

Two alternative routes for starch consolidation of mullite green bodies

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Abstract

The starch consolidation forming method can be used in the manufacture of porous ceramics. In this method, based on swelling and gelatinization properties of starch in aqueous suspension at temperature (55–80 °C), the starch granules perform as both consolidator/binder of the green body and pore former at high-temperature.

Commercially available powders of mullite and cassava starch were employed as raw materials. Mullite/starch aqueous suspensions (0.25 starch volume fraction of 40 vol.% total solid loading) were prepared by intensive mechanical mixing and homogenization in a ball mill.

Two alternative forming routes of thermogelling mullite/starch aqueous suspensions—the Conventional Route (CR) and the Pre-Gelling Route (PGR)—were studied. With the CR, disks were formed by pouring the mullite/starch suspension at room temperature directly into metallic molds and heating at different temperatures (70 and 80 °C) and times (1 and 2 h). With the PGR, disks were shaped by pouring pre-gelled mullite/starch suspensions at 59 °C into heated molds and heating at the same experimental conditions. Once the consolidation process was finished, samples were removed of the mold and dried. Green bodies shaped by the two processing routes and obtained before (CR_{bb} and PGR_{bb}) and after (CR_{ab} and PGR_{ab}) burning out the starch, were characterized by bulk density and apparent porosity measurements and microstructural analysis by SEM/EDAX on the external and fracture surfaces. The homogeneity of the distribution of raw materials and pores, and the volume porosity were taken into account to establish the optimum consolidation conditions to be used in the preparation of mullite porous materials with homogeneous microstructures.

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1. Introduction

Porous ceramic materials exhibit several specific properties, such as low density, low specific heat, low thermal conductivity, high surface area, and high permeability. Ceramic materials with these properties can potentially be used in a wide range of technological applications, such as catalyst supports, bioceramics, filters, combustion burners, and thermal or acoustic insulators, among others. In particular, mullite (3Al₂O₃·2SiO₂) porous materials are employed as thermal insulators, among other applications, because of their low thermal expansion coefficient and thermal conductivity, and their good mechanical properties at high-temperature.^{1–5}

Each one of the mentioned applications requires the development of a specific volume porosity homogeneously distributed, pore size distribution and pore morphology as well as the selection of the ceramic matrix composition. The control of

these porosity parameters is one of the critical points to be considered in the processing of porous ceramics. The high demand of these materials with controlled porous microstructures in order to meet specific properties for a determined application has driven the development of new processing methods.^{6,7}

It is well known that forming is a key issue in the production of ceramic materials. Among forming methods by direct consolidation, in which the ceramic suspension consolidates into non-porous moulds (e.g. metal moulds) without compaction or removal of water, a new non-contaminating technique of low-cost, based on the gelling capability of starch in aqueous media at temperature (55–85 °C), has been developed for use in the manufacture of porous ceramics. It has been thus successfully employed for the production of porous bodies of alumina,^{8,9} cordierite⁶ and mullite,¹⁰ among others. In this method, the starch acts as a consolidator/binder agent of the ceramic particles and a pore former after burning out at high-temperature.^{6,7} Besides the favorable gelling properties of starches, they are environmentally friendly, easy to burn-out and, not least important, they possess a low-cost.

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When a ceramic aqueous suspension with starch is heated, the intermolecular bonds holding the granules together are weakened. During this process the granules undergo¹¹ different changes that take place in a process called gelatinization. The gelatinization process involves several physical and chemical changes such as water diffusion, granule swelling, amylose leaching, the disruption of crystalline structures, and the realignment and formation of new intermolecular and intramolecular bonds.¹² Consequently, the amount of water available gradually diminishes, the suspension viscosity increases and a transition to viscoelastic behavior and the formation of an elastic gel between 55 and 85 °C occurs (depending on the type of starch and other factors), which causes the consolidation of ceramic particles into a solid body. The variation of the rheological and morphological characteristics of the starch suspension as a function of variables such as temperature and time is one of the factors that affect the kinetic of green ceramic body formation and their microstructural features. Consequently, these changes also affect the final porous microstructure developed. In addition, particularly in the colloidal processing, when mixtures of powders with different densities (i.e. mullite (3.16 g/cm³) and starch (1.5 g/cm³)) are used, the sedimentation of particles during the forming process is a problem that must be avoided or minimized in order to develop homogeneous microstructures.

In the present work, two alternative forming routes of thermogelling mullite/starch aqueous suspensions—the Conventional Route (CR) and the Pre-Gelling Route (PGR)—were studied with the aim to developing porous green bodies with homogeneous microstructures, particularly with regard to distributions of raw materials (starch and mullite particles) and pores. The pre-gelling process of the suspension was proposed with the following objectives: (a) to increase the viscosity of the mullite/starch suspension and, consequently, minimize the possible segregation of mullite particles and starch granules and (b) to decrease the necessary time in order to achieve an uniform consolidation temperature in the total volume of suspension and, therefore, minimize possible thermal gradients in the sample which can produce microstructural inhomogeneities and defects caused principally by differential shrinkage.

The behavior of the starch in aqueous suspension at temperature (gelatinization process including swelling of the granules) and the characteristics of the gelatinized granules were taken into account in the analysis of the results.

Table 1

Particle size distribution parameters of raw materials.

	D_{50}	D_{10}	D_{90}
Cassava starch	13.6	5.6	21.8
Mullite	1.5	0.5	6.9

2. Experimental description

2.1. Raw materials and characterization

Cassava native starch commercially available in Argentina (Avebe S.A., Argentina) was used as a consolidator agent and binder of the ceramic particles. Real density of the starch ($\rho_p = 1.49 \text{ g/cm}^3$) was determined by He-pycnometry (Mulptipycnometer QuantaChrome Co., USA). The particle size distribution (Mastersizer S, Malvern Instruments Ltd., UK) was determined using an aqueous suspension of starch with an ammonium polyacrylate solution (Dolapix CE-64, Zschimmer & Schwarz, Germany) as dispersant and applying ultrasound for 15 min to disperse and stabilize the starch particles. Values of the median volume diameter (D_{50}), and granule diameters for 90 vol.% (D_{90}) and 10 vol.% (D_{10}) are given in Table 1. The starch presented a bimodal granulometric distribution, with a low volume percentage (<5%) of small granules (0.5–4 μm) that can be associated to impurities or broken granules. The weight percentage of humidity (11.5 wt.%) was determined by thermogravimetric analysis (Shimatzu TGA-50, Japan) at 10 °C/min up to 120 °C, in air. The starch transition temperature (T_p ; endothermic peak temperature = 67.5 °C) was determined by differential scanning calorimetry (DSC) (Shimadzu DSC-50, Japan) up to 120 °C at 5 °C/min using a highly diluted aqueous starch suspension (>70 wt.% water) placed into a sealed aluminum pan. Dry starch granules with some polyhedral morphology (Fig. 1) were observed by scanning electronic microscopy, SEM (Jeol JSM-6460, Japan).

The pycnometric density, humidity weight percentage and starch transition temperature obtained for the starch employed agreed with the values reported for cassava starches in similar experimental conditions.^{6,7,13,14}

A high-purity mullite (3Al₂O₃·2SiO₂) powder (MULS, Baikowski, France) was employed as ceramic raw material. The content of the elements was determined by wet chemical analysis. From this analysis, an impurity level <0.2 wt.% and an excess of alumina (3.0 wt.%) respect to the stoichiometric composition (Al₂O₃ = 71.8 wt.%, SiO₂ = 28.2 wt.%) were determined.

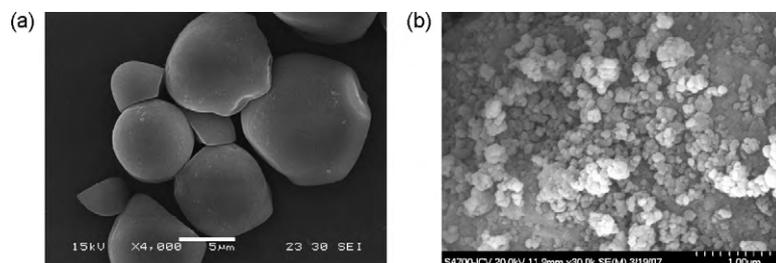


Fig. 1. SEM micrographs of (a) cassava starch and (b) mullite powder.

The last fact indicates that approximately 1 wt.% of Al_2O_3 does not form solid solution with mullite (up to 74 wt.% of Al_2O_3 forms solid solution with mullite¹⁵). This result is in agreement with the crystalline phases (mullite as majority phase and α -alumina and cristobalite as secondary phases) identified by XRD (Philips PW1830, $\text{CoK}\alpha$ radiation, at 30 mA and 40 kV), and with the pycnometric density value measured in kerosene at 37 °C ($\rho_p = 3.35 \text{ g/cm}^3$) which was discovered to fall midway between the theoretical densities of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (3.16 g/cm^3) and $\alpha\text{-Al}_2\text{O}_3$ (3.98 g/cm^3). The particle size distribution (Mastersizer S, Malvern Instruments Ltd., UK) was determined using an aqueous suspension of mullite powder and same experimental conditions than starch. The powder presented a bimodal particle size distribution with low values of D_{50} and D_{10} (Table 1) and agglomerates of up to 50 μm which were associated with the presence of very fine particles (Fig. 1). These results are in agreement with its high specific surface area ($13.5 \text{ m}^2/\text{g}$) determined by the BET method (Monosorb, Quantachrome Co., USA).

2.2. Preparation of mullite/starch suspensions

Mullite/starch aqueous suspensions (0.25 starch volume fraction of 40 vol.% total solid loading) were prepared by: (a) mixing (impeller mixer) mullite powder in water (40 vol.%) with 0.45 wt.% of Dolapix CE-64 (Zschimmer & Schwarz, Germany) as a dispersant (pH 8.7) with respect to the content of solid loading, (b) homogenizing in a ball mill for 6 h and (c) mixing the starch in the mullite suspension (impeller mixer) for 5 min. The optimum stability conditions of both mullite and mullite/starch aqueous suspensions were determined in a previous work¹⁶ from measurements of zeta potential (Zetasizer Nano ZS, Malvern Instruments, UK) and shear flow properties in controlled stress and controlled rate operating modes employing a rotational rheometer (Haake RS50, Thermo Electron Corp., Germany) with a double-cone/plate sensor configuration (DC60/2°, Haake, Germany).

Furthermore, the viscoelastic behavior (RDA-II, Rheometric Scientific, USA) of starch and mullite/starch aqueous suspensions as a function of temperature (30–95 °C) and strain (0.1–625%) was studied in a previous work¹⁷ in order to determine the consolidation experimental conditions. Based on the results obtained, isothermal heating at a temperature close to the corresponding onset of gelatinization temperature promoted the development of starch gels with both a higher resistance and structural stability to time. Consequently, in the context of ceramic-forming by starch direct consolidation, a specific dwell time at the gelling temperature of the suspension will provide green bodies with better properties than those obtained with treatments carried out at higher temperatures, as it is usually performed.^{6,7,10}

2.3. Starch consolidation of green bodies

Two alternative forming routes (Conventionally Route and Pre-gelling Route, labeled as CR and PGR, respectively) of thermogelling mullite/starch aqueous suspensions were studied. With the CR, disks were formed by pouring the mullite/starch

aqueous suspension at room temperature directly into stainless steel molds (diameter = 2.2 cm; height = 1 cm) kept at room temperature and heating in air (Memmert UFP 400, Germany, electric stove with circulation of forced air) at two temperatures (70 and 80 °C) and times (1 and 2 h). With the PGR, disks were shaped by pouring of pre-gelled mullite/starch suspensions at 59 °C (temperature slightly lower than the onset gelatinization of cassava starch (64 °C)), into stainless steel molds heated at 70 and 80 °C in thermostated water bath, and heating in electric stove (Memmert UFP 400, Germany) at the same temperatures and times employed with the CR. With both routes, the molds were coated with Teflon tape. Once the consolidation process was finished, samples were removed from the molds and dried in a ventilated oven at 40 °C for 24 h (labeled as CR_{bb} and PGR_{bb}). Finally, mullite green bodies (CR_{ab} and PGR_{ab}) were obtained by burning out the starch. This treatment was carried out at a heating rate of 1 °C/min up to 650 °C for 2 h in an electrical furnace with SiC heater elements. The debinding temperature was chosen from thermogravimetric analysis results (Shimadzu TGA-50, Japan; at 10 °C/min up to 900 °C, in air).

2.4. Characterization of green bodies

The weight loss percentage of water (WL) by drying was calculated from $100 \cdot (m - m_d)/m$ (where m and m_d are the masses of the samples before and after drying, respectively). The green densities (ρ_g) of the disks obtained before (CR_{bb} and PGR_{bb}) and after (CR_{ab} and PGR_{ab}) burning out were determined by immersion in Hg (Archimedes method), with an error associated of $\pm 10\%$. Porosities ($\% P_g$) were calculated from $100 \cdot (1 - \rho_g/\rho_p)$. For CR_{bb} and PGR_{bb} , the real density of the powdered mixture of mullite and starch ($\rho_p = 2.66 \text{ g/cm}^3$) was determined by He-pycnometry. For CR_{ab} and PGR_{ab} materials, ρ_p was 3.35 g/cm^3 (pycnometric density of the mullite powder). The microstructural analysis of the green materials by SEM (Jeol JSM-6460, Japan) was carried out on the external and fracture surfaces of the disks obtained before and after burning out. In addition, elementary analysis of carbon by EDAX (Genesis XM-2-Sys) was also carried out on the external and fracture surfaces of disks obtained before burning out. In this case, the starch distribution throughout the thickness of the samples was analyzed from carbon profiles obtained by C lineal scanning (EDAX).

3. Results and discussion

3.1. Characterization of green disks

The weight loss percentage of water (WL) by drying, and porosity of the green disks prepared by both forming routes (CR and PGR) and obtained before ($\% P_{g\text{-bb}}$) and after ($\% P_{g\text{-ab}}$) burning out are shown in Table 2.

For both processing routes, an increase of the consolidation temperature produced a slight decrease in the weight loss percentage of water (WL) by drying. However, an increase of the consolidation time at 70 or 80 °C caused a notable decrease in WL. This last fact indicates the presence of a lower amount of free water before the drying process in the samples consolidated

Table 2
Weight loss percentage (WL) and porosity (% P_{g-bb} and % P_{g-ab}) of the green disks.

Processing route	Temperature (°C)	Time (h)	WL (wt.%)	% P_{g-bb}	% P_{g-ab}
CR	70	1	7.8 ± 1.9	55	63
		2	0.6 ± 0.2	54	62
	80	1	4.3 ± 0.4	54	64
		2	0.1 ± 0.01	52	64
PGR	70	1	12.3 ± 0.2	52	65
		2	0.8 ± 0.3	53	66
	80	1	11.0 ± 2.8	55	69
		2	1.5 ± 0.9	53	69

for 2 h, facilitating the handling and, consequently, the removal of green compacts from the molds.

CR_{bb} and PGR_{bb} disks prepared at both temperatures and times achieved similar porosity values (52–55 ± 5%). On the other hand, the porosity of mullite green disks obtained by two forming routes significantly increased after burning out the starch (CR_{ab} and PGR_{ab}), achieving values higher than 62% (Table 2). These values resulted consistent with calculated values (% $P_{g-c} = 65 ± 4$) assuming that whole the added starch was removed during burn-out process. However, CR_{ab} disks presented a slightly lower porosity than % P_{g-c} , which could indicate that part of the removed starch did not generate pores into the body volume.

Typical SEM free surface micrographs of CR_{bb} and PGR_{bb} disks are presented in Fig. 2. One of the most significant differences between the microstructures developed by CR and PGR is the presence or absence of starch granules (confirmed by EDAX¹⁹) that preserved their integrity. These starch granules together with granules without integrity and, principally, amylose molecules leached by the granules as they swell, form the gel structure in the green disks providing a binding effect between ceramic particles. In several SEM micrographs, fine particles of

mullite forming agglomerates coated a certain area of the starch granule surface. The slight porosity differences determined from density measurements (Table 2) are not clearly seen in SEM micrographs.

A high amount of starch granules with morphology similar to the dry starch granules (Fig. 1) were observed in CR_{bb} obtained at 70 °C for 1 and 2 h (Fig. 2.a). The granule sizes observed by SEM (15–30 μm) are within the range of the values determined for dry starch granules and granules swelled at temperatures lower than 70 °C.¹⁸ This could indicate that a great proportion of granules (smaller granules) did not swell or were slightly swollen. However, the presence of swollen granules without integrity cannot be ruled out. For CR_{bb} prepared at 80 °C for 1 and 2 h, a slightly lower amount of starch granules were observed (Fig. 2.b) which showed similar sizes to those observed at 70 °C for 1 and 2 h. This result is consistent with the fact that by increasing the consolidation temperatures, a higher rupture of granules during gelatinization process is facilitated.

In all the PGR_{bb} disks, a limited amount of starch granules of lower size than those present in CR_{bb} was observed (Fig. 2). At both temperatures the starch granule sizes did not change by increasing the consolidation time, while an increase in consoli-

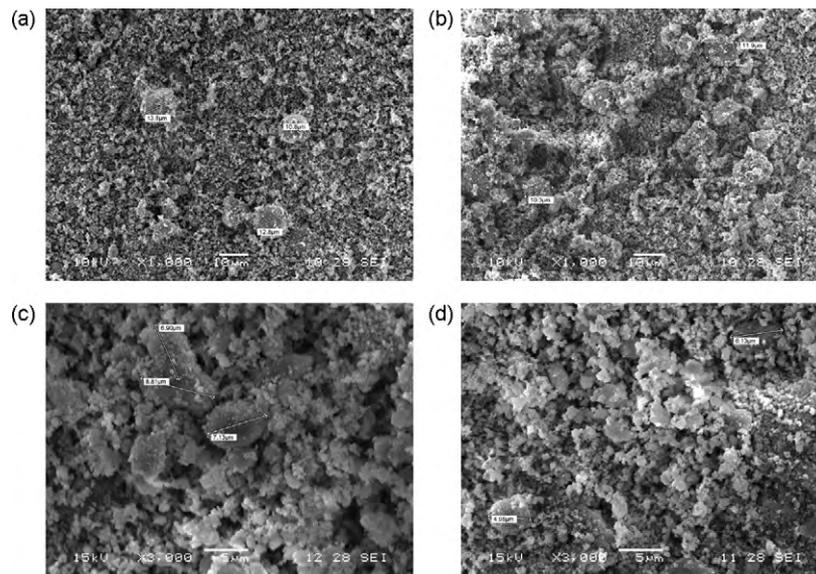


Fig. 2. Typical SEM free surfaces of CR_{bb} materials prepared at (a) 70 °C and (b) 80 °C, and PGR_{bb} materials prepared at (c) 70 °C and (d) 80 °C.

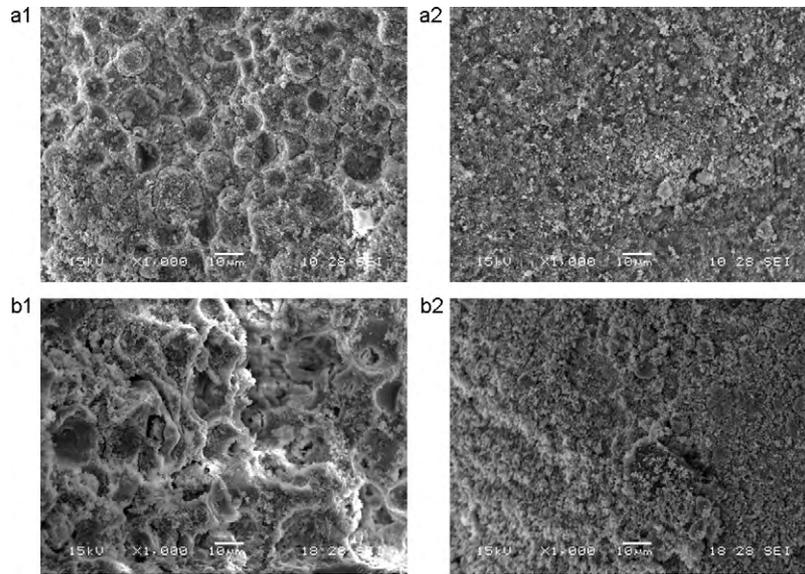


Fig. 3. SEM fracture surface images characteristic of upper (a1 and b1) and bottom (a2 and b2) regions of (a) CR_{bb} and (b) CR_{ab} disks.

ation temperature from 70 up to 80 °C allowed the observation of lower size granules (3–9 µm for 70 °C, and < 5 µm for 80 °C). These results could be attributed to the occurrence of a high gelatinization degree in the larger number of the starch granules at the higher temperature, which would produce the loss of integrity or rupture of the granules, mainly, those of greater size.

Typical SEM fracture surface micrographs of the green disks prepared by CR and PGR and obtained before and after burning out are shown in Figs. 3 and 4, respectively.

The CR_{bb} and CR_{ab} images correspond to the upper region (close to the free surface) and the bottom region of the disks. For these materials, as the temperature and time of consolidation did not determine significant changes in their microstructural features, typical microstructures are shown (Fig. 3).

On the other hand, the fracture surface microstructures of the materials prepared by PGR in each experimental condition and

obtained before and after burning out the starch were found to be similar throughout the whole thickness of the disks. Moreover, as was observed in CR_{bb}, the time was not a determinant variable in the developed microstructures. Therefore, for PGR_{bb} and PGR_{ab} materials, only a typical microstructure developed for each temperature is shown (Fig. 4).

It is noteworthy that the proposed processing routes notably influenced the microstructural homogeneity in green compacts, principally, with respect to starch distribution.

In CR_{bb} fracture surfaces, for both times (1 and 2 h) and temperatures (70 and 80 °C) of consolidation, the region next to the free surface presented a significantly different microstructure to that of the bottom region of the disk. In the upper region (Fig. 3a1), a high amount of starch granules that preserved their integrity were easily observed while in the bottom region (Fig. 3a2) of the disk, a very limited amount of granules was

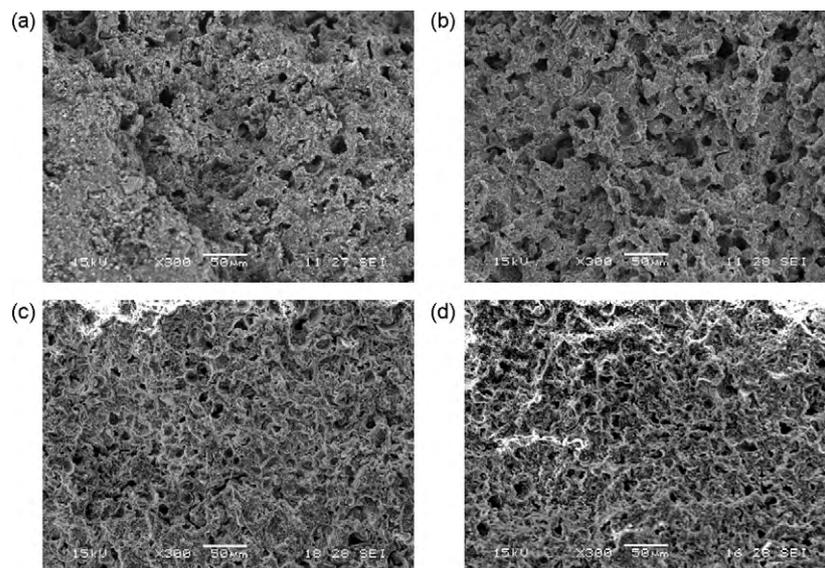


Fig. 4. Typical SEM fracture surfaces of PGR_{bb} disks prepared at (a) 70 °C and (b) 80 °C, and PGR_{ab} materials prepared at (c) 70 °C and (d) 80 °C.

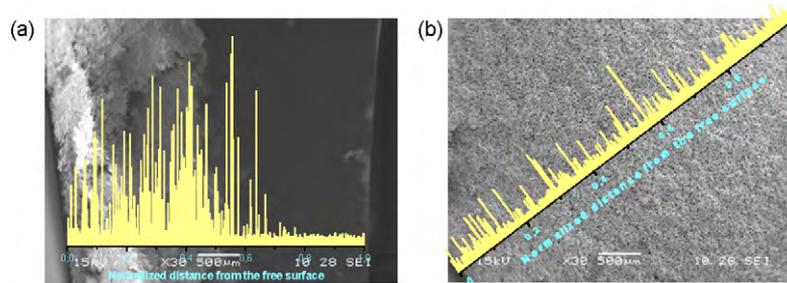


Fig. 5. Carbon profiles obtained by lineal scanning (EDAX) throughout the thickness of samples prepared by (a) CR and (b) PGR.

observed with difficulty. The starch granules in the upper region presented a similar morphology to the dry starch granules and similar sizes (15–30 μm) to those observed by SEM in the free surface (Fig. 2). These results indicate the occurrence of a certain degree of sedimentation of the mullite particles in all the CR_{bb} disks. Consequently, a great proportion of starch granules swelled slightly or did not swell due to a deficit of available free water, remaining in the upper region. Thus, it results highly probable that a great amount of these granules did not contribute to increase the volume porosity of the green body by burning out.

In this manner, this inhomogeneous distribution of raw materials is the origin of the density gradients in the green disks. Therefore, the given porosity values should be only considered as global values.

In the upper region of the CR_{ab} disks, it is observed the apparition of holes whose morphology and sizes resulted determined by the starch granules present in CR_{bb} materials (Fig. 3b1). Conversely, the bottom region of these materials (Fig. 3b2) did not present significant changes in the microstructures developed after removal starch.

On the other hand, according to the fracture surface microstructures of PGR_{bb} disks obtained at all the studied consolidation conditions (Fig. 4), in which starch granules with integrity were not observed, the degree of segregation could be considered insignificant. This consideration is supported, in part, taking into account that a high degree of gelatinization occurs in all the starch granules when a high amount of water is available for all of them. In these materials, a higher porosity was observed by increasing the temperature from 70 up to 80 °C, as much for 1 as 2 h (Fig. 4a and b), which was not clearly evidenced from determined porosity values (Table 2). Channels with high tortuosity degree were observed throughout the whole thickness of disks. This result could be associated with a higher proportion of granules involved in a much more advanced gelatinization process (total loss of the granule morphology in the gel structure), in particular, due to the effect produced by the high-temperature. In the PGR_{ab} materials a significant increment in the porosity amount was observed, keeping the tortuous morphology of the channels developed in whole the volume (Fig. 4c and d).

In addition, from the semi-quantitative analysis of the carbon distribution accomplished by C lineal scanning (EDAX) throughout the thickness of the disk, it was possible to corroborate the different distributions of the starch obtained in the green materials prepared by the CR and the PGR. In Fig. 5, typical

average carbon profiles obtained in CR_{bb} and PGR_{bb} samples are shown.

Thus, it is inferred that a high advance degree of the gelatinization can be obtained for a homogeneous distribution of raw materials (PGR_{bb}), which is supported for the null amount of starch granules observed by SEM.

4. Conclusions

A more homogeneous distribution of raw materials, and therefore, porous homogeneous microstructures, before and after of the burn-out process, were developed by including a pre-gelling step in the conventional forming process by starch direct consolidation. Thus, the segregation of mullite particles and starch granules, and consequently, the generation of thermal gradients in samples, were minimized due to the increase of the viscosity of the mullite/starch suspension and decrease of the necessary time to achieve a uniform consolidation temperature in the total volume of suspension.

For the proposed PGR processing, before and after of the elimination of the starch, a slight increase of the green porosities by increasing the consolidation temperature was observed. Conversely, an increase of the time of permanence at the consolidation temperature did not produce a relevant effect on microstructures since the gel formation process occurred during the first moments after pouring. However, a high consolidation time facilitated the removal of the mold and handling of the green disks, in particular, when the Conventional Route was employed.

Based on the obtained results, materials with high porosity and a more homogeneous distribution of pores can be developed by the proposed pre-gelling processing route.

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