

# Porous Ceramics Made Using Potato Starch as a Pore-forming Agent

Eva Gregorová\* • Zuzana Živcová • Willi Pabst

Department of Glass and Ceramics, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

Corresponding author: \* eva.gregorova@vscht.cz

## ABSTRACT

Starch, in particular potato (*Solanum tuberosum*) starch, is a common auxiliary material in ceramic technology. Beside its traditional function as a pore-forming agent, which is pyrolyzed and burned out during the heat-up stage of the ceramic firing process, it has become an important body-forming agent for ceramics during the last decade. In particular, the so-called starch consolidation casting process is based on the ability of starch to swell in aqueous media at a moderately elevated temperature (below 100°C) and thus on the ability of starch granules to absorb free water from a particulate suspension, which leads to the transformation of the more or less viscous ceramic suspension to a viscoelastic (and finally elastic) solid after heating. In this contribution we give a brief review of the uses of potato starch in ceramic technology, especially as a pore- and body-forming agent in traditional slip casting and starch consolidation casting. The discussion includes the most important aspects of using potato starch in ceramic technology, ranging from size and shape characterization, suspension rheology, swelling kinetics and burnout behavior to the characterization of the resulting ceramic microstructures and the properties of the final ceramic materials.

**Keywords:** functional gradient ceramics, pore size, porosity, slip casting, starch consolidation, swelling

**Abbreviations:** DTA, differential thermal analysis; PFA, pore-forming agent; SCC, starch consolidation casting; TG, thermogravimetry; TSC, traditional slip casting

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## INTRODUCTION

Porous ceramics have many fields of application, ranging from catalyst supports to filters for molten metals, aerosol filters and gas adsorbers, filters for hot corrosive gases and particulate-containing diesel engine exhaust gases, refractory furnace linings, kiln furniture and high-temperature thermal insulation, separators in electrochemical reactors, electrodes battery supports and solid oxide fuel cells, ceramics with electrically conductive coatings, magnetic filters, bioreactors and chemical engineering microreactors, space mirror supports, heat exchangers, thermal protection components for space vehicle re-entry, high-temperature acoustic insulation, light-weight sandwich structures and impact absorbing structures, radiant gas burners and volumetric solar receivers, microporous membranes for water purification and waste water treatment, macroporous filters for microbial filtration and macroporous implant materials and bone fillers, drug delivery systems and bone tissue engineering scaffolds (enabling bone ingrowth) (see e.g. Liu

1996; Liu and Dixit 1997; Rice 1998; Kitamura *et al.* 2004; Scheffler and Colombo 2005; Yang *et al.* 2005, 2007; García-Gabaldón *et al.* 2006; Sopyan *et al.* 2007; Colombo 2006, 2008).

Of course, porous ceramics also play a role as preforms for ceramic-metal and ceramic-polymer composites. Due to their relatively low bulk density (light weight), thermal stability, high-temperature structural stability, chemical inertness and corrosion resistance (even in hot corrosive gases and liquids) ceramics may outperform their metal and polymer competitors in many applications (Scheffler and Colombo 2005). The electric (and magnetic) properties, including conductivity (or resistivity), permittivity (dielectric constant) and piezoelectric coefficients, can be tailored by controlling the microstructure of the ceramic, in particular porosity (i.e. the volume fraction of pores) and other pore space characteristics (pore size, size distribution, shape, and connectivity). The thermal conductivity (or resistivity) and permeability for fluids can be tailored in a similar way (Rice 1998). On the other hand, from the viewpoint of

mechanical properties, ceramics, like glasses, are typically brittle materials with high rigidity, and this has to be taken into account in engineering design. A definite disadvantage of ceramics in general (in contrast to most metals and polymers) is their low fracture toughness, but pores do not cause any additional problems from this point of view; in many cases they may even improve the fracture toughness (Rice 1998). Rather complicated is the situation with thermomechanical properties such as the thermal shock resistance. There are several competing factors which may lead either to an increase or a decrease of the thermal shock resistance with increasing porosity (Arnold *et al.* 1996).

Depending on the intended application, the requirements on the ceramic microstructures are different. For example, fluid transport (with fluids ranging from gases to suspensions) requires open pores and permeability and separation efficiency depend on the degree of pore opening, connectivity, size, cross-section shape and uniformity. Thermal insulation requires closed pores, and the thermal conductivity of porous ceramics may be lower than that of air, when the pore size is small enough (nanosized, i.e. below the mean free path of the gas molecules enclosed). On the other hand, porous bioceramics for bone ingrowth require open pores with a high degree of connectivity and minimum pore size of order 100-200  $\mu\text{m}$ , and catalyst supports are often in the form of gradient material systems with a layered structure of variable porosity and/or pore size and a functional high-surface area top layer. Rather special applications exist for porous ceramics with tailored electric properties. For example, porous piezoelectric ceramics are of interest for hydrophones and medical imaging because of their enhanced coupling with water or biological tissue due to acoustic impedance matching (Palmquist *et al.* 2007). Their use of porous silica as a core material in sandwich-like electromagnetic windows is envisaged (Mao *et al.* 2006). Porous barium titanate ( $\text{BaTiO}_3$ ) ceramics exhibit higher electrical resistivity and a larger jump in the (positive) temperature coefficient of resistance than their densely sintered counterparts (Kim *et al.* 2006; Park *et al.* 2008). Similarly, porous pyroelectric materials with functional gradients have been produced (Shaw *et al.* 2007).

For a general review concerning the preparation methods of macroporous ceramics the reader is referred to (Colombo 2006; Studart *et al.* 2006). One of the most widely applied methods for the preparation of porous ceramics uses carbon (e.g. graphite or carbon black), organic polymers (e.g. polyethylene beads and poly-methyl-metacrylate) or natural biopolymers (ranging from starch-based products and lycopodium spores to wood flour, poppy seed and peas) as pore-forming agents which after burnout at temperatures of a few hundred  $^\circ\text{C}$  leave residual voids that determine the final microstructure of the fired ceramics (Lange *et al.* 1990; Slamovich and Lange 1992; Woyansky *et al.* 1992; Lopes and Segadaes 1996; Liu 1997; Rice 1998; Corbin and Apte 1999; Corbin *et al.* 2001; Maca *et al.* 2001; Boaro *et al.* 2003; Rice 2003; Mattern *et al.* 2004; Chen *et al.* 2005; Piazza *et al.* 2005; Praveen Lumar *et al.* 2005; Prabhakaran *et al.* 2007; Gregorová and Pabst 2007a; Gregorová *et al.* 2008a; Živcová *et al.* 2007, 2008). Among all pore-forming agents, starch has become the most widely used pore-forming agent in ceramic technology today (Corbin and Apte 1999; Davis *et al.* 2000; Galassi *et al.* 2002; Kim *et al.* 2002a, 2002b; Diaz and Hampshire 2004; Kitamura *et al.* 2004; Mattern *et al.* 2004; Barea *et al.* 2005; Reynaud *et al.* 2005; Gregorová *et al.* 2006d; Gregorová *et al.* 2007, 2008a; Kovalevsky *et al.* 2007; Nakahira *et al.* 2007; Zhang *et al.* 2008; Živcová *et al.* 2008). This is partly due to its universal availability and relatively low price, but also due to its unproblematic processing behavior in connection with ceramic systems, non-toxicity and environmentally friendly character. Apart from being a convenient pore-forming agent, for example in cold pressing or traditional slip casting (TSC) of ceramics (Reed 1995), the swelling and gelatinization effect of starch in hot water can be exploited to assist in ceramic shaping processes, in parti-

cular a process called starch consolidation or starch consolidation casting (SCC), in which starch swelling and gelatinization transforms a viscous ceramic suspension into an elastic (rigid) body, cf. (Lyckfeldt and Ferreira 1998; Alves *et al.* 1998; Lyckfeldt 1999; Lemos and Ferreira 2000; Bowden and Rippey 2002; Týnová *et al.* 2002; Týnová *et al.* 2003; Bhattacharjee *et al.* 2007; Gregorová and Pabst 2007b; Gregorová *et al.* 2007; Chen *et al.* 2008; Mao *et al.* 2008).

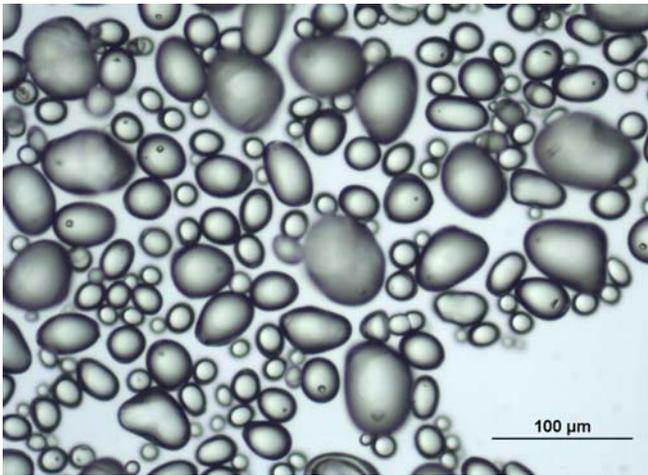
Despite the enormous significance of starch in ceramic technology today, only one review article on this field is available in the literature (Sikora and Izak 2006), and even this work does not contain a large amount of many recent developments. It contains an excellent overview on the international patent literature, where starch (including modified starches and starch derivatives) is used as one component of binder formulations in ceramic technology, but the important aspect of porosity and pore space control, where starch is an integral additive determining microstructural details of the final ceramics, is mentioned only peripherally. Therefore, in the present contribution, we try to fill this gap and give a brief review on what has been achieved in the development of porous ceramics shaping technology and microstructural control of ceramics using potato starch as a pore-forming agent, with special emphasis on its use in TSC and SCC.

## SIZE AND SHAPE CHARACTERIZATION OF POTATO STARCH

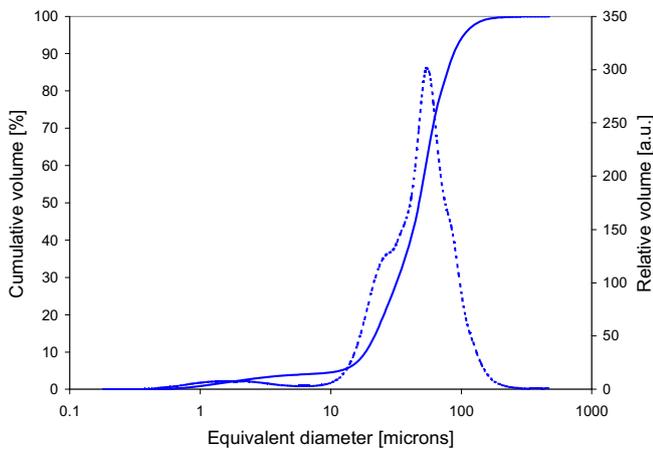
Potato starch is one of the largest starch types. **Fig. 1** shows a micrograph and **Fig. 2** shows a typical particle size distribution of potato starch, as measured via laser diffraction. The distribution looks essentially monomodal (with a mode of approx. 55  $\mu\text{m}$  in the frequency curve), but exhibits a distinct shoulder at approx. 20  $\mu\text{m}$ , which can shift the overall median (in the cumulative curve) to significantly lower values ( $< 50 \mu\text{m}$ ), cf. (Gregorová *et al.* 2006a). It has to be remembered that laser diffraction results are volume-weighted size distributions. In a number-weighted size distribution (measurable by image analysis), the 20- $\mu\text{m}$ -granules would appear as a second peak, so that the bimodality of the size distribution, which is evident from **Fig. 1**, would become more obvious. The small size fractions typically measured via laser diffraction in the range 1-2  $\mu\text{m}$  correspond to wear debris and impurities, which are unavoidable in commercial mass production processes.

Laser diffraction is one of the most common methods for particle size characterization today. However, because of the aforementioned fact that distribution curves measured by laser diffraction are volume-weighted, they cannot be directly compared with the results of microscopic image analysis, which are number-weighted. In order to do so it is necessary to transform the image analysis results to volume-weighted curves. These transformation procedures have been described in several papers, e.g. (Gregorová *et al.* 2006a, 2006c) and require knowledge of the size dependence of shape (characterized by an aspect ratio). The shape of potato starch granules is irregular but well-rounded. In contrast to wheat starch for example, oblate shapes are absent. It is therefore reasonable to approximate the shape of potato starch granules by a prolate spheroid (i.e. an elongated rotational ellipsoid). The appropriate quantitative measure to describe the shape of spheroids is the so-called aspect ratio, i.e. the ratio of the long to the short (semi-) axis. **Fig. 3** shows the frequency curve of the aspect ratio and **Fig. 4** shows the dependence of the arithmetic mean aspect ratio (and standard deviation) on size (here the projected area diameter). It is evident that the average aspect ratio, although exhibiting a large degree of scatter and a slight overall increase with size, is in the range 1.2–1.5. Most other starch types, e.g. rice, corn, or tapioca starch, are closer to 1, i.e. more isometric, cf. (Gregorová *et al.* 2006a).

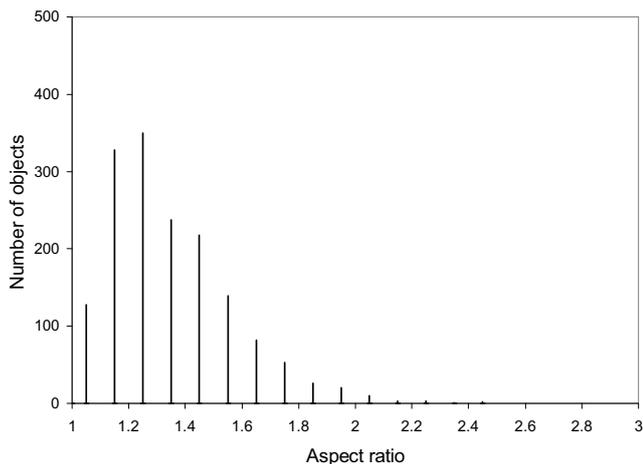
As soon as the size dependence of the aspect ratio is



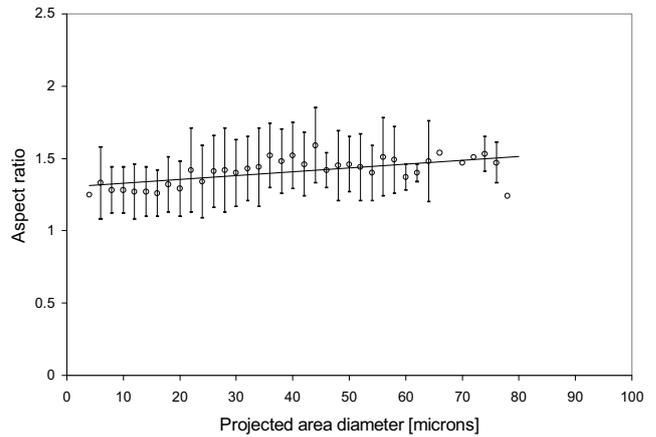
**Fig. 1** Optical micrograph of native potato starch.



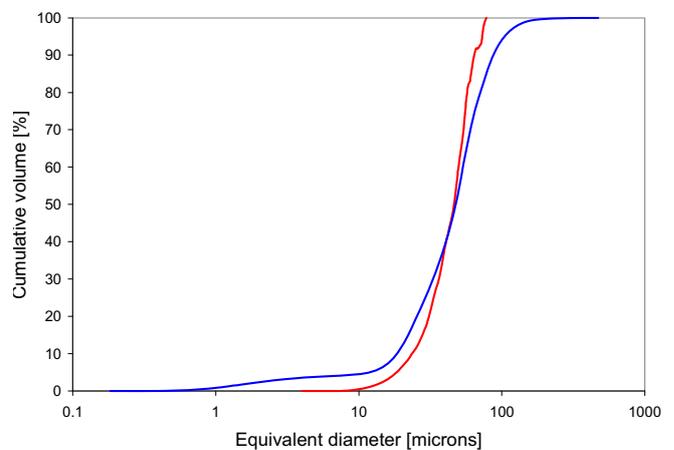
**Fig. 2** Size distribution of native potato starch granules, measured by laser diffraction (Fraunhofer approximation, full curve – cumulative, dotted curve – frequency). Reprinted from Gregorová E, Pabst W, Boháčenko I (2006a) Characterization of different starch types for their application in ceramic technology. *Journal of the European Ceramic Society* 26, 1301-1309, with kind permission of Elsevier, ©2006.



**Fig. 3** Frequency histogram of the aspect ratio of native potato starch granules, measured by image analysis (ratio of maximum to minimum Feret diameter). Reprinted from Gregorová E, Pabst W, Boháčenko I (2006a) Characterization of different starch types for their application in ceramic technology. *Journal of the European Ceramic Society* 26, 1301-1309, with kind permission of Elsevier, ©2006.



**Fig. 4** Size dependence of the aspect ratio of native potato starch granules. Reprinted from Gregorová E, Pabst W, Boháčenko I (2006a) Characterization of different starch types for their application in ceramic technology. *Journal of the European Ceramic Society* 26, 1301-1309, with kind permission of Elsevier, ©2006.



**Fig. 5** Comparison of the laser diffraction size distribution (blue curve) with the size distribution measured by image analysis (projected area diameters) and transformed to a volume-weighted curve. Reprinted from Gregorová E, Pabst W, Boháčenko I (2006a) Characterization of different starch types for their application in ceramic technology. *Journal of the European Ceramic Society* 26, 1301-1309, with kind permission of Elsevier, ©2006.

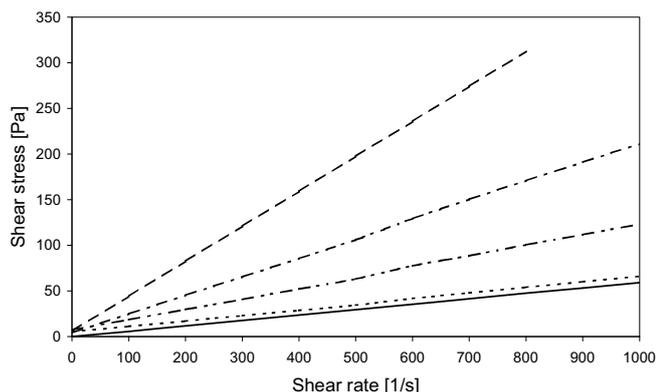
on manual evaluation of optical micrographs does not register the smallest size fraction (which is close to the resolution limit of optical microscopy), whereas laser diffraction may slightly overestimate the large-size fraction.

Although it seems that a systematic compilation of the size distributions of potato starches from different producers and suppliers is not available in the literature so far, the aforementioned findings are in good agreement with those of other authors (Bonekamp *et al.* 1989; Mattern *et al.* 2004; Wischmann *et al.* 2007), and we have obtained very similar results for potato starches from several producers, production dates and batches, so that they may be considered as quite representative for commercially available native potato starches. Nevertheless, it has to be kept in mind that starch granules are polymeric entities of biological origin, and thus the commercial end product may vary in dependence on the plant genotype, climate and weather conditions, as well as other environmental factors affecting plant growth (Kodet and Babor 1991; Zobel and Stephen 1995; Singh *et al.* 2008).

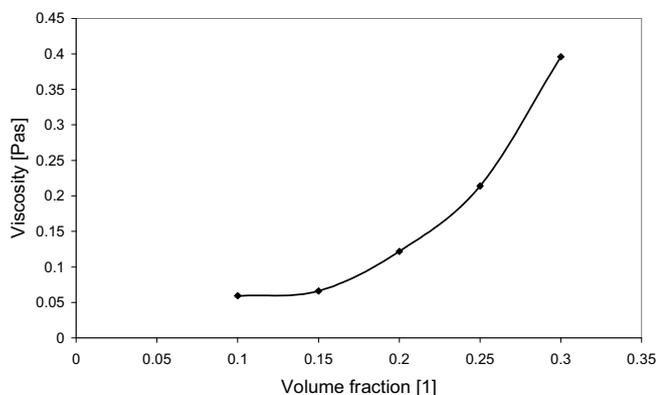
known, it is a simple task to transform the number-weighted size distributions to volume-weighted ones, cf. (Gregorová *et al.* 2006a, 2006c). **Fig. 5** compares the corresponding cumulative curves. It is evident that image analysis based

## RHEOLOGY OF STARCH-CONTAINING SUSPENSIONS, SWELLING AND GELATINIZATION

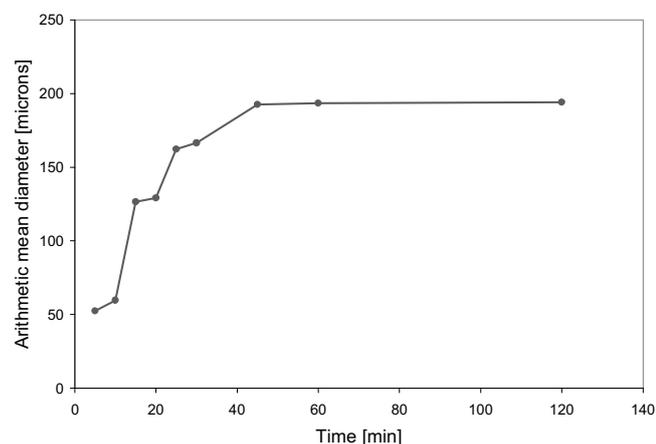
The rheology of starch-containing ceramic suspensions (mainly alumina and zirconia suspensions) has been investigated by several authors (Lyckfeldt and Ferreira 1998; Gregorová *et al.* 2006b, 2008b; Bhattacharjee *et al.* 2007; Li *et al.* 2007; Huang *et al.* 2008). As long as starch is used as a pore-forming agent in traditional slip casting, i.e. in water at room temperature, the suspensions remain purely viscous up to relatively high volume fractions. Such systems can be characterized via rotational viscometry. For low solids contents (ceramic powder and starch) the character of starch-containing ceramic suspensions is usually shear-thin-



**Fig. 6** Flow curves of native potato starch in 60% saccharose solution at room temperature (from bottom to top 10, 15, 20, 25, 30 vol.%, respectively).



**Fig. 7** Effective viscosity of starch suspensions (native potato starch in 60% saccharose solution at room temperature).



**Fig. 8** Swelling kinetics of native potato starch granules in excess water at 80°C (measured by laser diffraction).

ning (Lyckfeldt and Ferreira 1998; Gregorová *et al.* 2008b), whereas at higher solids contents shear-thickening behavior has been found as well (Gregorová *et al.* 2006b, 2008b). Of course, no general rules are applicable here and no absolute values for the transition from shear-thinning to shear-thickening behavior can be given, because the rheology of these mixed suspensions are critically dependent on the type of ceramic powder (chemical and phase composition, particle size and shape, surface state etc.), the effectivity of defloculation, and the starch type. In any case, ceramic suspensions with sufficient fluidity for slip casting (i.e. apparent viscosities of a few hundred mPas) can be obtained with starch contents up to 66 vol.% (related to the total solids content in the suspensions which is < 52 vol.%) in the classical paper on starch consolidation (Lyckfeldt and Ferreira 1998), and up to 50 vol.% of starch are routinely used in highly concentrated alumina suspensions in our laboratory (total solids content > 54 vol.%), cf. (Gregorová *et al.* 2006d; Gregorová and Pabst 2007b). **Fig. 6** shows typical flow curves and **Fig. 7** shows the increase of the relative viscosity of suspension of starch in a 60 wt.% saccharose solution. All these suspensions exhibit essentially Newtonian flow behavior (with negligible hysteresis), see **Fig. 6**. Therefore, it is the rheological behavior of the ceramic suspension itself, rather the starch addition, that is responsible for the frequently observed non-Newtonian behavior of starch-containing ceramic suspensions. Starch granules, being insoluble in water at room temperature (Biliaderis 1998), behave like other rigid particles, increasing the effective suspension viscosity (in dependence of the starch volume fraction) in a strongly nonlinear manner, see **Fig. 7**.

In starch consolidation casting, where starch is used as a combined pore-forming and body-forming agent, the volumetric and rheological changes occurring at elevated temperature are crucial for the consolidation of the ceramic suspension into a rigid body. After casting the suspension into the mold, the system is heated to approx. 80°C, and after some time a rigid body is formed, which can be taken out of the mold (demolded) and subsequently dried and fired to give a ceramic “green” body (unfired ceramic bodies are called “green bodies”). In aqueous systems starch absorbs water when the temperature is increased. This water uptake results in swelling. **Fig. 8** shows the swelling kinetics of potato starch in water. The data points are arithmetic mean diameters from size distributions measured via laser diffraction. It is evident that the arithmetic mean diameter increases by a factor of approx. four (400%), which is considerably more than for cereal starches, where the swelling factor is approx. two (200%), cf. (Gregorová and Pabst 2007b). Note that a linear swelling factor of 4 implies a relative volumetric swelling of 64, which is enormous (beyond this value the laser diffraction signal cannot be evaluated anymore, indicating that the starch granules have lost their identity and are more or less dissolved in the surrounding water). The relative volumetric swelling  $\varepsilon$  (with  $V$  being the volume after swelling and  $V_0$  the volume before swelling) is related to the actual size (equivalent diameter) of the swollen starch granule  $D$  via the relation

$$\varepsilon = \frac{V - V_0}{V_0} = \left( \frac{D}{D_0} \right)^3 - 1, \quad (1)$$

where  $D_0$  is the diameter of the dry starch granule (before swelling), cf. (Pabst *et al.* 2002). Several empirical relations can be used for fitting the measured sigmoidal swelling kinetics, e.g. the three-parameter logistic model,

$$\varepsilon = \frac{a}{1 + b \exp(-ct)}, \quad (2)$$

where  $t$  is the time (includes heating and swelling time) and  $a$ ,  $b$ ,  $c$  are adjustable fit parameters. In a ceramic suspension, where ceramic powder particles are present in addition to starch, the swelling starch granules push the ceramic parti-

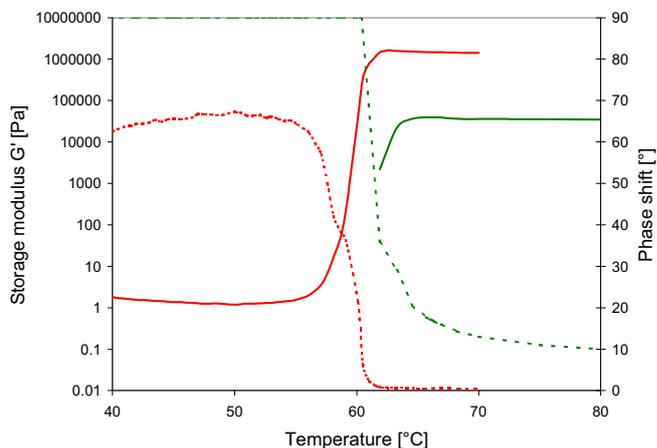
cles (which are typically much smaller than the starch granules, i.e. mostly of submicron size) aside and press them into a dense “random close packed” (rcp) or “maximally random jammed” (mrj) structure. For monodisperse spheres the packing density of such a rcp or mrj system is 64% (Torquato 2002), and in practice this value is often a reasonable approximation even for nonspherical particles, as long as the size distribution is not too broad. However, it is clear that the degree of swelling cannot attain its maximum value, because the excess water present in the suspension will be exhausted before this value is attained. Note that a certain amount of water will remain in the interstitial voids between the ceramic particles (36% of the pressed powder-water mixture volume) and is not available for starch swelling. According to this simple “excluded-volume” model the maximum relative volumetric swelling of the starch phase is given by the expression

$$\varepsilon^* = \frac{(\phi_0^{\max} - \phi_0) \cdot (1 - \phi_s)}{\phi_s \phi_0 \phi_0^{\max}}, \quad (3)$$

where  $\phi_0$  is the volume fraction of ceramic powder in water (without starch),  $\phi_0^{\max}$  is its maximum value (usually approx. 0.64) and  $\phi_s$  the starch content in the suspension (more precisely, the volume fraction of starch related to the solids content without water). When the free swelling kinetics (in pure water) is measured, the time dependence of swelling can be fitted using the logistic model and used to predict the minimum time needed for the consolidation step in the partially constrained system, i.e. the suspension in the mold (by setting  $\varepsilon = \varepsilon^*$ , i.e. combining Eqs. (2) and (3)).

After absorption of a sufficient amount of water and after attaining a sufficiently high temperature (for a sufficiently long time) further swelling results in granule breakup and, finally, gelatinization. Swelling is to a certain extent reversible (as long as the granules remain intact), whereas gelatinization is irreversible, because it is accompanied by the diffusion of starch components (in particular, amylose) out of the granules, thus forming a colloidal or macromolecular solution of swollen starch granules in a solution of dissolved amylose, a so-called paste, cf. e.g. (Owusu-Apen-ten 2005). In practice, both swelling and final breakup are statistical processes, i.e. they cannot be predicted for individual granules but only be described in an average sense for a large ensemble of granules (Týnová *et al.* 2003). For the mechanisms of swelling and gelatinization the reader may refer to (Macrae 1993; Zobel and Stephen 1995; Biliaderis 1998). It has been shown in (Pabst *et al.* 2002) that starch swelling cannot be the only consolidation mechanism in starch consolidation casting, because the consolidation time predicted on the basis of the swelling kinetics alone is significantly too short for demolding in practice. Other important factors for the consolidation of starch-containing suspensions into rigid ceramic green bodies are therefore the rheological changes occurring during gelatinization and the subsequent transformation of the starch solution into a gel during cooling, i.e. the gelation step, cf. e.g. (Owusu-Apen-ten 2005).

Of course, rotational viscometry is not the appropriate tool for characterizing the rheological behavior of viscoelastic and gelling systems in a physically correct way. Oscillatory rheometry has to be applied. In practice, measurements are usually performed in small amplitude shear, so that the results can be evaluated under the assumption of linear viscoelastic behavior (Gregorová *et al.* 2004). **Fig. 9** shows the storage moduli and phase shifts of potato starch in water and in a 70 wt.% alumina suspension. It is evident that the starch-in-water suspension is purely viscous up to temperatures of approx. 60°C (phase shift 90°, storage modulus undefined), while the starch-containing alumina suspension is slightly viscoelastic (i.e. exhibits a measureable storage modulus and a phase shift < 90°) already at temperatures as low as 40°C. At approx. 60°C (for the alumina suspensions 57–58°C) the starch-in-water suspension becomes strongly viscoelastic, whereas the starch-con-



**Fig. 9** Storage modulus (full curves) and phase shift (dotted curves) of potato starch/water systems (green curves) and potato-starch containing alumina suspensions (red curves).

taining alumina suspension becomes is transformed into a purely elastic solid, as indicated by the phase shift of 0°. Similar results have been found for other starch types (Gregorová *et al.* 2006b, 2008b) and by other authors (Lyckfeldt and Ferreira 1998; Bhattacharjee *et al.* 2007).

## TRADITIONAL SLIP CASTING OF CERAMIC SUSPENSIONS WITH POTATO STARCH

Slip casting is one of the most widely used shaping techniques for ceramics (Reed 1995), and the use of pore-forming agents is one of the favourite methods to prepare porous ceramics from aqueous ceramic suspensions via slip casting (Rice 2003). The principle of slip casting consists in casting a well-deflocculated, highly concentrated, stable suspension into a porous mold (in traditional slip casting (TSC) usually a plaster mold). Excess water is then sucked through the mold wall via capillary forces and what remains is a (water-saturated) ceramic green body, ready for demolding (Reed 1995; Rice 2003). When pore-forming agents of organic or biopolymeric origin are mixed into the suspension before casting, the resulting ceramic green body will contain these pore-formers even after drying. However, during heating up to the firing temperature (which is usually significantly higher than 1000°C, e.g. between 1400 and 1600°C for zirconia and alumina ceramics), the biopolymer pore-formers are burned out at temperatures below 600°C. The space occupied by the pore-formers remains in the form of voids (closed or open pores) after firing the ceramic, whereas the ceramic matrix around these voids may be completely dense (fully sintered). Note that the ash content should be negligibly low in order not to affect the properties of the final ceramics.

In the course of the last few years, potato starch has become one of the most popular pore-forming agents in ceramics. Apart from potato starch other starch types are used as pore-forming agents in TSC and tape casting, e.g. rice, corn (maize), wheat and tapioca (cassava) starch (Davis *et al.* 2000; Kim *et al.* 2002a, 2002b; Díaz and Hampshire 2004; Navarro *et al.* 2004; Gregorová *et al.* 2006d, 2007, 2008a; Bhattacharjee *et al.* 2007; Mao *et al.* 2008; Živcová *et al.* 2009), and many other biopolymer-based pore-forming agents have been proposed and tested as well, including lycopodium spores (Živcová *et al.* 2007), poppy seed (Gregorová *et al.* 2007a), peas and other seed (Luyten *et al.* 2003; Thijs *et al.* 2004), as well as wheat flour and semolina (Gregorová *et al.* 2008a; Prabhakaran *et al.* 2007; Živcová *et al.* 2008). Of course, many of these pore-forming agents, especially starches, are appropriate also in connection with other ceramic shaping techniques, e.g. cold isostatic pressing or extrusion (Reed 1995; Rice 2003), where they may at the same time act as binders and/or plasticizers.

When preparing ceramic mixtures with starch, a key question concerns the density of starch, since for many purposes it is important to determine the volume fraction of starch in the mixture. Answering this question is complicated by the fact that starch is hygroscopic. Literature values vary from approx.  $1.4 \text{ g/cm}^3$  (for starch with high water content) to  $1.6 \text{ g/cm}^3$  (for completely dry native starch), cf. (Batson and Hogan 1949; Kodet and Babor 1991). The values most frequently mentioned by producers-suppliers and researchers-scientists are in the range  $1.45\text{--}1.55 \text{ g/cm}^3$ . Thus, in the absence of a more precise information, a value of  $1.5 \text{ g/cm}^3$  should be a reasonable estimate of the starch density (at ambient humidity).

### STARCH CONSOLIDATION CASTING OF CERAMIC SUSPENSIONS WITH POTATO STARCH

Starch consolidation or starch consolidation casting has been invented by Lyckfeldt and Ferreira in Stockholm (Sweden) and Aveiro (Portugal) and was first published in 1998 for alumina ceramics (Lyckfeldt and Ferreira 1998). In the meantime, SCC has been applied to several other types of ceramics, including cordierite (Alves *et al.* 1998), calcium carbonate (Lemos and Ferreira 2000), hydroxyapatite (Rodríguez-Lorenzo *et al.* 2002), bioactive glass-ceramics (Vitale-Brovarone *et al.* 2004, 2005), kaolin-based mullite ceramics (Barea *et al.* 2005), zirconia (Pabst *et al.* 2004; Tichá *et al.* 2005; Garrido *et al.* 2009), and it has, of course, been extensively used for alumina ceramics (Bowden and Rippey 2002; Týnová *et al.* 2002; Gregorová *et al.* 2006c, 2006d; Gregorová and Pabst 2007b). The key idea is very simple: using the swelling (and gelatinization) capability of starch in hot water for the transformation of a ceramic suspension (viscous) into a rigid ceramic green body (elastic). Thus, instead of dewatering via the plaster mold wall (acting as a semipermeable interface) in TSC, ceramic green body formation occurs in SCC in the whole volume more or less simultaneously (only determined by the heat transfer kinetics and temperature gradients). As a consequence, the microstructure of ceramics prepared via SCC can be expected to be essentially gradient-free and isotropic, in contrast to TSC, where microstructural gradients (and anisotropy, if anisometric particles, for example clay minerals, are present) are unavoidable.

A practical advantage of SCC over TSC is the fact that impermeable molds can be used and that the mold materials are more or less arbitrary. For example, polymer and metal molds may be used. In contrast to injection molding, which is restricted to small shapes with a few mm wall thickness because of the critical and time-consuming binder removal step (which is necessary because of the high content of organic waxes and paraffins), SCC is a water-based shaping technique, in which the green bodies can be dried after demolding in a classical drying step. This drying step as well as starch burnout in the temperature range approx.  $300\text{--}550^\circ\text{C}$  is relatively uncritical and defects (cracks, warping) have to be expected only for very high starch contents, very large bodies or very fast heating rates.

### BURNOUT BEHAVIOR OF POTATO STARCH

After drying (i.e. the elimination of capillary and adsorbed water, usually performed first for several hours under ambient condition, followed by drying in a convective drier up to a temperature of approx.  $105^\circ\text{C}$  until mass changes become negligible) the ceramic green body is ready for firing. The heating schedule (temperature ramp) up to the maximum firing temperature (for oxide ceramics typically in the range  $1400\text{--}1600^\circ\text{C}$ , e.g. for alumina and zirconia ceramics, for silicate ceramics often significantly lower) may be adapted to reduce the danger of introducing defects, e.g. microcracks as a result of too violent gas evolution. For example, Lyckfeldt, Ferreira and coworkers (Alves *et al.* 1998; Lyckfeldt and Ferreira 1998) proposed a slow temperature increase of  $1^\circ\text{C}/\text{min}$  up to  $500^\circ\text{C}$ , interrupted by 60

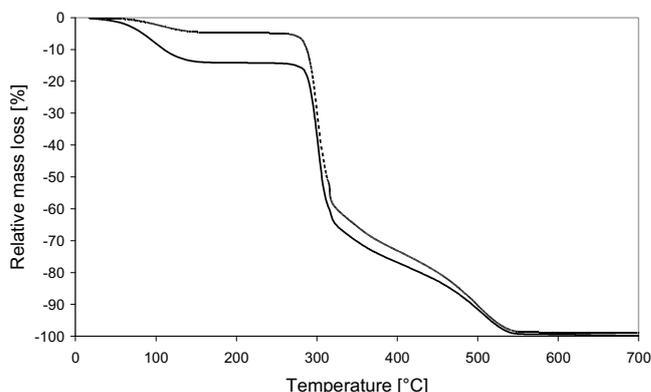


Fig. 10 Thermogravimetric (TG) curves of potato starch with two different humidity (water content 5 and 15%, respectively), heating rate  $5^\circ\text{C}/\text{min}$ .

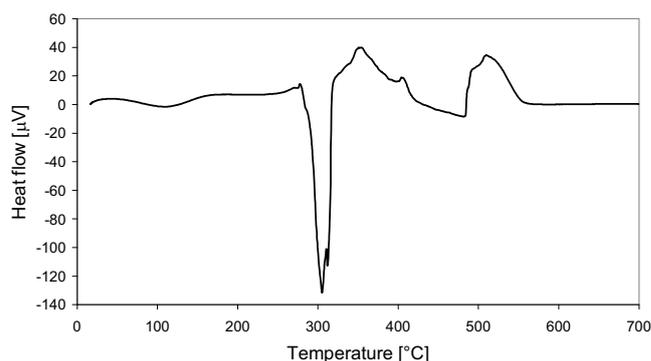
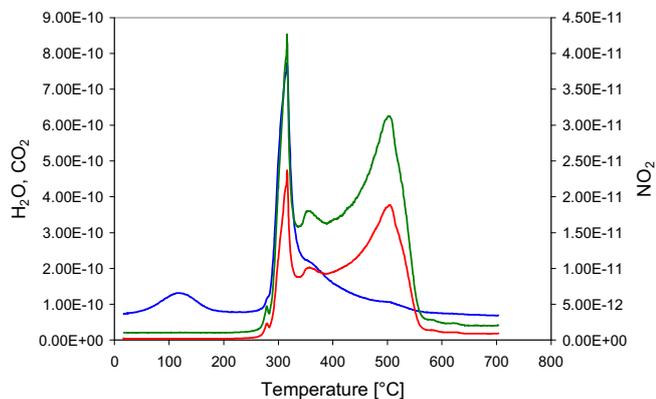


Fig. 11 Differential thermal analysis (DTA) curve of native potato starch (heating rate  $5^\circ\text{C}/\text{min}$ ).

min holdings at  $200$ ,  $300$  and  $500^\circ\text{C}$ , followed by a faster ramp ( $5^\circ\text{C}/\text{min}$ ) up to the final sintering temperature (with a hold time of 1-2 h) and subsequent cooling in the furnace down to room temperature. The rationale of this sophisticated firing schedule is to be sought in the burnout behavior of starch.

Fig. 10 shows typical thermogravimetric (TG) curves of potato starch (upper curve with a water content of approx. 5%, lower curve with 15%; note that starch is hygroscopic and different starch types may absorb different amounts of water). Fig. 11 shows a typical differential thermal analysis (DTA) curve. Both measurements have been performed in air, with constant heating rate of  $5^\circ\text{C}/\text{min}$ . It is clear that the mass loss in TG and the weak endothermic effect around  $100^\circ\text{C}$  in DTA result from the evaporative elimination of water (i.e. corresponds to drying). Thermal decomposition of the starch starts at approx.  $280^\circ\text{C}$  and is accompanied by a large mass loss (TG) and a significant endothermic effect, peaking at approx.  $300^\circ\text{C}$ . Similar endothermic effects at relatively low temperature have been found in nitrogen atmospheres (Aggarwal *et al.* 1997) and are therefore attributed to non-oxidative processes (charring). At slightly higher temperature in air (peak around  $350^\circ\text{C}$ ), this endothermic effect is overrun by an exothermic effect (absent in nitrogen atmospheres) due to gaseous or “flaming” combustion, where the gaseous degradation products ignite. Concomitantly, TG reveals a further mass decrease with increasing temperature. At even higher temperatures (in the range  $420\text{--}470^\circ\text{C}$ ) a second endotherm occurs. This is interpreted as being a consequence of a local environment over the sample formed by the gaseous products that prevent them from catching fire (Aggarwal *et al.* 1997). The second significant exothermic peak (at approx.  $500^\circ\text{C}$ ) corresponds to a “glowing” combustion, where mainly the carbonaceous residues burn to give simple products such as  $\text{CO}$  and  $\text{CO}_2$ . Fig. 12 shows mass spectrometric measurements of some of the evolving gases ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}_2$ ). Evidently, chemically bonded  $\text{H}_2\text{O}$  leaves the structure mainly at around  $300^\circ\text{C}$ ,



**Fig. 12** Evolution of gases during heating of native potato starch in dependence of the temperature (mass spectrometric measurement); H<sub>2</sub>O – blue, CO<sub>2</sub> – red, NO<sub>2</sub> – green.

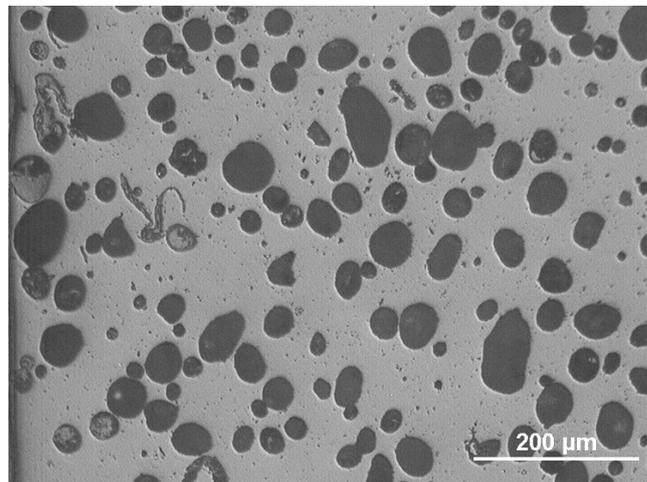
whereas CO<sub>2</sub> and NO<sub>2</sub> are eliminated in a multistage process, with main effects at 300 and 500°C. Other gases that may possibly be formed during starch burnout are acetaldehyde, furan and 2-methyl furan (Aggarwal *et al.* 1997). The burnout of potato starch is completed at approx. 550°C. What remains is ash, i.e. inorganic residues, which may enter in the crystalline or glassy ceramic phases. Generally, the ash content should be as low as possible. For advanced ceramic applications the ash content must be carefully controlled.

In spite of the importance of knowing the details of burnout behavior, in our laboratory we have successfully used a very simple heating schedule (2°C/min up to the maximum firing temperature, followed by 2 h hold and in-furnace cooling) for many years, without finding it necessary to follow the schedule of (Alves *et al.* 1998; Lyckfeldt and Ferreira 1998). Even this simple schedule did not result in any macroscopic damage of the samples and there is no evidence of microscopic defects originating from the firing step. Thus, it may be considered as confirmed that the burnout of starch is not a serious problem as long as the samples are not too large, and our simplified heating schedule can safely be used for samples of a wall thickness up to at least 10 mm with a porosity (nominal starch contents) of at least 60%. Of course, for significantly larger thicknesses and/or starch contents (porosities) it might in some cases be necessary to modify this schedule. Based on thermal analysis (TG and DTA information) concerning the individual starch type used this can easily be done. Doubtlessly, for industrial production of porous ceramic using starch as a PFA, thermal analysis of the starch burnout step is a necessary precondition to optimize the firing process in order to achieve fastest possible firing and thus save time and energy.

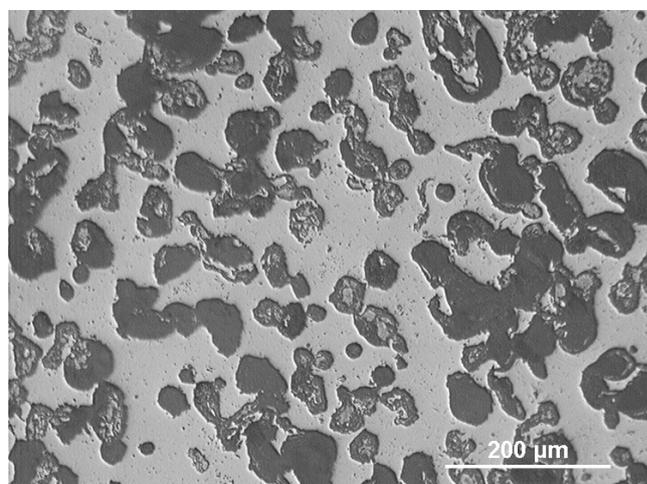
### MICROSTRUCTURE OF POROUS CERAMICS

**Figs. 13–15** show typical microstructures of alumina ceramics prepared with potato starch as a pore-forming agent (TSC and SCC). These micrographs have been obtained by optical microscopy (using reflected light) from polished sections of as-fired ceramic samples prepared by diamond-saw cutting, grinding, and polishing. The resulting polished sections can be observed by optical microscopy using reflected light.

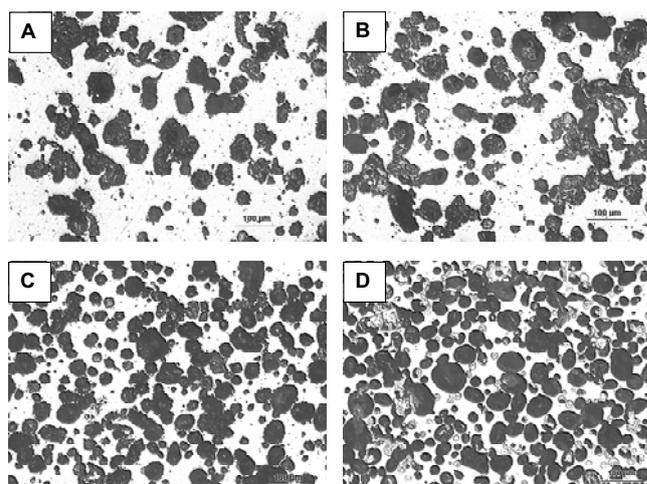
It is evident that the large pores correspond to the voids remaining after starch burnout. Since the ceramic powder is typically more than one order of magnitude smaller than the starch, the large pores remain (or may even grow), whereas the small (submicron) interstitial voids between the ceramic particles vanish during sintering (German 1996). Due to their large size, the driving force for pore closure (which is determined by the surface curvature) is negligible for these pores, and thus they do not contribute to the overall shrinkage of the ceramic body during firing. That means, shrinkage is entirely determined by the “matrix“, or – more precisely – the small (submicron) interstitial voids between ceramic particles, and the large pores may shrink during firing only to the same degree as the body as a whole, leaving the total porosity (volume fraction of pores) unchanged. Thus, the microstructure is essentially of the matrix-inclusion type.



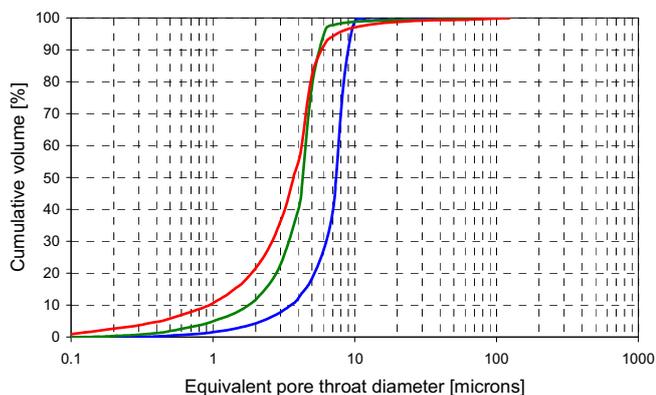
**Fig. 13** Porous alumina ceramics prepared via TSC with 25 vol.% of potato starch as a PFA; the pores correspond to the unswollen starch granules.



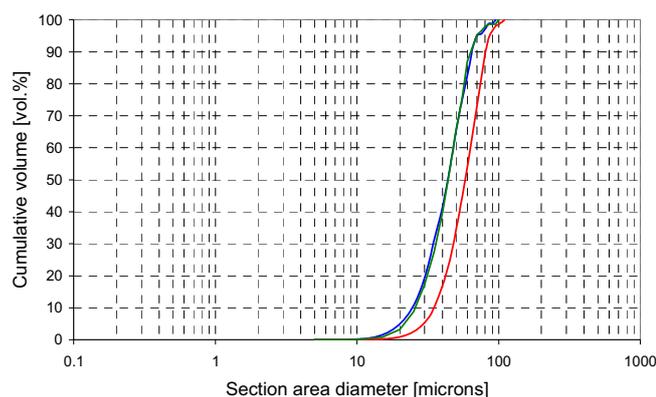
**Fig. 14** Porous alumina ceramics prepared via SCC with 25 vol.% of potato starch as a PFA and body-forming agent; the pores correspond to the starch granules after swelling.



**Fig. 15** Porous alumina ceramics prepared via SCC with 10 (A), 15 (B), 30 (C) and 50 vol.% (D) of potato starch, respectively.



**Fig. 16** Pore throat diameter distributions in porous alumina ceramics prepared by SCC, with 10 (red curve), 30 (green curve) and 50 vol.% (blue curve) of potato starch; measured by mercury intrusion.



**Fig. 17** Pore size distribution in porous alumina ceramics prepared by SCC, with 10 (red curve), 30 (green curve) and 50 vol.% (blue curve) of potato starch; measured by microscopic image analysis on polished sections.

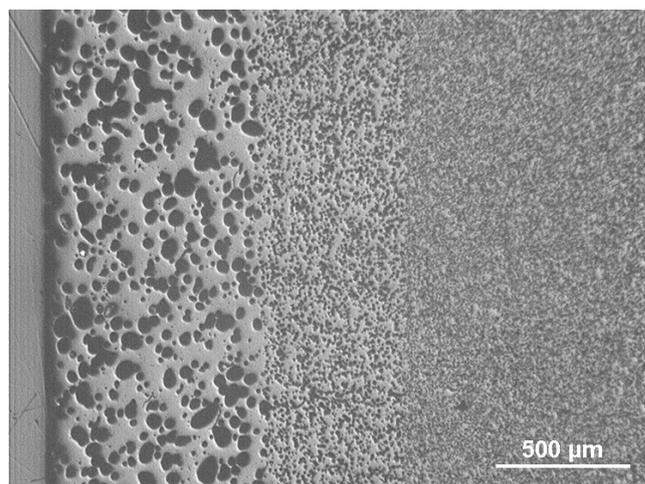
However, only for small starch contents the pores are completely closed, and even this is the case only when the starch is used as a mere pore-forming agent (PFA), i.e. in TSC but not in SCC (where starch is at the same time a body-forming agent).

Experience has shown that at total porosities higher than 15-20% the percolation threshold for open porosity (and thus, fluid permeability) is exceeded and the pore space begins to form a network of open, interconnected channels (Bonekamp *et al.* 1989; Gregorová *et al.* 2006d). Mercury intrusion measurements are indicative of the size of these small-diameter channels (pore necks or “throats”), see **Fig. 16**. Nevertheless, the large pores originating from starch burnout constitute the major part of the pore volume fraction (porosity). **Fig. 17** shows typical size distributions of starch-produced pores, as measured by image analysis (via section area diameters). After transforming the image analysis results from number-weighted to volume-weighted curves it is admissible to compare them directly with mercury intrusion results (after rescaling of the cumulative curves to 100%).

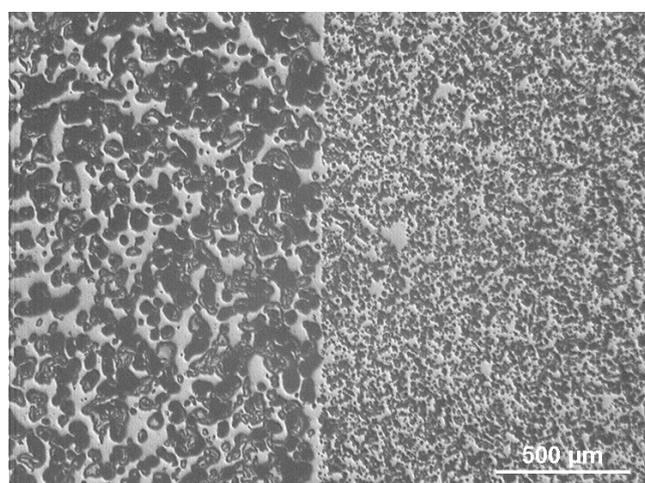
It is evident, that the size-distribution measured by mercury intrusion is smaller by approx. one order of magnitude. This finding has been confirmed by many authors (Bonekamp *et al.* 1989; Alves *et al.* 1998; Lyckfeldt and Ferreira 1998; Gregorová *et al.* 2006d; Garrido *et al.* 2009) and is usually interpreted in terms of the cylindrical tube model used for the evaluation of mercury intrusion curves via the Washburn equation (Gregg and Sing 1982). Thus, the mercury intrusion curves represent more or less the pore throat size, i.e. the diameter of the interconnections between adjacent bulk pores. This explains in a natural way the common finding that the throat size increases with increasing starch volume fraction, see **Fig. 16**, although the bulk pore size

exhibits the opposite tendency, see **Fig. 17**, due to the steric (excluded-volume) effects that restrict the degree of swelling.

Since the microscopic image analysis results are obtained from polished sections (random cuts), the pore size distribution, as determined from the equivalent section area diameters, is principally affected by the Wicksell problem (random section problem), see (Russ and Dehoff 2000), and corrections may be applied to infer the real size distribution (Gregorová *et al.* 2006d). On the other hand, the porosities measured via image analysis are in most cases grossly overestimated (when compared to porosities determined via the Archimedes method or direct volume-and-mass measurement), particularly in the case of high porosities. This finding is surprising, because the Delesse-Rosiwal law (Russ and Dehoff 2000) predicts area fractions to be equal to volume fractions of pores, when the microstructure is isotropic, uniform, and random (which is always the case for porous ceramics prepared by SCC and, with some reservation, also TSC). This apparent contradiction to the Delesse-Rosiwal law must be attributed to the breaking and pull-out of pore ledges during sample preparation (sawing, grinding, polishing), especially in those operations where normal forces act on the porous samples (note that ceramics, albeit strong, are highly brittle). However, when the ledges are eliminated, the maximum (i.e. real three-dimensional) pore diameter is directly visible in the two-dimensional section, rendering an additional correction of the random section



**Fig. 18** Ceramic laminate with pore size gradient (functional gradient material consisting of porous alumina layers prepared with 25 vol.% of potato starch, corn starch and rice starch, respectively), using TSC on a flat plaster support.



**Fig. 19** Interface between two alumina layers in a ceramic laminate prepared using SSC with 25 vol.% of potato starch (left hand side) and corn starch (right hand side), respectively.

problem (via a Saltykov transformation, say) unnecessary or even unjustifiable. Cum grano salis it may be said that the worse the porosity measurement via image analysis, the better the pore size measurement via image analysis.

Total porosities of up to 70% have been achieved using starch as a PFA (Lyckfeldt and Ferreira 1998). Using TSC, arbitrarily low porosities can be achieved (and easily controlled), whereas SCC seems not to be possible with starch contents significantly below 10 vol.% (Gregorová *et al.* 2006d; Gregorová and Pabst 2007b). Due to swelling, porosity control in SCC is more difficult than in TSC, and porosities below the percolation threshold (15–20%) have not been achieved by SCC. **Figs. 18, 19** give an impression of the further possibilities inherent in ceramic processing using starch as a PFA. **Fig. 18** shows a ceramic laminate (functional gradient material) with a pore-size gradient, consisting of porous alumina layers prepared via TSC with 25 vol.% of potato, corn and rice starch, respectively. Note that the porosity is the same in the three different layers, i.e. in TSC the final porosity in the ceramic corresponds very well to the starch content in the suspension. Similarly, the pore size in TSC corresponds to the original size of the starch granules. **Fig. 19** shows an interface between two alumina layers prepared via SCC with 25 vol.% potato and corn starch, respectively. Note the significant increases in pore size and porosity (compared to the TSC-produced laminate in **Fig. 18**), which are due to starch swelling in SCC. However, both micrographs indicate that defect-free interfaces with excellent adhesion and absence of delamination effects can be produced via either TSC or SCC.

## PROPERTIES OF POROUS CERAMICS PRODUCED WITH POTATO STARCH

The introduction of porosity generally changes the macroscopic properties of materials. Mechanical strength, elastic moduli (stiffnesses) and thermal conductivity generally decrease (implying that their inverse properties such as elastic compliances and thermal resistivity increase), whereas other parameters or properties remain constant (e.g. the thermal expansion coefficient) or may even increase (e.g. fracture toughness, thermal shock resistance). An enormous amount of literature is available on the properties of porous materials, see Torquato (2002) and the references cited therein. The properties of porous ceramics have been discussed in great detail in Rice (1998).

With respect to this situation it is rather surprising, that until recently no relations were available for the prediction of the porosity dependence of even such well-defined properties as the Young's modulus and the thermal conductivity for ceramics produced with starch as pore-formers. In other words, all models de facto relied on measured values, which were then (a posteriori) fitted with at least one adjustable parameter. Recently, a parameter-free predictive model has been derived via a functional-equation approach (Pabst and Gregorová 2004). The resulting modified exponential relations were shown to predict the relative Young's modulus and thermal conductivity for starch-processed porous ceramics reasonably well (Tichá *et al.* 2005; Pabst *et al.* 2005, 2006; Pabst and Gregorová 2006a, 2006b, 2007, 2008; Živcová *et al.* 2009). These relations are

$$E_r = \frac{E}{E_0} = \exp\left(\frac{-2\phi}{1-\phi}\right) \quad (4)$$

for the tensile or Young's modulus (with  $\phi$  being the porosity and  $E_r$  the relative modulus, i.e. the ratio between the effective modulus of the porous ceramic  $E$  and the modulus of the solid phase  $E_0$ , i.e. the densely sintered ceramics) and

$$k_r = \frac{k}{k_0} = \exp\left(\frac{-1.5\phi}{1-\phi}\right) \quad (5)$$

for the thermal conductivity (with  $k_r$  = relative conductivity,  $k$  = effective conductivity,  $k_0$  = solid phase conductivity).

Note that these modified exponential relations are always lower than the so-called Hashin-Shtrikman upper bounds,

$$E_r = \frac{1-\phi}{1+\phi} \quad (6)$$

and

$$k_r = \frac{1-\phi}{1+\phi/2} \quad (7)$$

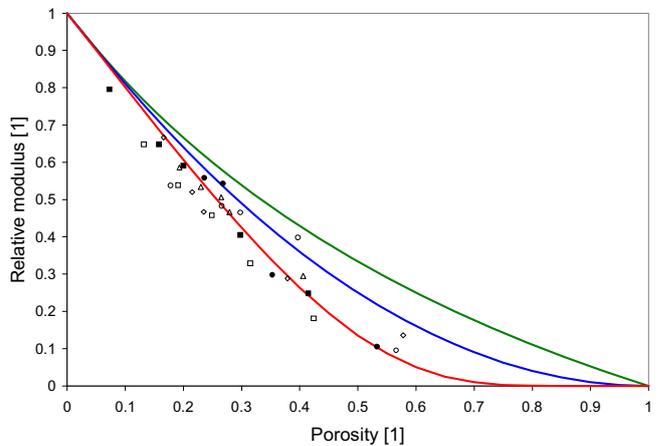
(which cannot be exceeded by any isotropic porous material), and also well below the popular power-law relations,

$$E_r = (1-\phi)^2 \quad (8)$$

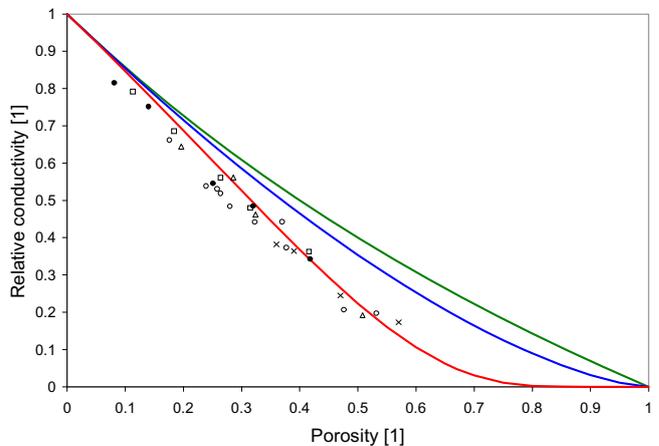
and

$$k_r = (1-\phi)^{3/2}, \quad (9)$$

which can be derived using variational methods and a differential scheme approach, respectively, see e.g. (Torquato 2002; Pabst *et al.* 2007) and the references cited therein.



**Fig. 20** Porosity dependence of the relative tensile modulus (Young's modulus); alumina (circles), alumina-rich alumina-zirconia composite ceramics with 15% zirconia (rhombos), zirconia-rich alumina-zirconia composite ceramics with 20% alumina (triangles) and zirconia (squares) prepared with potato starch (empty symbols) and corn starch (full symbols) – Hashin-Shtrikman upper bound (green curve), power law relation (blue curve), Pabst-Gregorová exponential relation (red curve); measured data from Pabst *et al.* 2004, 2005.



**Fig. 21** Porosity dependence of the relative thermal conductivity; alumina (empty circles: SCC, full circles: TSC), zirconia-rich alumina-zirconia composite ceramics with 20% alumina (triangles), zirconia (squares) and mullite (crosses) – Hashin-Shtrikman upper bound (green curve), power law relation (blue curve), Pabst-Gregorová exponential relation (red curve); literature data and measured data from: Barea *et al.* 2005; Tichá *et al.* 2005; Živcová *et al.* 2009.

**Figs. 20, 21** show the predictive curves following from theory, together with experimentally measured values. Although it is clear that the porosity dependence is not the same for all microstructures, it seems that the effective properties of starch-processed ceramics are best predicted by our modified exponential relations Eqs. (4) and (5). Moreover, there is no indication of systematic differences between different starch types so far, although it might be argued that this is due to insufficient measurement precision and reproducibility. In particular, with respect to currently achievable measurement precision and reproducibility, pore size effects (in the range covered by starch, i.e. from 1–100  $\mu\text{m}$ , with median values ranging from 5–50  $\mu\text{m}$ ) are undetectable, so that the properties of porous ceramics made with potato starch do not differ measurably from those made with other starch types at comparable porosity.

## MODIFIED STARCHES AND OTHER USES OF POTATO STARCH IN CERAMIC TECHNOLOGY

In their classic paper (Lyckfeldt and Ferreira 1998), Lyckfeldt and Ferreira emphasize that modified starches are in many respects more useful for ceramic processing than native starches. According to these authors, modified starches enable easier processing and give more reproducible results. While these statements may be true for certain starch products, the ceramic community has been hesitant if not reluctant to adopt this standpoint in general. Actually today, the majority of authors prefer native starches for ceramic processing applications; exceptions are, for example (Alves *et al.* 1998; Barea *et al.* 2005; Li *et al.* 2007; Chen *et al.* 2008; Huang *et al.* 2008). Doubtlessly, one of the reasons is that the palette of modified starch products is too widespread for the non-specialist, cf. (Kodet and Babor 1991; Blanchard and Katz 1995; Wurzburg 1995). A further reason may be that a detailed knowledge of the modification methods is necessary in order to assess the effects of chemical and physico-chemical changes introduced via the modification procedures and their auxiliary chemicals. Note that any chemical components that do not completely burn out during firing may leave elemental residues that may be harmful for the intended application of the final ceramic, especially alkali (Na) and earth alkali (Ca) ions, but also phosphorus P (and to some extent sulphur S). Therefore the intrinsic inorganic ash content of the starch should be as low as possible, and the content of additives introduced in the starch modification procedure must be carefully controlled, especially when the ceramic application requires extremely high purity (e.g. implant or bone tissue engineering applications).

Apart from being a pore former, starch, modified starches, starch derivatives, and starch pastes are extensively used in ceramic technology as binder or plasticizer components (Greenwood *et al.* 2001; Lidén *et al.* 2001; Sikora and Izak 2006; Islam and Kim 2007; LeBeau and Boonyongmaneerat 2007). In these cases the main purpose is usually to replace the plastic clay fraction (in clay-free ceramics) and not to obtain a porous ceramic material after firing. Since the starch granules are usually destroyed during high-shear mixing, kneading, chemical or thermal treatment before extrusion or injection molding, aqueous solutions of the starch components (amylose and amylopectin) are free and fluid enough to fill the interstitial voids between the ceramic particles. In very special cases, starch may also serve as an additional carbon source, for example in the preparation of carbides or nitrides (Rafaniello *et al.* 1981; Kuang *et al.* 2004), or as a gelling additive to produce ceramics via polymeric sol-gel routes (Egger *et al.* 2005).

Apart from applications of starch for the preparation of sintered ceramics and ceramic composites, two vast fields have recently emerged, where starch is used as a matrix material component of hybrid organic composites with ceramic raw materials as inclusions. In the field of biomaterials, new hybrid starch-based composites have been prepared with hydroxyapatite and calcium silicate (Vaz *et al.*

2002; Marques and Reis 2005; Miyazaki *et al.* 2007a, 2007b; Ohtsuki *et al.* 2007). In contrast to porous implants with a ceramic matrix these hybrid materials have the advantage that they are not brittle and have elastic properties relatively close to (cancellous) bone. Their bone-bonding capability makes them promising implant materials (the starch matrix is bioresorbable while hydroxyapatite is bioactive). Apart from implant applications, starch can be used for porous scaffolds in bone tissue engineering (Salgado *et al.* 2004) and to modify acrylic bone cement, making it bioactive and partially bioresorbable (Espigares *et al.* 2002). Similarly, starch-based hybrid composites with kaolin and other clays as fillers have been developed as environmentally friendly (renewable and biodegradable) packaging materials (Chiou *et al.* 2005; Sinha Ray *et al.* 2005). Not less important is the application of starch as a binder for dry-pressed tablets in the pharmaceutical industry, where the purpose of starch consists in enhancing the mechanical strength of inorganic and organic crystalline pressed powders (van Veen *et al.* 2000). Recent variants of this binder application use potato starch as a binder for syntactic foams made of ceramic microballoons (hollow micro-spheres) and in other contexts, cf. (Sikora and Izak 2006; Islam and Kim 2007).

## SUMMARY AND CONCLUSION

Starch, in particular potato starch, is an important additive in ceramic technology and has been used for a long time as a binder component, often replacing plastic clay in clay-free ceramics. In the last two decades potato starch has been used as a pore-forming agent in advanced ceramics, deliberately introduced to prepare porous ceramics with controlled microstructure. Ten years ago (1998), a new process was published, called starch consolidation or starch consolidation casting (SCC), where the swelling and gelatinization capability of starch is used for the purpose of ceramic green body solidification. That means, in this process starch serves as a combined pore-and-body-forming agent. In this contribution the size and shape characterization of native potato starch, rheology of potato-starch containing suspensions, swelling kinetics and burnout behavior of starch have been discussed in some detail, and the fundamental differences between traditional slip casting (TSC) and starch consolidation casting (SCC) have been explained. Microstructural issues have been commented upon and selected microstructure-property relations have been mentioned. In particular, it has been demonstrated, that our modified exponential relations give a reasonable prediction of the Young's modulus and thermal conductivity of porous ceramics prepared with potato starch. A total porosity of up to 70% can be achieved in ceramics prepared with potato starch as a pore-forming agent.

## ACKNOWLEDGEMENTS

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