

ORIGINAL ARTICLE

Macroporous mullite materials prepared by novel shaping strategies based on starch thermogelation for thermal insulation

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Abstract

A rigorous microstructural analysis of porous mullite materials developed using novel shaping strategies based on the starch consolidation casting, and their thermal properties in relation to the processing and starch type were accomplished in view of their use as thermal insulators. In order to characterize the size and morphology of pore, basic size and 2D shape factors, and global 3D stereological parameters were determined using microscopy techniques. Results indicated that the porosity volume, pore connectivity degree, and mean free path were the determining factors of the lowest heat transfer by conduction registered in materials prepared with cassava starch. This material is the best candidate to be used in thermal insulation.

KEYWORDS

microstructure, mullite, porous materials, thermal conductivity

1 | INTRODUCTION

High porosity mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) materials can be widely used as thermal insulators because of their low thermal expansion coefficient ($\alpha \approx 5 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$) and thermal conductivity ($k \approx 5\text{--}6 \text{ W m}^{-1} \text{ K}^{-1}$), as well as their good mechanical properties at high temperature (e.g., high strength as well as high creep resistance). In recent years, the increasing demand for materials that help reduce energy consumption and use energy efficiently has required the development of high performance thermal insulators.^{1,2} For applications involving heat transfer, as in the case of thermal insulating, the thermal properties of materials, particularly thermal conductivity, are especially important. Moreover, the effective thermal conductivity of porous ceramics may significantly influence other properties such as thermal shock resistance.³ However, in spite of the technological interest in highly porous mullite materials, the number of research papers found in the literature regarding the thermal properties is not very high.⁴⁻⁶

Regarding the processing of porous ceramics, which determines their microstructure-properties relationships, methods based on the direct consolidation of ceramic suspensions into nonporous molds, among which are those

that use pore-forming agents, have been developed in recent years in order to obtain controlled porous microstructures. When heating at high temperature, these pore-forming agents are burned out, leaving pores in the ceramic. Thus, among the various direct consolidation methods, a noncontaminating low-cost consolidation technique in which the starch is used not only as a pore-forming agent at high temperature after burning (e.g., as an additive in traditional slip casting, TSC) but also as a body-forming agent of the ceramic suspension when the system is heated between 50 and 85°C (i.e., as a consolidating agent in so-called starch consolidation casting, SCC), and has gained a prominent position among the most popular processing methods for porous ceramics.⁷⁻¹² When the aqueous ceramic-starch suspension is heated, the starch granules swell by water absorption, decreasing the available free water, and the ceramic particles, usually of smaller size than the starch granules, are thus pressed together in the interstitial space to consolidate into a solid body. Finally, after thermal treatments, a porous material is obtained whose porosity, which is associated with highly interconnected open pores (essentially convex cavities), particularly when the starch content is high, depends on the amount, shape, and size of the swollen starch granules.

Starches are cheap, nontoxic, environmentally friendly, and, most importantly, from an engineering point of view, provide residual-free burnout (the ash content is negligible). The first reported investigations^{7,8} on starch consolidation casting method showed that highly deformed green bodies were obtained by using native starches from different botanical sources. In contrast, it is possible to obtain more satisfactory results by using chemically or physically modified starches.⁷⁻¹⁰ However, we have recently reported that the inclusion of modifications into the conventional route of processing allows developing high-quality ceramic green bodies with controlled porous microstructures.^{11,12}

The proper analysis of applications for porous materials requires a global microstructural characterization, which includes at least the nontrivial determination of the total porosity amount and the pore size. The total porosity can be calculated by measuring the bulk density when the real or theoretical densities are known. This method is usually more reliable than determining the total porosity via image analysis, for which “the pores” are referred to as the isolated intersections of a planar cross section with the 3D pore space.^{13,14} In addition, the accurate determination of pore size presents major difficulties. In general, the pore size is considered as the equivalent diameter, mean area, or some other more or less well-defined geometric quantity measured by applying image analysis to the planar cross sections through the 3D pore space. Besides the fact that the pore size must be given in terms of either equivalent or statistical values, the concept of pore size requires that the pores are well-defined isolated objects arranged in a matrix, preferentially with a convex shape. Only under these conditions, a 2D pore equivalent diameter distribution can be measured via image analysis and subsequently transformed into a 3D pore equivalent diameter distribution, provided that the pore shape does not deviate much from an isometric form. Therefore, microscopy image analysis can be used to determine an unambiguous pore size distribution only when the isotropic microstructure is of the matrix-inclusion type. The accurate measurement of pore size by image analysis requires that they are all single and isolated. Unfortunately, this does not always occur, as in the case of the porous materials obtained by SCC, which generally have interconnected single pores. In some cases, moreover, agglomerates of pores originating from the rupture of the pore wall or from the overlapping or joining of adjacent granules during the forming process are also formed, which leads to an overestimated pore size by image analysis. Also, it is worth noting that even the qualitative interpretation of the microscopy images is not always easy, as when planar images do not adequately display the complexity of the three-dimensional (3D) details, and therefore cannot offer any conclusions as for the pore type in 3D.¹⁵ In spite of the abovementioned considerations, an arithmetic

average of a number-weighted size distribution¹⁴ could be determined in low density materials by microscopy image analysis using the mean intercept length, even if the pores are not well-defined isolated objects. On the other hand, if a pore size distribution is required, mercury porosimetry is the traditional method of choice.

Considering that the image analysis implies reducing the complex visual information contained in the images to easily interpretable quantitative information, generally in the form of size distributions or even average or mean values, the loss of some information is inevitable; therefore, the extraction of essential information must be ensured.¹⁶

On the other hand, stereology, which can be considered as a subdiscipline to stochastic geometry, is defined as the method to derive a quantitative description of 3D geometry from data obtained by the quantitative image analysis of 2D images. This method aims at obtaining information on the 3D microstructure from 2D cuts (planar sections). Stereology is based on the assumption that mean values exist characterizing the microstructure of the material, which are invariant under nondistorting translations and rotations. Therefore, unless stated otherwise, it is assumed that the microstructure of the material under investigation is isotropic, uniform and random. Stereological techniques are considered the most effective way to evaluate the complex 3D geometry in quantitative terms. In general, there are two ways to describe the 3D geometry of microstructures by these techniques. One way is to take measurements of a large number of 2D features and to convert them into 3D distributions with specific characteristics, which usually requires an unrealistic approximation. However, the way most advocated by several authors is that which describes the microstructure by a set of so-called “global parameters”. The data for determining the most relevant global parameters are derived from counting measurements performed on 2D cross sections using stereological equations. The strength and generality of these equations are based on the fact that no geometric assumptions are necessary for their derivation. Each of the global parameters provides an unbiased estimate of a specific geometric characteristic of the entire microstructure if the tested sample is representative for the specimen and properly described. Moreover, each global parameter can be expressed by a simple value without reference to other parameters, as well as provide an accurate, although limited, description of the 3D geometry of real microstructures and define those quantities which can be directly related to the properties and functions of a material by physical reasoning. The two most useful global parameters are volume fraction and surface density. With these few basic data, mean size, mean spacing, orientation, and connectivity can be quantitatively described by simple and easily comprehensible equations relating 2D measurements to 3D quantities.

Several researches^{13,15,17} agree to and advocate the use of the global stereological parameters, but with certain exceptions (e.g., the microstructure is not statistically homogeneous, among others). Based on their experience, mean linear grain/pore size or grain/pore boundary density and volume fraction and size or surface density are fully adequate to deal with the majority of practical problems which can arise in the microstructural characterization of materials from the viewpoint of the material science. Thus, stereology will remain or become the method of first choice when it is selectively optimized.

Based on the abovementioned, the aim of this study is to perform a rigorous analysis of both the microstructural features of the porous mullite materials developed by using two novel shaping strategies based on the starch consolidation casting method and their thermal properties in relation to the processing and starch type used in view of their use as thermal insulators. The combined use of both image analysis and stereology is proposed in order to carry out a microstructural analysis more integral, and thereby, to determine for design purposes the main parameters that characterize the porosity of the developed materials.

2 | EXPERIMENTAL PROCEDURE

2.1 | Processing of porous mullite materials

A high-purity commercial mullite powder (MULSM, Baikowski, Charlotte, NC) and commercial native starches (AVEBE Argentina, Buenos Aires, Argentina) derived from cassava, corn, and potato were used as raw materials. A complete characterization of these powders was reported in previous works of the authors.^{12,18} It is worth noting that the used starches were selected taking into account their granulometric distributions (particularly, the mean particle size, D_{50}) and swelling capacities (they were obtained from the analysis of optical microscopy images corresponding to aqueous starch suspensions at different temperatures) of granules.¹⁸ These characteristics are considered relevant in the context of the present work because of the size of starch granules determines the pore size which is one of the microstructural parameters that might affect the thermal conductivity. The three starches presented bimodal granulometric distributions with a low volume percentage (<5%) of small granules, which can be linked to impurities or broken granules. Potato starch exhibited the largest granules ($D_{50}=47.8\ \mu\text{m}$), whereas corn and cassava starches presented smaller granules ($D_{50}=13.6$ and $D_{50}=14.8\ \mu\text{m}$, respectively). In addition, potato and cassava starches possessed a swelling capacity notably greater than that of corn starch, with potato starch presenting the greatest swollen granule size.

Green mullite disks were formed by using two novel previously designed routes called the “Sub-gelatinization

Route” (SGR) and the “Mixing Route” (MR). These routes are based on the thermal consolidation process of aqueous mullite suspensions with native starches. Based on the fact that the processing method determines the porous microstructures developed, the used routes could also affect the parameters that characterize the porosity. As was already reported in previous work,¹² the use of both routes prevented the segregation of starch granules and mullite particles and allowed a homogeneous distribution of raw materials is obtained in each green mullite ceramics.

By following an experimental procedure and conditions that were previously selected and studied,¹⁹ aqueous mullite-starch suspensions (40 vol% total solid loading) were prepared for both routes by: (i) mixing mullite powder in water to a solid content of 40 vol% and dispersing with 0.45 wt% Dolapix CE-64 (Zschimmer & Schwarz, Lahnstein, Germany) with respect to the powder amount; (ii) homogenizing the mixture in a ball mill for 6 hours; and (iii) adding an aqueous starch suspension (40 vol%) and mixing for 5 minutes to obtain final starch and mullite contents of 10 and 30 vol% (with respect to the total volume of suspension), respectively.

For SGR, aqueous mullite-starch suspensions were heated at temperatures lower than the onset temperature of gelatinization for each system (59°C for the mullite-cassava starch and mullite-potato starch suspensions, and 64°C for the mullite-corn starch suspension) in order to activate the gelatinization process when reaching the necessary temperature (80°C). This is also done in order to decrease the required time to achieve a uniform consolidation temperature throughout the total volume of suspension and, therefore minimize not only possible thermal gradients in the sample but also the segregation of mullite particles and starch granules caused by their very different densities and particle sizes.

Regarding MR, which was proposed with the aim of increasing the viscosity of the mullite-starch suspensions and, consequently, preventing the segregation of mullite particles and starch granules, a mixture of ungelatinized native starch and the same type of starch previously gelatinized (10 vol% starch in water at 80°C for 10 minutes) was used to prepare the aqueous mullite-starch suspensions. The ratio of previously gelatinized to total starches was 1:10.

Using both routes, mullite-starch disks were formed by pouring the aqueous mullite-starch suspensions into stainless steel cylindrical molds (diameter=2.20 cm; height=1.00 cm) covered on the inside with adhesive PTFE (polytetrafluoroethylene, Teflon) tape to facilitate the removal of the samples and prevent the generation of defects due to deficient wetness. They were then heated in an electric stove (UFP 400; Memmert, Schwabach, Germany) at 80°C for 2 hours and subsequently dried at 40°C for 24 hours, at which time the consolidation was finished and the samples were taken out of their molds.

The burning-out process to completely remove the starch and organic additives was performed at a heating rate of $1^{\circ}\text{C min}^{-1}$ up to 650°C for 2 hours. Finally, porous mullite bodies were obtained by sintering at 1650°C for 2 hours. Mullite 3/2 (File 74-2419) was the single crystalline phase present after the sintering process. In addition, the pycnometric density value of the powdered sample (ρ_{ps}) treated at 1650°C was 3.11 g cm^{-3} . Based on these results, it was reported that a complete mullitization reaction occurred after treatment at 1650°C for 2 hours.^{10,12}

2.2 | Analysis of the porous mullite microstructures

Open, closed, and total porosities as well as the pore connectivity degree (defined as the open porosity/total porosity ratio) were presented in a work of the authors previously reported,¹² but a deeper analysis of these results is carried out in the present work.

The final developed microstructures were analyzed by SEM on the fracture surfaces of disks with thermal etching (this treatment was carried out for 30 minutes at 50°C below the sintering temperature by using heating and cooling rates of $20^{\circ}\text{C min}^{-1}$) and optical microscopy (PMG-3, Olympus, Tokyo, Japan) on their free surfaces. For observation via optical microscopy, the surfaces were prepared by inlaying the samples into an epoxy resin (EpoFix Resin, Struers, Ballerup, Denmark) using vacuum impregnation, grinding them with 600-grit SiC paper using water as lubricant, and finally, polishing them with diamond pastes of 3 and $1 \mu\text{m}$ on nylon cloth lubricated with a commercial solvent (DP-Lubricant Green, Struers).

A qualitative analysis of the microstructure was carried out using SEM images captured at low and high magnifications in order to appreciate, on one hand, a large area field of view, and on the other, the most important details of the developed porous microstructures (e.g., homogeneity, grain size, grain morphology, presence of windows).

In addition, a quantitative analysis of these microstructures was performed by using two specific methodologies—2D image analysis and global 3D stereology—from which mean values and the standard deviation of different parameters were obtained. The analysis of the corresponding images captured by optical microscopy was carried out by using open source programs (ImageJ v1.48, NIH, Bethesda, MD; Goitacá v4.43, UENF, Rio de Janeiro, Brazil) employing three samples of each processing route for each starch type. For both methodologies, each gray-level image was transformed into a binary image that was further processed by interactive editing, amending operations such as erosion and dilation, hole filling, separation of touching objects, and smoothing outlines.

2.2.1 | Basic size measurements and shape factors in 2D

2D basic size and shape factors measurements of the pores (~300 objects were measured in each sample) developed in the porous mullite materials were obtained. The following basic parameters were analyzed:

1. Feret diameters, which take into account the two mutually perpendicular normal values for each object so that the area of the rectangle enclosing the object outline becomes a minimum (this area is determined by the minimum Feret diameter, DF^{min} , and the dimension perpendicular to it, called the maximum Feret diameter, DF^{max}).
2. The aspect ratio, which refers to the relation between the major and minor axis lengths of the object. This parameter was calculated from maximum and minimum Feret diameters and indicates object elongation.
3. Circularity or roundness, which is the ratio of the projected area times 4π to the perimeter squared ($4\pi \cdot A_p / P^2$), provides a combined measure of anisometry and nonsmoothness for convex and nonconvex objects. This parameter takes values ≤ 1 (i.e., equal to 1 for circles and < 1 for noncircles).

2.2.2 | Global 3D stereological parameters

With the second methodology, a set of global parameters were determined by counting measurements performed on binarized optical micrographs using stereological equations with the status of mean value theorems in statistics. The objects (cavities) were measured using image analysis software (Goitacá v4.43, UENF) by superimposing a square grid on the micrograph and dividing the integral chord length inside pore sections by the number of intersections (equal to half the number of intersection points with the pore perimeter). Each global parameter is a simple sum and, irrespective of shapes, sizes, and arrangements, can be expressed by a simple value without reference to other parameters.

In this study, the volume fraction (V_V) of a specific microstructural feature in 3D (e.g., the porosity) and the surface density (S_V) of features (e.g., pores) per unit volume in 3D space are considered the most useful global parameters. In general, the quantities “per unit volume” (i.e., V_V and S_V , among others) cannot be directly measured and are indirectly determined from other directly measurable parameters such as P_P , L_L , A_A , and P_L considering the most fundamental stereological relationship of Delesse-Rosiwal ($P_P=L_L=A_A=V_V$, where P_P is the number of points hitting the feature (pore) of interest divided by the total number of points placed on the image, L_L the length of intersection lines per unit test line, and A_A the area of intercepted features per unit test area) for a particular phase and

by using the stereological relation, $S_V=2P_L$, where P_L is the number of intersection points per unit length of test line. In addition, other stereological parameters were also determined from the directly measured parameters, such as the mean intercept length in 3D (mean linear size), which is considered the mean pore size, and the mean linear distance (mean free path) between pores. These parameters were defined as $\bar{L}=4V_V/S_V=P_L/P_P$ and $\bar{D}=(1-P_P)/P_L=4\cdot(1-V_V)/S_V$, respectively. The experimental results are reliable to a 5% probability of error (i.e., 95% significance level).

2.3 | Evaluation of thermal properties

The thermal diffusivity (α) was measured by the laser-flash method (Thermaflash 2200; Holometrix-Micromet, Bedford, MA) with a precision of 5%. Tests were carried out in air up to 800°C using duplicate mullite disks of 12.6–12.7 mm in diameter and 1.0 mm thick. Three measurements were performed at each temperature and then an average value for each set of measurements was calculated. In order to adjust the disk dimensions to the required values, mullite disks were first green machined with 600-grit SiC paper and, once they were sintered, a diamond drill refrigerated with water was used. Sample surfaces were coated with a thin $\sim 0.1\ \mu\text{m}$ gold layer in order to prevent direct transmission of the laser radiation through the samples. Then, they were additionally coated with a $\sim 10\ \mu\text{m}$ layer of colloidal graphite to increase the efficiency of radiation absorption and ensure uniform absorption of the radiation and heat emission. The experimental data were analyzed by the Koski procedure to the Clark-Taylor model.

The thermal conductivity (k) can be directly deduced from the thermal diffusivity values by $k=\rho_s\cdot C_p\cdot\alpha_c$, where C_p is the specific heat of the mullite material at each temperature and ρ_s is the sample density. C_p data as a function of the temperature for the mullite material were taken from other research.²⁰ In the particular case of porous mullite materials, the error in the thermal conductivity values associated with the volume change as a function of the temperature (the anisotropy of the mullite bond system is considered so that the major thermal expansion occurs in the direction of the b axis) is negligible for the calculus of this parameter from the diffusivity measurements by laser-flash method⁴ compared to the error associated with the method itself.

3 | RESULTS AND DISCUSSION

3.1 | Porous mullite microstructures

Total porosities were in the range 39–44%. Even though for both processing routes the total porosity values were

not notably different (43–44% for SGR and 39–42% for MR), the porosities obtained for materials prepared by SGR were the greatest. Moreover, samples consolidated by MR presented a higher amount of closed pores (2.4%, 4.2%, and 5.2% for samples prepared with cassava, corn, and potato starches, respectively) than those prepared by the other processing route (2.0%, 3.6%, and 4.7% for samples fabricated with cassava, corn, and potato starches, respectively). These results could be explained taking into account that for MR, the swelling and the gelatinization processes of some starch granules might have been limited because of the increase in the suspension viscosity produced by the presence of previously gelatinized starch. On the other hand, considering the results obtained for each route, the total porosity values registered slightly depended on the used starch. When the cassava starch was used, the samples presented greater total porosity values (44% and 42% for SGR and MR, respectively) than those obtained for samples prepared with corn (43% and 39%) or potato (43% and 40%) starches. In addition, the samples prepared with cassava starch presented a higher pore connectivity degree (0.95) than that registered in the remaining samples (0.90 and 0.88 for samples prepared with corn and potato starches, respectively). The dependency of these parameters (total porosity and pore connectivity degree) on the starch type could be attributed to the different swelling capacities that present the used starches (cassava starch granules have the highest swelling capacity) and three-dimensional gel structures formed, which depending on the botanical source of the starch.¹⁸ In addition, the occurrence of constrained swelling due to steric effects (excluded volume effect) could explain the small differences determined in the parameters analyzed as yet.

On the other hand, nondifference was appreciated in the SEM micrographs corresponding to the samples obtained by both processing routes due to the complex microstructure developed by SCC method. Thus, typical SEM images with high and low magnification of the porous mullite materials obtained by using cassava, corn, or potato starches are shown in Figure 1.

As reported in previous works^{10,12} and in several papers published by other authors,^{7,8,14} large convex pores (cavities) with nonspecific tortuous morphology embedded in the mullite matrix were created in all the materials by the removal of native starch granules. In addition, much smaller pore channels or throats (cell windows) interconnecting the cavities were developed throughout the entire thickness of the disk after the sintering treatment. The cavity size (10–20 μm for materials prepared with cassava and corn starches, and 30–70 μm for materials obtained with potato starch) was mainly determined by the native starch type, and was not only related to dry starch granule sizes or those having suffered some degree of swelling, but also

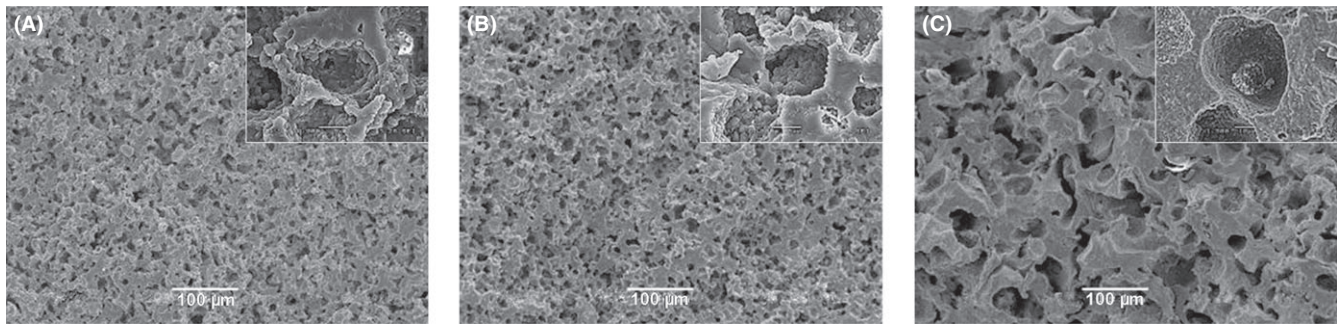


FIGURE 1 Typical SEM micrographs of fracture surfaces of the disks obtained with cassava (A), corn (B), and potato (C) starches, after sintering at 1650°C

larger cavities generated from the joining of various cavities. The mullite matrix presented a high degree of densification promoted by the presence of phases based on silicates with low melting points, with submicronic, mainly equiaxial ($\sim 0.5 \mu\text{m}$) grains and elongated grains slightly larger (“aspect ratio” <2.5).

Optical micrographs of polished sections of porous mullite materials are shown in Figures 2 and 3. In these images, the pores correspond to gray areas, whereas white areas denote the ceramic matrix. Starting from the observation of the obtained images, it is clear that distinguishing between single pores and apparent pore agglomerates, which may have originated from pore wall breaking or from overlapping or joining of adjacent starch granules during forming of green bodies, was not possible. Thus, the pore sizes determined by analyzing the images with respect to the swelled granule sizes are always overestimated due to the overlapping or bonding of pores. On the other hand, it is well known that the pores may appear isolated in a 2D cut; however, this analysis prevents any conclusion to be drawn about the type of pore in 3D.

The mean and standard deviation values of basic 2D parameters used to characterize the size and morphology of pore cavities developed in the materials which were formed by both consolidation routes are given in Table 1. The high dispersions obtained for each parameter are due not only to

the fact that in these materials, natural agents as pore formers with a large size distribution (in original condition as well as after swelling) were used, but also by the gelatinization process itself.

According to the obtained circularity and aspect ratio values, all the consolidated materials, independently of the route and starch used, showed cavities with a similar degree of elongation (aspect ratio values between 1.8 and 2 ± 0.3).

Concerning the obtained mean values of the minimum Feret diameter (DF^{min}) and maximum Feret diameter (DF^{max}), all the developed materials presented values that depended on the starch type used for each processing route. The highest Feret diameter values were obtained for the materials prepared with potato starch, while the materials prepared with corn and cassava starches presented similar values for these parameters. These results can be also related to the starch granule sizes. In addition, for the materials prepared with potato starch, the tendency registered for the values of these parameters suggests that using MR allows slightly smaller pore cavities to develop, probably due to the limited starch granule swelling because of the high suspension viscosity generated in this route, as was abovementioned. In contrast, variations in the values of the considered parameters were not recorded for the materials prepared with remaining starches due to the fact that the

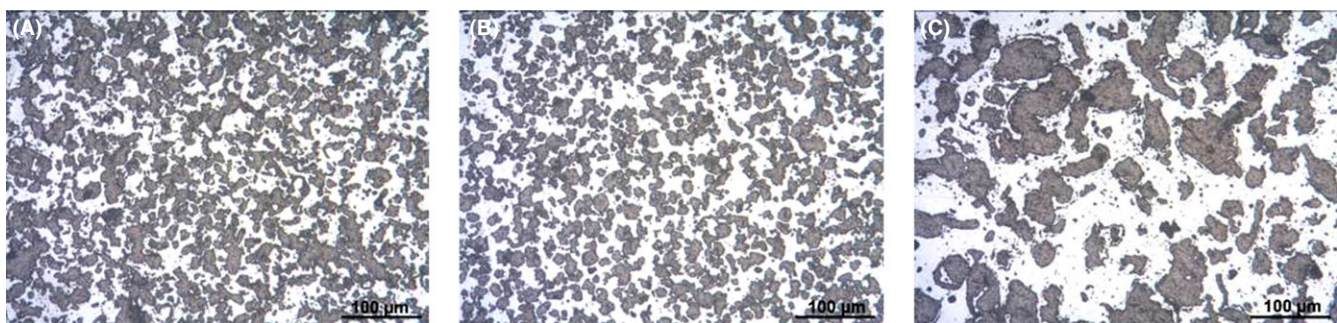


FIGURE 2 Optical micrographs of polished disks formed with cassava (A), corn (B), and potato (C) starches by SGR, after sintering at 1650°C [Color figure can be viewed at wileyonlinelibrary.com]

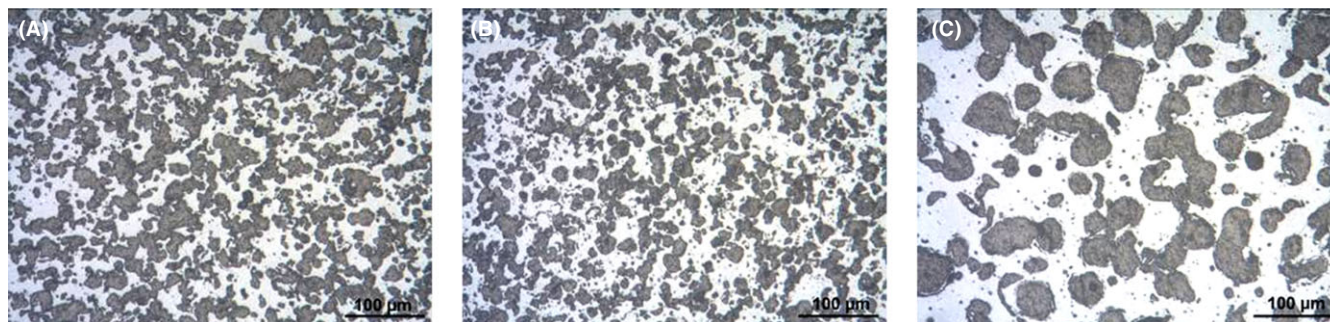


FIGURE 3 Optical micrographs of polished disks formed with cassava (A), corn (B), and potato (C) starches by MR, after sintering at 1650°C [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Basic size measurements (minimum and maximum Feret diameters) and shape factors (aspect ratio and circularity) in 2D for the developed porous mullite materials

Forming route	Starting system	DF ^{max} (μm)	DF ^{min} (μm)	Aspect ratio	Circularity
SGR	Mullite-cassava	29±4	17±2	2.0±0.3	0.3±0.1
	Mullite-corn	27±4	16±2	1.8±0.3	0.4±0.1
	Mullite-potato	80±13	53±8	1.9±0.3	0.3±0.1
MR	Mullite-cassava	28±4	16±2	1.9±0.3	0.4±0.1
	Mullite-corn	30±5	18±2	1.9±0.3	0.4±0.1
	Mullite-potato	70±10	42±6	1.8±0.3	0.4±0.1

viscosity of their suspensions was not so highly influenced by the presence of the gelatinized starch (i.e., the suspensions with corn and cassava starches used in MR presented viscosity values lower than that with potato starch).¹²

On the other hand, the global 3D stereological parameters corresponding to the developed porous mullite materials obtained by using the second methodology are given in Table 2.

Determining these parameters enabled a complete characterization of the developed microstructures to be made.

As for V_V , which is the primary parameter when relating properties of a material to its microstructure, the values obtained for the materials prepared with the different starches and processing routes were consistent with those

TABLE 2 Global 3D stereological parameters (volume fraction, mean intercept length, mean linear distance, and specific surface density) for the developed porous mullite materials

Forming route	Starting system	V_V	\bar{L} (μm)	\bar{D} (μm)	S_V/V_V (μm ⁻¹)
SGR	Mullite-cassava	0.48	23	26	0.17
	Mullite-corn	0.44	21	27	0.19
	Mullite-potato	0.43	53	71	0.075
MR	Mullite-cassava	0.46	22	26	0.18
	Mullite-corn	0.41	20	29	0.20
	Mullite-potato	0.41	52	75	0.077

determined by the density measurements and calculated porosities.

The mean intercept length values (\bar{L}) for the materials prepared with cassava and corn starches using SGR and MR were similar due to their similar microstructures and lower than those measured for the materials prepared with potato starch. This methodology did not allow determining significant differences between the pore size values (\bar{L}) obtained for samples prepared by SGR and MR. Moreover, the values obtained for each material and processing route were between the values corresponding to minimum and maximum Feret diameters, although they were closer to the minimum Feret diameters (Table 1) probably due to the high tortuosity of the formed pores.

As for \bar{D} , the values determined for all the materials followed the tendency determined previously for \bar{L} , as was expected when considering that this parameter geometrically links together \bar{L} and V_V parameters. Particularly, the \bar{D} value obtained for the samples formed with potato starch by using MR was higher than that obtained for the samples prepared by SGR, which indicates that a higher mean linear distance between pores is present in these materials in agreement with the behavior of this starch in this processing route, which was already mentioned.

Finally, the S_V/V_V ratio (specific surface density) takes into account the degree of dispersion (dispersiveness) of pores by specifying the area of the interface shared with the other phase (ceramic phase) with respect to the volume

density. The values obtained (~ 0.2 for the materials prepared with cassava and corn starches and ~ 0.08 for the material formed with potato starch, independently of the forming route) were in agreement with the fact that the lower pore size, the higher surface density.

3.2 | Thermal properties of developed porous mullite materials

Heat transfer in porous media generally occurs via three possible mechanisms: conduction, convection, and radiation. In many cases, the two last mechanisms can be disregarded depending on the porous solid characteristics and the temperature range. Thus, several expressions relate the relative thermal conductivity (k_r ; ratio of effective thermal conductivity of the porous material to thermal conductivity of the solid phase) to the porosity. This is the case with the Rusell and Ribaud expressions or the Maxwell-Eucken model, whose expression is identical to the Hashin-Strickman upper bound.^{2,21} In addition, other predictive relationships for thermal conductivity can be found by using the Coble-Kingery approximation ($k_r = 1 - 1.5\phi + 0.5\phi^2$, where ϕ is the volume fraction of pores) and that proposed by Živcová et al.³ This last predictive exponential relationship does not infringe on physical principles (in particular, it does not exceed the upper Hashin-Strickman upper bound), and is derived from the equivalent relationship of the Young's modulus with the porosity.

In the present work, the analysis of the influence of the volume fraction of pores on the thermal conductivity of the porous mullite materials and the comparison of the experimental data to the different analytical models were not performed because the developed materials presented a narrow porosity range.

In addition to its dependence on the microstructure, particularly with regard to porosity, solid thermal conductivity is a function of the temperature. When the heat transfer is governed by phonon scattering processes (conduction mechanism through the crystalline network), the thermal conductivity of the crystalline solid, in general, is decreased by increasing the temperature.³ There are few reports in which the simultaneous effect of the porosity and the temperature are considered,^{1,3,4} and still fewer that attempt to model the variation in the thermal conductivity with both parameters.

At first, the thermal diffusivity results for the porous mullite materials as a function of temperature (Figure 4) are discussed based on the abovementioned considerations.

For all the materials, the thermal diffusivity continuously decreased by increasing temperature, according to the decrease in the phonon heat transfer capacity of the matrix, with this decrease being more pronounced until reaching 400–500°C. On the other hand, none of the curves showed

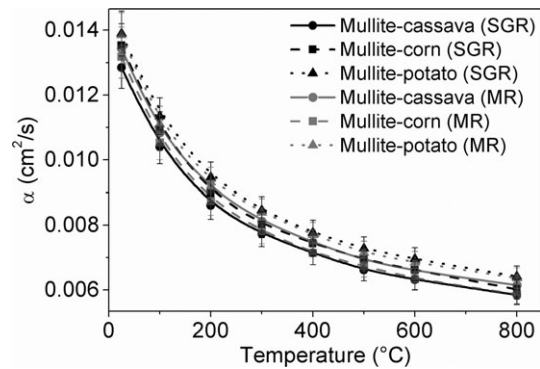


FIGURE 4 Thermal diffusivity as a function of temperature for porous mullite materials

the characteristic increase in the diffusivity values at the highest temperatures associated with the contribution of the heat transfer by gas convection and radiation at high temperatures in materials with high porosity. The obtained thermal diffusivity values for each material were similar to those reported by Barea et al.⁴ for similar mullite materials having the same porosity range (39–47%) as the studied materials. The obtained thermal diffusivity results were analyzed taking into account the precision of the laser-flash method. The samples prepared with potato starch by both processing routes presented the highest values of thermal diffusivity while those formed with cassava starch by SGR shown the lowest value. Thus, in a first insight into discussion of obtained results, it is evident that certain microstructural characteristics, in particular related to the material porosity, influenced this property.

As for the calculated thermal conductivities as a function of temperature for all the developed porous mullite materials, a moderate decrease ($\sim 27\%$) in this parameter (from $1.76\text{--}1.90\text{ W m}^{-1}\text{ K}^{-1}$ at 25°C up to $1.28\text{--}1.40\text{ W m}^{-1}\text{ K}^{-1}$ at 800°C) was observed by increasing the temperature (Figure 5). The behavior displayed and the obtained range of thermal conductivity were consistent

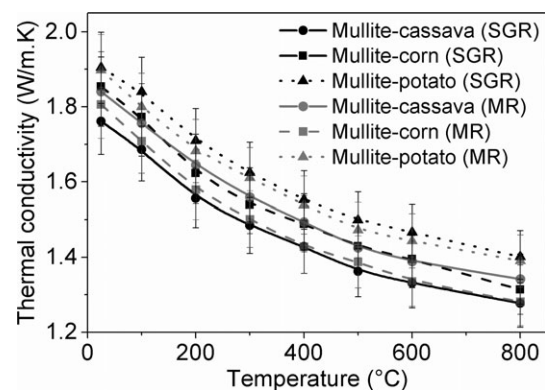


FIGURE 5 Thermal conductivity as a function of the temperature for porous mullite materials

with experimental data recorded by Barea et al.⁴ for porous mullite materials prepared also using SCC.

Considering the thermal conductivity value for denser mullite materials ($5.1 \text{ W m}^{-1} \text{ K}^{-1}$) reported by Barea et al.,⁴ the obtained thermal conductivity results indicate that the generated pore total volume allowed decreasing significantly the heat transfer in these materials. It is well known that, particularly with porous materials, the contribution of convection and radiation mechanisms begins to increase when the temperature is increased. This contribution depends on the pores and the mean free path of gas molecules which are inside them, and can be ignored at room temperature. It has been reported that the convection mechanism must be taken into account especially when the Grashof number exceeds a value of 1000, and that this mechanism in materials with pore sizes below $100 \mu\text{m}$ can be clearly ignored.³ On the other hand, although it has been established that the contribution of the radiation in porous ceramic materials is negligible even at 500°C ,³ other authors have considered the contribution of this mechanism as responsible for the increase in thermal diffusivity at the abovementioned temperature for materials with high porosity.^{1,22} Therefore, based on the characteristics of the developed mullite materials (mainly, porosity and pore size) and given considerations for this type of materials was assumed that the thermal conductivity is determined mainly by the mullite, with the contribution of the convection and radiation mechanisms being negligible.

As the tendency observed for the thermal diffusivity, the thermal conductivity values for samples prepared with potato starch by SGR and MR were the highest while the corresponding samples formed with cassava starch by SGR were the lowest. The lowest pore connectivity degree and the highest mean free path (\bar{D}) values determined for the samples prepared with potato starch support the obtained results due to the occurrence of a less hindered conduction into mullite matrix (Table 2). A similar justification could be given in order to explain the results obtained for samples prepared with cassava starch by using SGR. In this case, highest pore connectivity degree and the lowest mean free path values, besides the highest total pore volumes (total porosity and V_V), are consistent with the operation of a heat transfer mechanism by conduction more obstructed. According to abovementioned, the differences registered in the pore sizes (Feret diameters or mean intercept length, \bar{L}) for the analyzed materials were not decisive for the thermal conductivity. This result is in agreement with reported data which points out that, for a range of mean pore sizes between 1 and $100 \mu\text{m}$, the thermal conductivity does not depend on the pore size.^{3,23}

Finally, taking into account the range of obtained thermal conductivity values ($1.28\text{--}1.90 \text{ W m}^{-1} \text{ K}^{-1}$) along with the total porosity percentage (total porosity between

39% and 44% and $V_V=0.41\text{--}0.48$), the developed porous mullite materials are considered adequate to be used as thermal insulators. In particular, the porous mullite materials prepared with cassava starch by using SGR presented the lowest thermal conductivities in all the evaluated temperature range whereby they can be considered as the most promising candidates to be used as thermal insulators.

4 | CONCLUSIONS

Porous mullite materials with controlled microstructures were prepared by using different type of native starches and two novel shaping strategies which are based on the starch consolidation casting method. Porous associated with large cavities, whose size was determined mainly by the type of starch, with nonspecific tortuous morphology, embedded in a dense mullite matrix together with much smaller pore channels interconnecting the cavities were developed.

A complete characterization of the developed porous microstructures was carried out by analyzing 2D basic size and shape factors and global stereological parameters.

Minimum and maximum Feret diameters of pores for all the developed materials only depended on the starch type used for each processing route while the remaining 2D parameters analyzed were independent not only of the starch type but also the used processing route. Materials prepared with potato starch by both processing routes presented the highest values for these size parameters, although slightly smaller pore cavities were generated when MR was employed due to the occurrence of limited swelling in the gelatinization process.

Global stereological parameter values for all materials were consistent with the microstructural analysis carried out from SEM micrographs. In addition, the determined pore volume fractions were also consistent with density values. The mean intercept length and mean linear distance values for the materials prepared with cassava and corn starches using both routes were similar and lower than those measured for the materials prepared with potato starch. Moreover, for these last materials, the mean linear distance obtained by using MR was higher than that determined for the samples prepared by SGR.

The thermal behavior of the developed porous materials determined by the laser-flash method as a function of the temperature indicated that their thermal properties were determined mainly by the mullite phase. The accomplished analysis of the stereological parameters that characterize the porous mullite materials allowed delving in the study of the relationships existent between the pore parameters and the thermal properties. The highest pore connectivity degree and total pore volume values together with the lowest mean free path values presented for materials prepared

with potato starch were the characteristics that allowed explaining the obtained values of thermal conductivity. Moreover, the pore size represented by Feret diameter or mean intercept length, and the remaining microstructural parameters analyzed were not determining factors in the thermal conductivity of the developed mullite materials.

Finally, even though the range of obtained thermal conductivity values along with the total porosity percentage achieved for the developed materials allowed considering the porous mullite materials processed by both forming routes are adequate to be used as thermal insulators, the material prepared by SGR using the cassava starch can be considered as the most promising candidate for this application.

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