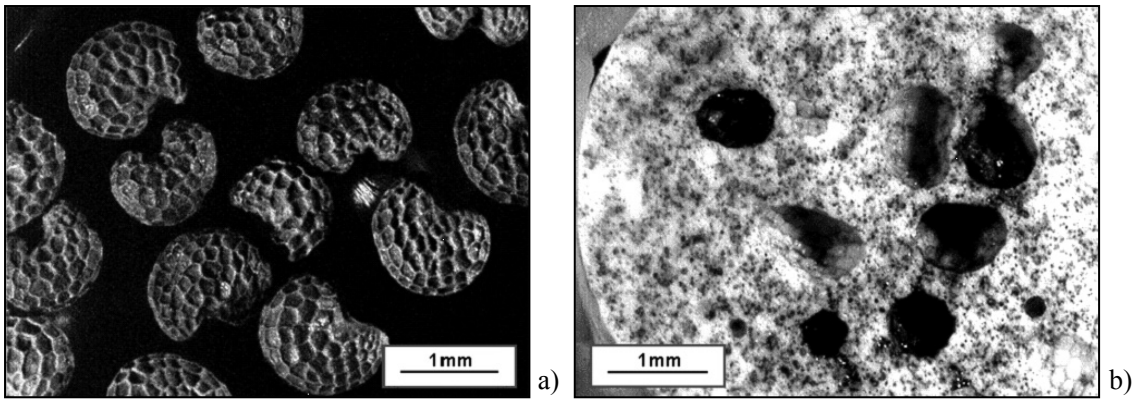

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Figure 5. Optical micrograph of poppy seed (left) and microstructure of porous alumina ceramics prepared with poppy seed (polished section, right)

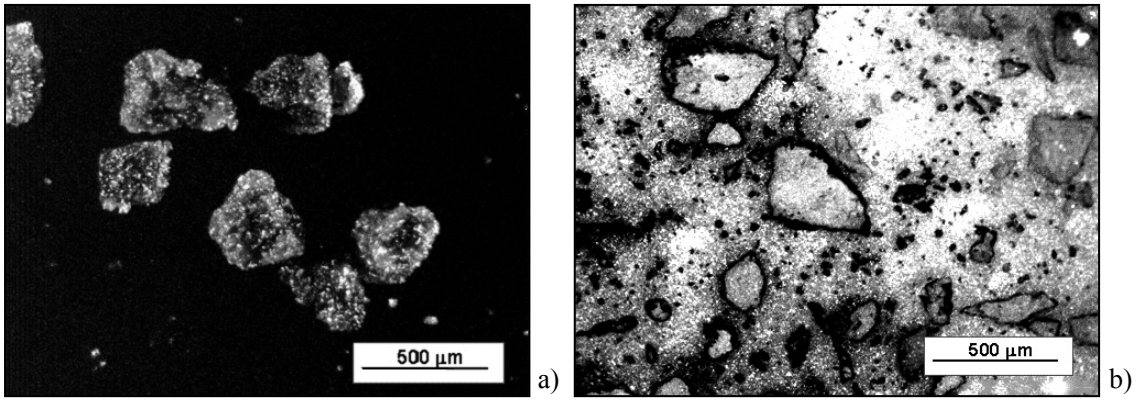

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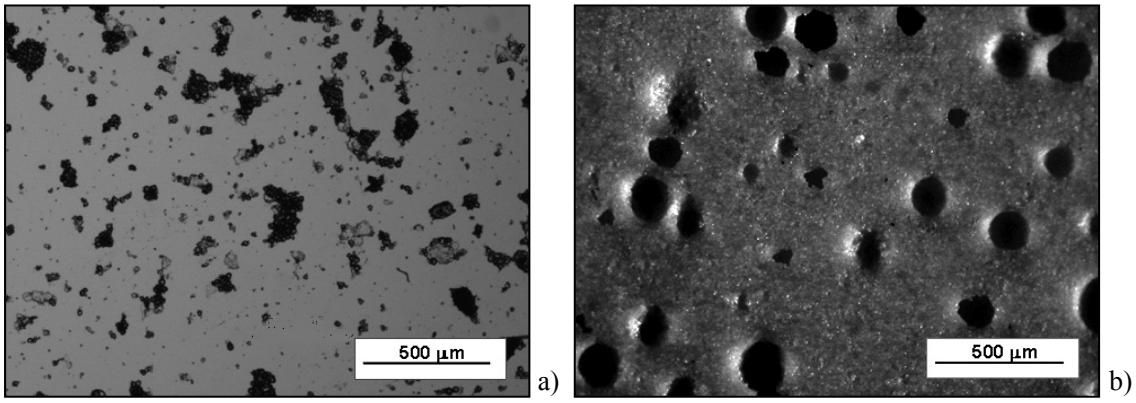
Figure 6. Optical micrograph of coffee (left) and microstructure of porous alumina ceramics prepared with coffee (polished section, right)



a) b)

Figure 7. Optical micrograph of fine flour (left) and microstructure of porous alumina ceramics prepared with fine flour (polished section, right)

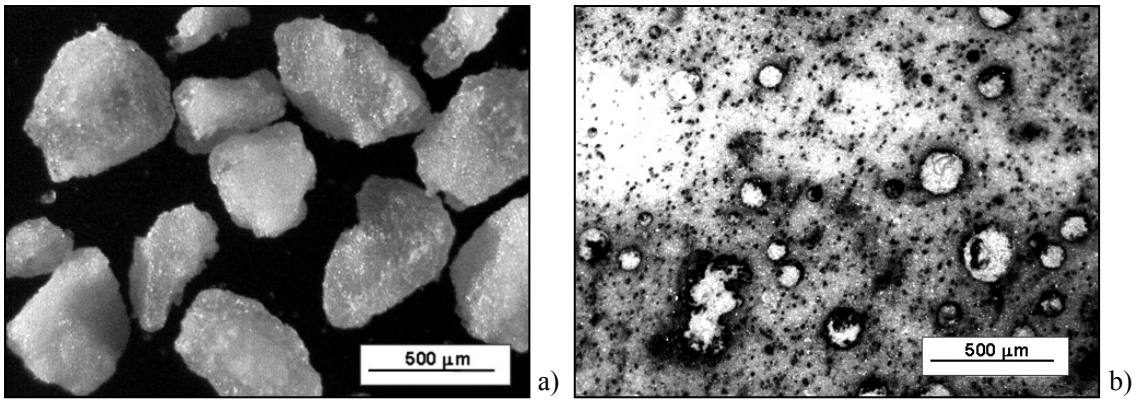


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Figure 8. Optical micrograph of semolina (left) and microstructure of porous alumina ceramics prepared with semolina (polished section, right)

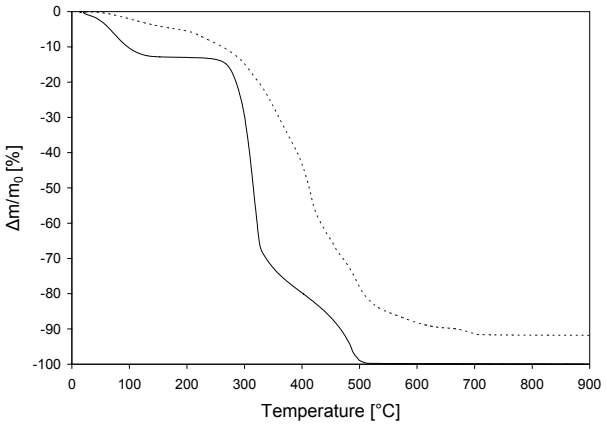

Figure 9. Thermogravimetric (TG) curves of starch (full line) and poppy seed (dotted line) measured with a heating rate of 10°C/min in air atmosphere

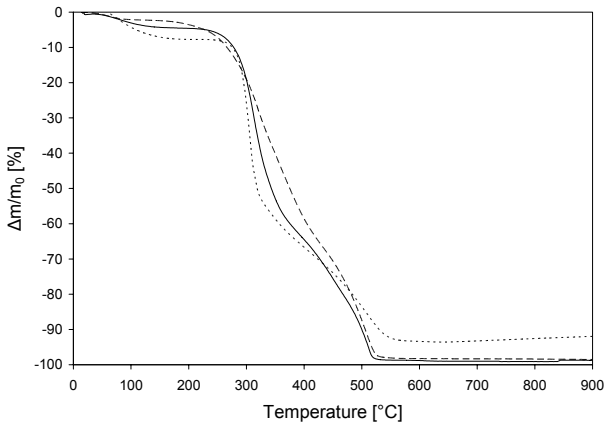

Figure 10. Thermogravimetric (TG) curves of lycopodium (dashed line), coffee (full line) and semolina (dotted line) measured with a heating rate of 10°C/min in air atmosphere

Figs. 9–12 show the thermogravimetric (TG) and differential thermal analysis (DTA) curves of the PFA powders. It is evident, that most PFAs burn out between 250 and 550°C, except for poppy seed, which requires a temperature of at least 600°C to be completely removed. For all PFAs the burnout stage corresponds to an exothermic overall reaction (but note that for starch the initial burnout phase is endothermic – this exceptional behavior has been confirmed for all starch types investigated here).

Table 2 lists the measured values of bulk density, open porosity and total porosity and pore size median values (determined from pore size distributions measured via microscopic image analysis and mercury intrusion porosimetry, respectively) for porous alumina ceramics prepared by traditional slip casting TSC (using starch as a pore-forming agent only) and by starch consolidation casting SCC (using starch as a pore-forming agent and body-forming agent). Optical micrographs of the corresponding microstructures are shown in the right-hand-side of Figs. 1b–3b. In the case of SCC the pore size depends on the degree of starch swelling and on the nominal starch content, therefore the pore size cannot be controlled in a completely arbitrary way just by choosing the appropriate starch type. The resulting median size values measured via microscopy image analysis (where the pore size distribution is generally underestimated due to the Wicksell problem → using the Saltykov transformation leads to an increase of median size values by approx. 4–15 %) for nominal starch contents of 10, 30 and 50 vol% (related to alumina) exhibit a clear trend to smaller size with increasing starch content (sterical hindrance during swelling), cf. Table 2. In the case of TSC (in Table 2 shown for corn starch) the resulting median pore size corresponds very well with the original size of starch granules, because swelling does not occur during the shaping step. That means, porosity and pore size can be more easily controlled in TSC, where starch is used only as a PFA (and not as a combined pore-forming and body-forming or consolidation agent as in SCC). For both SCC- and TCC-prepared porous alumina, comparison of pore siz-

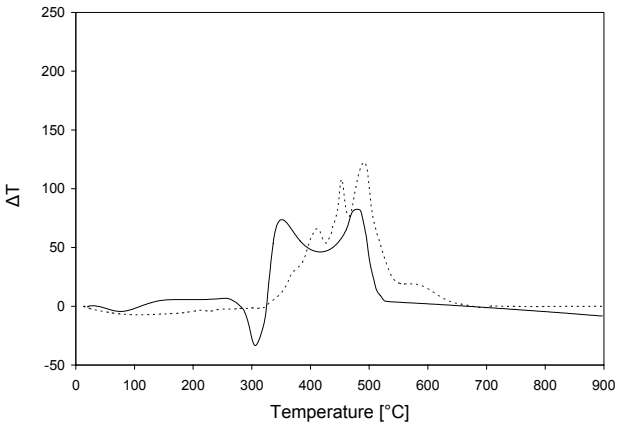

Figure 11. Differential thermal analysis (DTA) curves of starch (full line) and poppy seed (dotted line) measured with a heating rate of 10°C/min in air atmosphere

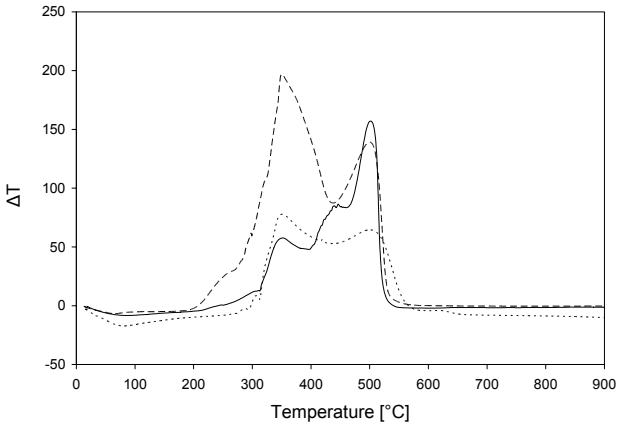

Figure 12. Differential thermal analysis (DTA) curves of lycopodium (dashed line), coffee (full line) and semolina (dotted line) measured with a heating rate of 10 °C/min in air atmosphere

Table 2. Microstructural characteristics of as-fired alumina ceramics prepared with several starch types as PFA: bulk density, open porosity, total porosity, characteristic pore size values – (medians determined from pore size distribution measured by mercury intrusion porosimetry and microscopy image analysis); ± denotes standard deviation

		Nominal starch content [vol%]	Bulk density [g/cm^3]	Open porosity [%]	Total porosity [%]	Median (MIA) [μm]	Median (Hg-porosimetry) [μm]
Rice starch	SCC	10	3.08 ± 0.01	14.5 ± 1.1	22.8 ± 0.2	7.3	0.66
		30	2.91 ± 0.02	24.0 ± 0.4	27.2 ± 0.6	6.1	0.65
		50	2.89 ± 0.04	26.7 ± 0.8	27.8 ± 0.9	5.9	0.65
Corn starch	TSC	10	3.52 ± 0.02	0	12.1 ± 0.5	13.2	-
		30	2.75 ± 0.01	25.7 ± 0.3	31.3 ± 0.1	12.8	1.6
		50	2.02 ± 0.02	48.7 ± 0.4	49.5 ± 0.5	12.1	2.7
	SCC	10	2.88 ± 0.04	25.4 ± 0.6	28.1 ± 0.9	21.0	4.0
		30	2.60 ± 0.01	32.6 ± 0.2	35.1 ± 0.1	13.9	1.9
		50	2.09 ± 0.07	47.1 ± 1.7	47.7 ± 1.7	11.5	2.5
Potato starch	SCC	10	3.00 ± 0.01	22.0 ± 0.3	25.8 ± 0.3	57.9	5.7
		30	2.50 ± 0.01	32.9 ± 1.3	37.0 ± 0.5	43.7	4.3
		50	1.90 ± 0.01	52.4 ± 0.1	53.9 ± 0.1	43.6	7.4

es (distributions and their median values) measured by image analysis with those measured by mercury porosimetry (cf. Table 2) shows that the latter are lower by approx. one order of magnitude, which is due to the fact that mercury porosimetry measures the interconnecting channels between pores (pore throats), while microscopic image analysis focuses on the pore bodies (cavities) resulting from the burnout of PFAs.

The total porosity achieved with nominal starch contents of 10, 30 and 50 vol% are in the range 23–54 % for SCC (with rice starch exhibiting worst controllability, resulting in a range of only 23–28 %) and 12–50 % for TSC (well controllable, example here: waxy corn starch). Only TSC enables the fabrication of a microstructure with completely closed porosity, i.e. below the percolation threshold, which has recently been shown to be at approx. 18 % total porosity [14].

Figs. 4b–8b show optical micrographs of the microstructures of polished sections of porous alumina ceramics prepared with the new PFAs lycopodium, poppy seed, coffee, flour and semolina and Table 3 lists the measured values of bulk density, open porosity, total porosity and pore size median values (determined from pore size distributions measured via microscopic image analysis and mercury intrusion porosimetry, respectively) for alumina prepared with lycopodium, poppy seed and coffee.

As expected, when lycopodium is used as a PFA in TSC the total porosity can be relatively well controlled. A recent study showed that the percolation threshold (transition from closed to open porosity) is somewhere between 10 and 15 % [11]. Preparing porous alumina by SCC with poppy seed, it is clear that due to starch swelling the total porosity is increased over and above the nominal (i.e. weighed-in) total PFA content of 32.3 % related to alumina (with 47.6 vol% of poppy seed related to the overall PFA content). The resulting total porosity is 38.7 %, with 29.6 % being open porosity (in satisfactory agreement with the earlier result of 37.6 % total and 32.4 % open porosity, cf. [10]). A similar situation occurs for porous alumina made by the SCC technique with coffee as a PFA and starch as a combined pore-forming-and-body-consolidating agent (total porosity 46.6 % versus nominal PFA content 36.7 %). However, surprisingly, an even larger difference exists when the TSC technique is used with coffee alone as a PFA (19.7 % nominal PFA

Table 3. Microstructural characteristic of as-fired alumina ceramics prepared with several PFAs (lycopodium, coffee, poppy seed): bulk density, open porosity and total porosity

		PFA content [vol%]	Bulk density [g/cm^3]	Open porosity [%]	Total porosity [%]
Lycopodium	TSC	10	3.56 ± 0.01	0	10.9 ± 0.2
		20	3.21 ± 0.02	6.9 ± 0.4	19.7 ± 0.4
		40	2.17 ± 0.05	43.7 ± 1.1	45.6 ± 1.2
Poppy seed	SCC	32.3*	2.45 ± 0.05	29.6 ± 1.6	38.7 ± 1.3
Coffee	TSC	19.7	2.69 ± 0.03	25.7 ± 1.5	32.7 ± 0.9
	SCC	36.7**	2.14 ± 0.01	44.6 ± 0.7	46.6 ± 0.4

*(poppy / PFA = 47.6 vol%)

**(coffee / PFA = 42.5 vol%)

content and 32.7 % total porosity resulting in the ceramics after firing). This difference is still unexplored and clearly needs further experimental confirmation before a final explanation can be attempted. It is not unlikely, however, that it is connected with a relatively high degree of open porosity of the coffee particles, which makes their effective volume larger than the volume corresponding to their measured density (which has been measured with all open pores filled with liquid).

Concerning porous alumina prepared with fine flour and semolina as PFAs, respectively, quantitative microstructural investigation is still ongoing and definite results are not yet available. It seems, however, that with these PFAs the final microstructure is very strongly dependent on the processing conditions. For example, porosities in the range 22–48 % and 32–48 % have been achieved using 20 vol% of flour and semolina, respectively, the higher porosities resulting from longer homogenization steps. Moreover, from Figs. 7b and 8b it can be seen, that the pores have a totally different character (size and shape) than the PFAs. They are approximately spherical and often of a size of more than 100 μm (but never more than 500 μm, which would correspond to the size of the original semolina grains). Apart from that they are relatively similar for fine flour and semolina, which is at first sight remarkable with regard to the different initial size of these two PFAs. To explain these results, it has to be taken into account that the homogenization procedure applied during the preparation of the suspensions served at the time as a milling step for the semolina (and possibly the flour) and resulted in the disintegration of large agglomerates (mainly semolina grains), so that the state of the suspension before casting might have been very similar in the two cases. Further, due to the impact of the milling media (alumina balls), the small residual starch agglomerates might be in a mechanically and / or thermally activated state, which makes them prone to release entrapped gases after casting. Microscopic investigation of green bodies after drying confirmed that this microstructure develops before firing. Thus, the possibility that it results from the pyrolysis of PFA agglomerates, can definitely be excluded.

IV. Conclusions

The various biopolymeric pore-forming agents (PFAs) used for this work are in size range from 5 μm (rice starch) to approx. 1 mm (poppy seed). The density of the investigated PFAs is in the range 1.1–1.5 g/cm^3, which is appropriate for use in ceramic suspensions. The shape of all PFAs is more or less isometric (aspect ratio < 2 in all cases), with starch, lycopodium and poppy seed being more rounded and coffee, flour and semolina more irregular. Thermal analysis showed, that all biopolymeric PFAs investigated here exhibit burnout between 250 and 550°C, except for poppy seed, which shows thermal effects up to at least 600°C. For the sample sizes fabricated here (less than 7 mm diameter), defect-free burnout was possible with a conventional heating schedule (heating rate 2°C / min without hold up to the maximum firing temperature 1570°C). In the case of larger bodies, it might be necessary to chose a slower heating rate in the pyrolysis range from 250–600°C. Using traditional slip casting (TSC) with starch and lycopodium, precise porosity and pore size control is possible. This is not the case for coffee, probably because of its internal porosity which leads to larger effective volume. The use of poppy seed alone in connection with TSC was not successful, because starch is needed to create pathways for gas release during pyrolysis in order to avoid stresses and cracking. All starch-containing systems, including flour and semolina, can be used as combined pore-forming and body-forming agents in the SCC process (starch consolidation casting). With this process the pore size is intimately connected to the porosity (due to starch swelling) and thus control is less trivial than in the TSC process. Moreover, porosities lower than approx. 20 % are difficult to achieve with SCC. However, using the SCC process, greater microstructural uniformity can be achieved, and the typical characteristics between the performance of different starch types can be exploited (e.g. for nominal starch contents from 10–50 vol% rice starch leads to porosities in the narrow range 23–28 %, which makes the process less flexible but robust).

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