Green mechanical evaluation of mullite porous compacts prepared by pre-gelling starch consolidation

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ARTICLE INFO

ABSTRACT

The mechanical behavior of green porous mullite disks (volume porosity > 55%) prepared by the thermogelation of mullite aqueous suspensions with different native starches (i.e. potato, cassava and corn starches) was studied. One set of disks was prepared by thermal consolidation (70–80 °C, 2 h) of aqueous mullite suspensions (40 vol.%) containing 10 vol.% of starch pre-gelled at 55–60 °C and dried at 40 °C for 24 h. Another set of specimens was prepared by additional firing at 650 °C for 2 h to burn-out the starches. Both sets of disks were characterized by density measurements (Archimedes method), apparent porosity calculus, and microstructural analysis by SEM. Mechanical parameters such as fracture strength, apparent elastic modulus, fracture and final deformations and yield stress were determined from apparent stress–strain relations derived from load-displacement curves obtained by diametral compression testing. Moreover, typical crack patterns were evaluated and fractographic analysis was carried out by SEM. Mechanical results were analyzed in relation to the behavior of the starches in aqueous suspension and the properties of the developed gels, together with the respective microstructures before and after the burn-out process. Mechanical data were also considered taking into account the possibility of machining the green compacts formed by pre-gelling starch consolidation.

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1. Introduction

Green machining of pre-forms is currently used for forming small, symmetrical parts. However, machining is generally limited to grinding and cutting because the green bodies are not strong enough to withstand the conventional processes of milling, drilling and lathing [1,2]. Consequently, in the optimization of the overall production cycle of ceramic pieces, the improvement of the green bodies' mechanical properties is one of the key points that must be considered. In particular, the key parameter for machining ceramic pieces is fracture strength: the green body must be strong enough to resist the stresses induced by machining and clamping without fracturing. As a reference, a mechanical strength of 2 MPa is considered high enough to bear the stress induced by the machining process [3,4]. The use of gelling agents for shaping ceramic bodies improves the mechanical properties with respect to those materials prepared by conventional forming methods [5,6], particularly by increasing mechanical resistance. Therefore, the binder system (gelling agents) and its content must be chosen carefully since it is critical for achieving high ceramic solid loading and strong interfacial bonding between ceramic particles. The toughness, the work

of fracture and the hardness of the ceramic compacts are other properties considered in the optimization of the green machining process [2,3,7,8].

Among the new colloidal processing methods, the starch direct consolidation technique has been developed in the manufacture of porous ceramics. Thanks to the control of the pieces' dimensions that can be achieved by this method, it is a promising near net-shaping technique [9]. Moreover, the use of starches has additional advantages, such as reduced environmental impact and low cost. With this method [10–13], the starch acts as a binder of the suspended ceramic particles and as a consolidator agent by thermogelation of the ceramic aqueous suspension at 55–85 °C. It is also a pore former after consolidation by burn-out at high-temperature. As a consequence of the formation of an elastic starch gel, which occurs due to the starch gelatinization process, the green body's mechanical resistance is increased. The authors' use of native starches [14] in the consolidation of mullite porous compacts had the disadvantage of causing inhomogeneous green microstructures, partially due to the different densities of the raw materials (starches and oxide particles). An alternative to this conventional starch consolidation forming route was conceived in order to surmount this problem: the pre-gelling route (PGR) [14]. This alternative forming route enabled us to obtain porous homogeneous microstructures both before and after the burn-out process.

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In the present work, green porous mullite disks formed by the pre-gelling of a ceramic–starch aqueous suspension prepared with different native starches (cassava, corn and potato) were mechanically evaluated in diametral compression. The results were analyzed in relation to developed microstructures before and after the burn-out process, the behavior of the starches in aqueous suspension and the properties of the formed gels. Burned mullite disks were also mechanically evaluated. The machinability of the green mullite compacts was thus evaluated using the experimental mechanical data and the main properties for optimizing green machining

2. Experimental

2.1. Preparation and characterization of green bodies

A high-purity mullite ($3Al_2O_3 \cdot 2SiO_2$) powder (MULS, Baikowski, France) and native potato, cassava and corn starches commercially available in Argentina were used as the ceramic raw material and the consolidator/binder agent, respectively. The physical and viscoelastic properties of the employed starches were already studied in previously reported work [15]. The elementary analysis of the mullite powder was performed by wet chemical analysis, which revealed an impurity level less than 0.2 wt.%. An excess of alumina (3.0 wt.%) with respect to the stoichiometric composition ($Al_2O_3 = 71.8$ wt.%, $SiO_2 = 28.2$ wt.%) was estimated, indicating that approximately 1.0 wt.% of Al_2O_3 does not form a solid solution with mullite (up to 74 wt.% of Al_2O_3 dissolves mullite) [16]. This result agrees with the X-ray diffraction analysis (XRD; Siemens D5000, CuK$_\alpha$, at 30 mA and 40 kV, and at 1° 2θ/min) performed on the crystalline phases (mullite as primary phase and α-alumina and cristobalite as secondary phases) as well as the pycnometric density value measured in kerosene at 37 °C ($\rho_m = 3.35$ g/cm^3) which was discovered to fall midway between the theoretical densities of $3Al_2O_3 \cdot 2SiO_2$ (3.16 g/cm^3) and α-Al_2O_3 (3.98 g/cm^3). The powder presented a bimodal particle size distribution (Mastersizer S, Malvern Instruments Ltd., UK) with a low mean volume diameter ($D_{50} = 1.46$ μm), and a high volume percentage of fine particles <1 μm, and contained agglomerates up to 50 μm associated with the presence of the very fine particles. These results are consistent with the high value of specific surface area (13.5 m^2/g) determined by the BET method (Monosorb, Quantachrome Co., USA).

Real densities determined by He-pycnometry (Multipycnometer, Quantachrome Co., USA) were 1.47 g/cm^3 for potato starch and 1.49 g/cm^3 for cassava and corn starches. The particle size distributions (Mastersizer S, Malvern Instruments Ltd., UK) were determined using an aqueous suspension of starch with a carboxylic acid based polyelectrolyte solution (Dolapix CE-64, Zschimmer & Schwarz, Germany) as a dispersant and by applying ultrasound for 15 s to disperse and stabilize the starch particles. All the starches presented bimodal granulometric distributions with a low volume percentage (<5%) of small granules (0.5–4 μm for corn and cassava starches and 0.6–10 μm for potato starch), which can be linked to impurities or broken granules. The median volume diameter for potato starch ($D_{50} = 47.8$ μm) was notably greater than the corresponding values of the other starches ($D_{50} = 13$–15 μm). The granule morphology analysis of the dry starches was carried out by SEM (Jeol JSM-6460, Japan). Potato starch exhibited the largest granules, with smooth surfaces and oval or spherical forms. The rest of starches presented granules with some polyhedral morphology, with corn starch granules exhibiting the most. The variation in size and morphology of starch granules is attributed to their biological origin.

Aqueous mullite–starch 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) homogenization in a ball mill for 6 h to stabilize the suspension, and (c) adding starch and mixing (impeller mixer) for 5 min. The optimum stability conditions for preparing the aqueous mullite [17] and mullite–starch [18] suspensions and forming experimental conditions by thermogelation of aqueous suspensions had been determined previously [15].

The pre-gelling process [19] of the each mullite/starch suspension was carried out at a temperature slightly lower than the onset gelatinization temperature of the starch. This process was proposed with the following objectives: (a) to increase the viscosity of the mullite/starch suspension and, consequently, to minimize the possible segregation of mullite particles and starch granules, and (b) to decrease the time required to achieve a uniform consolidation temperature throughout the entire suspension and, therefore, to reduce microstructural inhomogeneity and defects caused mainly by differential shrinkage. The experimental conditions suitable for achieving these objectives when forming green mullite compacts were determined by the authors in previous works [14,18].

One set of disks was shaped by pouring pre-gelled mullite/starch suspensions at 55–60 °C into stainless steel molds coated with Teflon tape (diameter = 2.2 cm; height = 1 cm), which were previously heated at 70 or 80 °C in a sand bath and an electric stove (Memmert UFP 400, Germany) up 70 or 80 °C, respectively, for 2 h. Once the consolidation process was complete, samples were removed from the molds and dried in a ventilated oven at 40 °C for 24 h. Disks formed with cassava, corn and potato starches were labeled as Ca_{bb}, Co_{bb} and Po_{bb}, respectively.

A second set of disks was prepared by burning out the compacts further in order to eliminate the starches. The burned disks were labeled as Ca_{ab}, Co_{ab} and Po_{ab} when cassava, corn and potato starches were used as the thermogelling agent. The thermal 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 (Shimatzu TGA-50, Japan; at 10 °C/min up to 900 °C, in air). A very low heating rate (1 °C/min) was employed in order to minimize the generation of defects in the green bodies or their rupture during the burn-out process due to the high volume of gas that evolved (mainly water vapor and carbon dioxide) brought on by the oxidative degradation of the starch.

The real density of the mullite–starch powder mixture (ρ_p) determined by He-pycnometry (Multipycnometer, Quantachrome Co.) was 2.66 g/cm^3. The bulk densities of disks (ρ_g) before and after the burn-out were determined by immersion in Hg (Archimedes method). Apparent porosities of disks before (% P_{bb}) and after burn-out (% P_{ab}) were calculated from the experimental densities as: $100(1 - \rho_g/\rho_x)$ where ρ_x is the pycnometric density of the starting mullite powder ($\rho_m = 3.35$ g/cm^3) or ρ_p.

The microstructures of the fracture surfaces on burned and unburned disks were analyzed by SEM (Jeol JSM-6460, Japan).

2.2. Mechanical testing

An INSTRON model 8501 servohydraulic machine was used for the mechanical testing, employing a load cell of ±5 kN maximum load (accuracy greater than 0.25% in the whole load range) and steel platens (R_c: 65). In all the tests, MoS_2 lubricant paste was applied on the platen surfaces in contact with the disk to reduce the effect of friction; white and carbon papers were placed together between each platen and the disk for load distribution (padding material) [20]. The tests were performed in displacement control; the displacement rates were previously adjusted in order to avoid temporal effects (e.g. subcritical crack grow) and to achieve

an adequate arrangement of the sample in the load system. Displacement rates of 0.8 mm/min were selected for Ca_{bb} and Co_{bb} disks, 0.6 mm/min for Po_{bb}, and 1 mm/min for burned disks. Eight to twelve specimens of each set of compacts were mechanically tested. The duration of each test was approximately 1 min.

From the load (P) versus displacement (d) curve, the apparent stress (σ)–strain (ε) relationship was obtained by calculus, employing the following equations [20,21]:

$$\sigma = \frac{2P}{\pi Dt} \tag{A}$$

$$\varepsilon = \frac{d}{D} \tag{B}$$

where P is the load, D and t are the diameter and the thickness of the disk, respectively, and d is the actuator displacement. The diameter (D) of the tested disks was four times larger than the thickness (t) to ensure that only a plane stress state was tested and to decrease the non-uniformity of the axial distribution of the applied load in order to validate the use of Eq. (A) [22]. From σ vs. ε curves, the following parameters were determined: mechanical strength (σ_F) using the maximum load; the fracture strain (ε_F) considered as the strain corresponding to the maximum load; the strain at the end of the test (ε_U); the apparent elastic modulus (E_a) determined as the slope of the linear part of the curves; and the apparent elastic limit (σ_Y) defined as the stress where the deviation from the linear behavior is 1% [21]. The percentage ratio σ_Y/σ_F, considered as the degree of deviation from the linear behavior caused by some irreversible strain mechanism (such as global plasticity and/or located plasticity, compacting and microcracking) was also calculated.

It is worth clarifying that the 'apparent elastic modulus' (E_a) is a stress–strain ratio corresponding to orthogonal space directions (i.e. X and Y axis). On the other hand, the actuator displacement (d) does not correspond to a direct measurement on the disk, although the high stiffness of the employed machine and the low load supported by the tested specimens make Eq. (B) a good estimation of disk deformation. Thus, all the contributions to the disks' overall deformation, independently of type (elastic, non-elastic, plastic) and the location—this point is relevant in this type of test because the contact zone is affected by the compression platens [20,21,23]—are included in the (value. These restrictions limit the value of E_a to an 'apparent elastic modulus'.

The fracture features of the tested disks were evaluated by ocular inspection during and after the mechanical tests. In addition, fractographic analysis was performed by SEM (Jeol JSM-6460, Japan).

3. Results and discussion

3.1. Characterization of disks

The mean apparent porosity values of the starch-containing mullite compacts (% P_{bb}) and the compacts after the burn-out process (% P_{ab}) are shown in Table 1. Considering the experimental error of the Archimedes technique, the standard deviation of the porosity values is ±10%.

Table 1
Mean apparent porosity values (% P_{bb} and % P_{ab}) of mullite disks.

Systems	Consolidation temperature (°C)	% P_{bb}	% P_{ab}
Mullite–cassava	70	56	69
	80	56	69
Mullite–corn	70	57	70
	80	56	69
Mullite–potato	70	59	70
	80	58	71

For each studied mullite–starch system, the consolidation temperature did not have a significant influence on the obtained porosity values for any of the sets of mullite compacts. However, the green disks consolidated with potato starch achieved higher porosities (% P_{bb}) than those prepared with the remaining starches (confidence limit higher than 99.5%). The differences in porosity between Co_{bb} and Ca_{bb} were not considered statistically significant. This variation is partially due to the differences in the capacity to retain the water both physically and chemically in the structure of the starch gel developed in the consolidation conditions employed in this study. The water retention capacity defined as the ratio between the mass of water in the gel and the mass of starch in the gel [24] was determined at a gelling temperature of 80 °C. Potato starch gel had the highest water retention capacity (8.3) while the corn and cassava starch gels exhibited lower values (6.9 and 6.5, respectively). Thus, the most open gel structure is generated by the potato starch, which explains why the green disks prepared with this starch develop the highest porosity. Moreover, the incidence of other differences in the gel's structural characteristics in the presence of the ceramic particles [18] cannot be ruled out.

On the other hand, the porosity of the green disks significantly increased after the starch was removed by the burn-out process (% P_{ab}), achieving values between 69 and 71%. In general, these values were consistent with those obtained by calculation (% $P_c \approx 69$) assuming that all the added starch was removed during the burn-out process. The highest porosity values (% P_{ab}) achieved in the disks after the burning out process were obtained when potato starch was used as the gelling agent (confidence limit higher than 92.5 and 82.5% when is compared Po_{ab} with Ca_{ab} or with Co_{ab}, respectively). However, the difference between the porosities of Ca_{ab} and Co_{ab} were not considered statistically significant.

Typical fracture surface micrographs obtained by SEM of the green disks before the burn-out process are shown in Fig. 1. No significant variation in the apparent porosity with the consolidation temperature was observed, in agreement with the calculated porosity values reported in Table 1. The porosity was mainly associated with the highly tortuous interconnected cavities distributed throughout the whole thickness of the disks. These features are attributed to the high proportion of granules involved in a much more advanced gelatinization process, i.e. the total loss of the granule integrity in the gel structure. All the burned disks showed a significant increase in porosity compared to the green bodies containing starch. Similar microstructural features to those observed in green disks before burn-out were observed throughout the whole volume of the burned disks (Fig. 1). In each set of disks, the largest cavities were observed in those materials obtained from potato starch Po_{bb} and Po_{ab} (approximately twice the size of the cavities observed in disks prepared using cassava and corn starches in both sets of compacts).

3.2. Mechanical evaluation

Stress–strain curves corresponding to green disks before and after the burn-out process are shown in Fig. 2, and the mean and standard deviation values of mechanical parameters are given in Table 2.

For each mullite–starch system, the differences between the mechanical parameters of the disks consolidated at 70 and 80 °C were not significant in either of the two set of disks (before and after the burn-out process), which is in agreement with the similitude in the microstructural characteristics (with respect to the amount, size and morphology of pores in particular) shown for these materials. For this reason, the values of the mechanical parameters corresponding to both consolidation temperatures were included in the same population for each
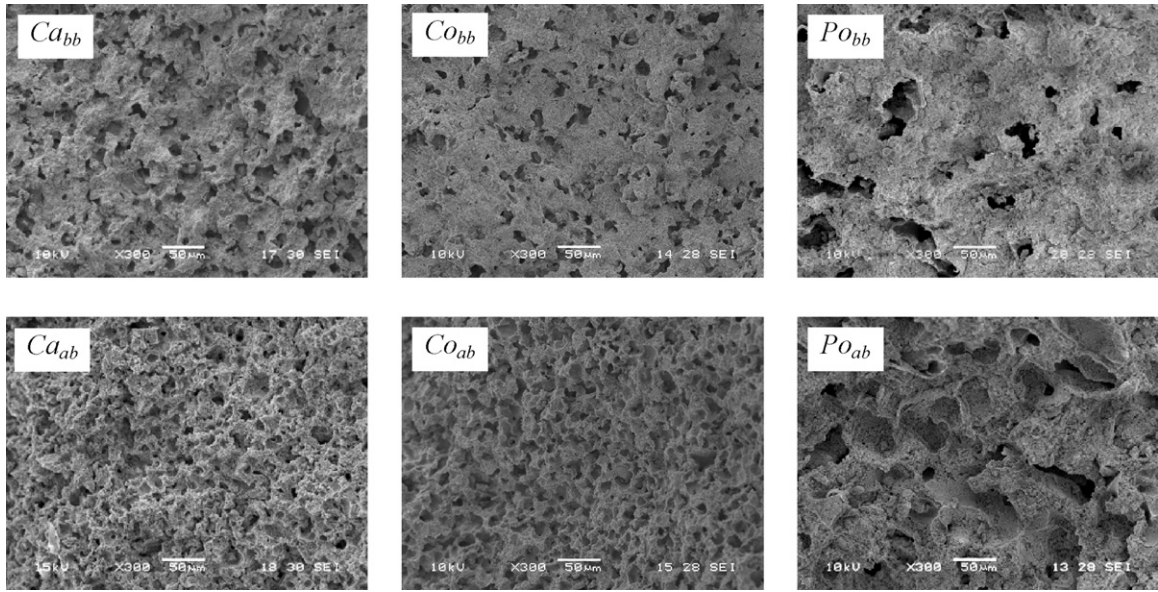
Fig. 1. SEM fracture surfaces of green disks, before and after the burn-out process.

mullite–starch system, and they were treated altogether to obtain the mean value and its standard deviation. On the other hand, the differences between all of the mechanical parameters of the compacts prepared from the three starches were significantly different, with limits of confidence higher than 99.5% in every case.

The stress–strain curves of the green disks before the burn-out process (Fig. 2a) show a deviation from linearity, in particular in Ca_{bb} and Co_{bb}. This behavior was attributed to a certain amount of irreversible deformation (although a non-linear elastic behavior of the materials cannot be ruled out) due to the starch's plastic behavior and microcracking; this last mechanism might predominantly occur in the contact zone between the disks and the compression platens. The densification by compacting [23], which can also lead to permanent deformation of the material, was not verified by SEM fractographic analysis, as shown below. On the other hand, the fracture of Ca_{bb} and Co_{bb} occurred suddenly once the maximum load was reached, whereas in Po_{bb}, fracture was less catastrophic and exhibited a more gradual decrease of the load. As a consequence, the fracture deformation value (ε_F) for Ca_{bb} and Co_{bb} coincided, or almost coincided, with the deformation at the end of the test (ε_U) whereas in Po_{bb}, ε_U was higher than ε_F. In any of the cases, the characteristics of the stress-strain curves manifest a quasi-brittle behavior.

The σ_Y/σ_F ratio (Table 2), as a quantitative estimation of the degree of deviation from linearity, was higher in Po_{bb} (lower deviation from the linear elastic behavior) than in the remaining materials. This fact was attributed to the low load-bearing capacity of these disks, which hindered the development of the mechanisms leading to a permanent deformation, or to the inherent characteristics of the mullite–potato starch matrix.

Typical crack patterns for each system before and after the burn-out process are shown in Fig. 3. Crack patterns characteristics of a diametral compression test were observed in all the unburned green disks [20].

In general, Ca_{bb} and Co_{bb} showed a slight deformation in the contact zones with the compression platens when low loads were applied, followed by small superficial chipping in these regions; the presence of a permanent deformed contact area confirmed the occurrence of irreversible deformation mechanisms. Afterwards, at higher loads, a crack begun at the center of the specimen and propagated diametrally toward the contact region. The presence of secondary cracks was also observed in some disks consolidated with cassava starch (33%). The early chipping in the contact region between the disk and the compression platens was attributed to the presence of shear stresses (at the beginning, stress is concentrated in this zone due to the finite rate of load transmission in the material) and the lower resistance of the materials to this sort of loading [25]. The sudden fall of the load observed in stress–strain curves is caused by the propagation of the diametral crack. The appearance of secondary cracks in Ca_{bb} was related to the high load-bearing capacity of these disks, which induces stress near the region of compression platens [23] high enough to initiate these cracks.

In Po_{bb}, the steps mentioned above (delamination, and then diametral fracture) occurred simultaneously; these specimens showed a principal diametral crack, and no permanent deformed contact area was observed in most of the cases. This last fact is in agreement with the low bearing–load capacity of Po_{bb}, which hindered the development of mechanisms causing permanent deformation, and is consistent with the high σ_Y/σ_F ratio and the low ε_F and ε_U values for this material in comparison with the compacts consolidated with the remaining starches.

Table 2
Values of the mechanical parameters.

	σ_F (MPa)	ε_F	ε_U	$(\sigma_Y/\sigma_F) \times 100$	E_a (GPa)
Ca_{bb}	2.5 ± 0.6	0.035 ± 0.004	0.035 ± 0.004	53 ± 8	0.11 ± 0.02
Ca_{ab}	0.21 ± 0.03	0.03 ± 0.01	0.04 ± 0.01	77 ± 9	0.017 ± 0.002
Co_{bb}	2.1 ± 0.4	0.029 ± 0.007	0.030 ± 0.007	60 ± 10	0.10 ± 0.02
Co_{ab}	0.24 ± 0.05	0.04 ± 0.01	0.05 ± 0.01	70 ± 9	0.018 ± 0.002
Po_{bb}	0.8 ± 0.2	0.016 ± 0.004	0.018 ± 0.002	80 ± 10	0.05 ± 0.01
Po_{ab}	0.18 ± 0.05	0.05 ± 0.01	0.07 ± 0.01	61 ± 6	0.007 ± 0.001

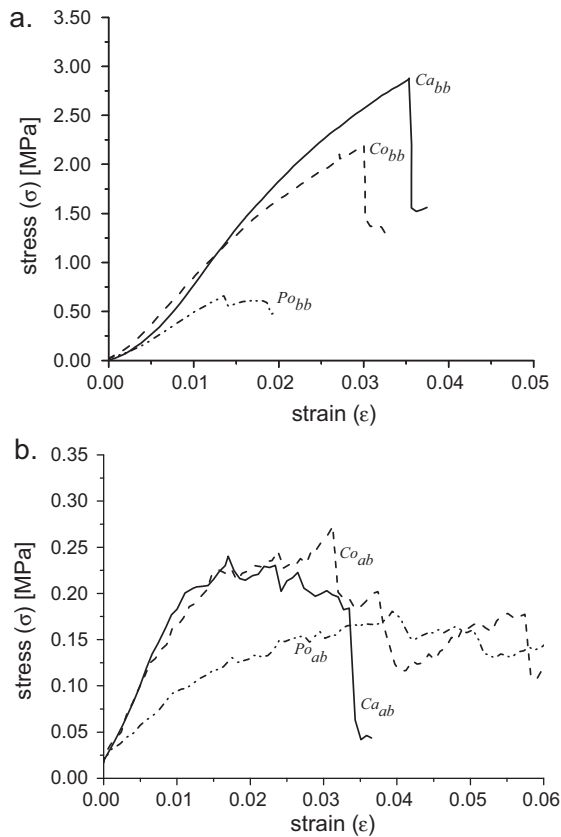**Fig. 2.** Typical stress (σ)–strain (ε) curves for mullite disks: (a) before and (b) after the burn-out process.

The stress–strain curves obtained for burned disks (Fig. 2b) show a significant deviation from linear behavior , which was attributed to the mechanisms of microcracking and compacting (this mechanism was verified by fractographic analysis, as will be described further on). Unlike the starch-containing green disks, the higher value of σ_Y/σ_F (Table 2) was estimated for those disks prepared using cassava starch, thus highlighting the higher brittleness of Ca_{ab} that is also reflected by the sudden fall of the load at the end of the test (Fig. 2b). Moreover, the stress–strain curves fall gradually as deformation increases; in particular, the curves of Ca_{ab} exhibit a remarkable and sudden drop in the load

at the end of the test, which is absent in Co_{ab} and Po_{ab}. The small differences in the maximum stress values supported by three types of burned disks indicate that in every case the irreversible deformation mechanisms are equally likely to be activated.

Typical crack patterns exhibited by burned disks are shown in Fig. 3. All the burned disks prepared with the three starch types showed a large deformation in the contact area with the compression platens. In addition, chipping was observed in these zones indicating the concentration of and/or susceptibility to shear stresses. The successive losses of flakes (delamination) lead to the sawed shape of the stress-strain curves. A high percentage of Ca_{ab} ($\sim$70%) had a diametral crack too, whereas this type of fracture occurred to a lesser extent in Co_{ab} and Po_{ab} ($\sim$30% for the two materials). The diametral propagation was linked to the sudden fall of the stress–strain curves (Fig. 2b); as for the high brittleness, Ca_{ab} exhibited the highest σ_Y/σ_F ratio and the lowest ε_F value (Table 2).

The mechanical strength of the green disks before the burn-out process (Table 2) is as follows: $Ca_{bb} > Co_{bb} \gg Po_{bb}$; a 68% difference in the values of Ca_{bb} and Po_{bb} disks was determined. The differences in pore sizes (Fig. 1) together with the different characteristics of mullite–starch gels were the main factors that determined the differences in the values of σ_F for the three systems. From dynamical rheological measurements reported by the authors in previous research [18], the structures developed by aqueous mullite–cassava starch and mullite–corn starch systems consisted of a three-dimensional gel network, with inclusion of the ceramic particles. On the other hand, in the aqueous mullite–potato starch system, a starch gel with a low inclusion of ceramic particles and aggregates of these particles bonded with weak interaction forces were formed as a consequence of a strong destabilization of the starting suspension due to a high and fast segregation of the components associated, in part, with the high water-retention index of the potato gel. Based on these facts, it was considered that the potato starch has a lower bonding power than the other two starches (cassava and corn) in the ceramic system and the processing experimental conditions used in this study.

Regarding the deformation parameters, the order of the strain-to fracture (ε_F) for mullite disks before the burn-out process was equivalent to that of the mechanical strength: $Ca_{bb} > Co_{bb} \gg Po_{bb}$, whereas the order of the final deformation values (ε_U) was: $Ca_{bb} \sim Co_{bb} \gg Po_{bb}$. The difference between the first and third systems was approximately 50% for both parameters. On the other hand, the apparent elastic modulus (E_a) decreased: $Ca_{bb} \sim Co_{bb} \gg Po_{bb}$ (the E_a value for Ca_{bb} was 55% higher than Po_{bb}). The differences in the ε_F, ε_U and E_a values between the
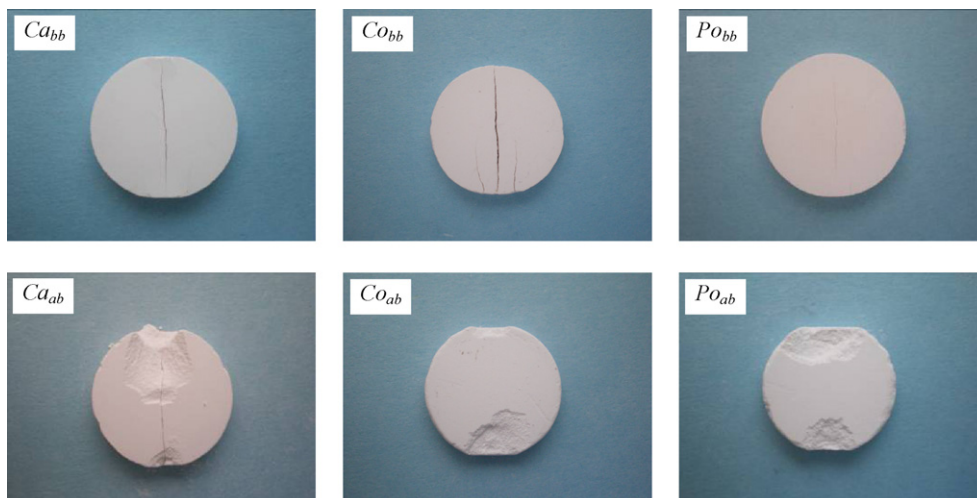

Fig. 3. Mullite disks before and after the burn-out process broken in diametral compression tests.
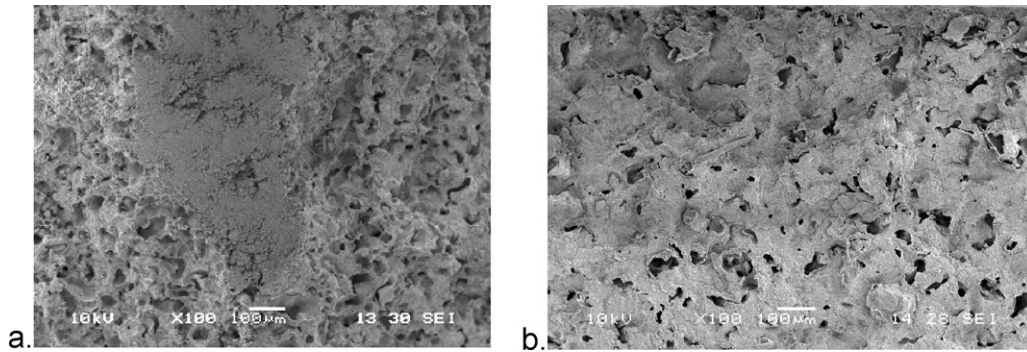
Fig. 4. SEM micrographs of fracture surfaces in the contact region: (a) burned and (b) unburned disks.

mullite-starch systems could be partially related to differences in the 'gel strength' (defined as the critical deformation value ε_c for which the gel behaving as an elastic solid becomes a viscous fluid) and the G'_{max} (maximum elastic modulus) values for the mullite–starch system [18], e.g. the mullite–cassava starch gel exhibited the highest G'_{max} (6.9×10^6 Pa) and was most susceptible to deformation ($\varepsilon_c = 157.5\%$). Finally, it is noteworthy that from the high mechanical strength and the large deformation at the end of the test (ε_U) for Ca_{bb} and Co_{bb}, a high toughness and/or work of fracture would be expected for these materials (higher for Ca_{bb}), higher than Po_{bb} disks.

Regarding the burned disks, their mechanical strength values were significantly lower than those of the green unburned disks due to the higher porosity of the former and the bonding capacity of the starch present in the latter. Moreover, Ca_{ab} and Co_{ab} were stronger than the disks prepared with potato starch, although the differences between the mechanical strength values were smaller than the values measured for unburned disks. From the very low heating rate used for the burn-out process ($1\,^\circ$C/min) together with the high porosity of the green bodies, which allowed the escape of the evolved gasses, a scarce or null development of cracks in the matrix would be expected when the starches were removed. For this reason, the pore characteristics, in particular their size (Fig. 1), seem to be the dominant factor in the differences between the mechanical strength values for burned bodies; therefore, the large pores present in Po_{ab} led to the lower σ_F exhibited by this material.

The apparent elastic moduli of the burned disks were significantly lower than the modulus of green unburned disks. The higher porosity of the former and the absence of the starch gel were the factors responsible for the low stiffness of these materials. In this case, the burned disks obtained by thermogelation of cassava and corn starches also showed higher E_a values than those of the compacts prepared with potato starch, which is associated with the size and morphology of the pores present in this last material. Furthermore, both strain parameters, ε_F and ε_U for burned disks were in general higher than the corresponding values for starch-containing disks, and the relative order was the opposite: $Ca_{bb} < Co_{bb} < Po_{bb}$. In spite of the large deformation at the end of the mechanical test, the toughness and/or the work of fracture was expected to be rather low for burned disks due to the very low strength values.

From fractographic analysis of both sets of mullite disk (Fig. 1), neither the critical defect nor the fracture mode could be identified in any case because of the microstructural characteristics of the materials and the stress distribution generated by the diametral compression, where the stress was uniform in a large region around the center of the disk [20,21,23]. However, the SEM images of the fracture surfaces of burned disks (Fig. 4) show densification in regions near where contact with the compression platens occurred, confirming the occurrence of compacting as an irreversible

deformation mechanism. This fact was attributed to the presence of a relatively small load bearing solid volume between a large amount of pores which collapse easily; moreover, this solid volume has a low mechanical resistance because of the absence of the binder. Conversely, no compacting was observed in any of the unburned green disks after mechanical testing (Fig. 4) due to the bonding effect of the starch gel that avoids the collapse of the matrix.

3.3. Relation with green machining

The mechanical properties and the microstructure of the green unburned mullite disks can be correlated with their green machinability (although 'machinability' is a parameter hard to define for green compacts, as asserted by [26]). One of the properties that clearly correlated with good behavior in green machining processes is the mechanical strength of the compact due to its effect on the clamping and the wear of the piece. A mechanical strength of 2 MPa was considered [3,4] high enough to bear the stress induced during the clamping and machining of the body. In this sense, the action of the binders is a key issue since these additives strongly determine the mechanical strength of green compacts as much as the quality of the surface finish and the wear of the machining tools do. Owing to their organic nature, these additives usually give a certain degree of plasticity to the system, which favors machining since this generally leads to an increase in the toughness and/or work of fracture that is also considered a favorable condition for a better green machinability [3,7]. The hardness of the compact has been also considered as a parameter to be taken into account in the analysis of the green machining behavior [2,7].

The elucidation of which properties influence the machining behavior is easier if the wear mechanism dominant in the operation is known. Regarding this aspect, it has been found that ductile [26] or brittle [3] mechanisms of chip formation could prevail; the type and content of the binder are two of the factors that strongly determining the dominant mechanism. Even in the case of brittle chip formation, in general the green compact has a more or less developed plastic–ductile behavior [3,7,8,25,26].

In this context, and bearing in mind the measured mechanical properties of mullite green bodies containing different starches, those compacts prepared from cassava and corn starches have sufficient mechanical strength to bear the green machining, using the above-mentioned limit value (2 MPa) as a reference. However, the tensile mechanical strength measured in flexural tests is always higher than that determined by diametral compression [27], up threefold higher. Taking this fact into account, the three types of unburned mullite compacts would have tensile mechanical resistances higher than 2 MPa (Table 1), with the values measured for compacts prepared with cassava and corn starches being even higher than those reported by Santacruz et al.

[5] and Millán et al. [28] for alumina compacts prepared using polysaccharides (agar, agarose and carragenate) with porosities similar to those of the green unburned mullite disks studied here.

In addition, there is evidence of non-linear behavior due to ductility and microcracking in both starch-containing materials, from which a high toughness and/or work of fracture is expected to benefit the green machining operation. However, from the way in which the specimens broke, a mainly brittle chip formation is expected. This behavior, whether associated with a certain ductility or not, has been considered even better than completely ductile behavior [24]. Taking into account the measured values of the mechanical parameters, the green compacts prepared from cassava starch are expected to be more easily machined than those prepared from corn starch. At the other extreme, the low bonding power of the potato starch (plus the microstructural characteristics of this material, with a high amount of large pores) prevents the compact from having the required mechanical strength to be green machined successfully. In addition, the toughness and/or the work of fracture, which is rather lower than the corresponding values of the other two starches, causes one to expect low performance in the machining process of the green mullite bodies prepared from potato starch.

Even though the experimental measurement of the Young modulus in relation to the green machining is carried out [24], a correlation between this parameter and the green machinability has not been reported. In this study, it has been verified that those compacts more able to be green machined were those with the higher values of the apparent elastic modulus (which is related to the Young modulus even with the above-mentioned restrictions).

As for the burned mullite disks, they do not have the required mechanical strength (>2 MPa, even taking into account the correction made for the type of mechanical test used) to withstand a machining operation due to their low toughness and/or work of fracture. This would be expected if it is taken into account that the burn-out process only removed the starch but did not favor any incipient cohesion of the matrix that would counteract the absence of the binder (to achieve this goal, a temperature rather higher than 650 °C would have to be used). Moreover, from the fracture pattern observed in this set of disks (Fig. 3), a high susceptibility to shear stress and a typical brittle mode of fracture become apparent. On the other hand, evidence of densification by compacting in the region of the specimen in contact with the compression platens indicates a tendency to generate density gradients in the materials that could negatively affect the integrity of the ceramic piece after sintering.

In short, based on the experimental data obtained in this study, native cassava and corn starches are the additives recommended for the preparation of porous mullite bodies by pre-gelling of ceramic–starch suspensions if green machining is considered as an alternative to reduce the production cost. It is also worth emphasizing the benefits associated with the use of native cassava and corn starches in the processing of porous mullite bodies: minimization of environmental impact, reduction of production cost and, as a key issue regarding the material, the generation of small pores before the burning-out process, which favors the thermal and mechanical properties of the final material.

For future work, the quality of the final pieces as a function of starch type and the presence of microcracking damage and surface roughness in particular still needs to be done. Moreover, even when the machining of the burned mullite compacts is advised against, the incorporation of a further step at a higher temperature to obtain a pre-sintered compact (white machining) might be evaluated as an alternative to green machining.

4. Conclusions

The green compacts prepared from the thermal consolidation of pre-gelled suspensions of mullite with cassava and corn native starches were shown to have better mechanical properties than those prepared using native potato starch. This was attributed to the features of the gel and the sizes of the pores developed for each starch and the positive effect of irreversible mechanisms of deformation, especially some degree of ductility. Once the starches were removed, the mechanical superiority of those disks prepared with cassava and corn starches was maintained due to the smaller pores generated during the burn-out; moreover, compacting of material was observed in the contact region of the specimens with the compression platens, together with a high susceptibility to shear stress. From the analysis of the experimental data, it was considered that the cassava native starch possesses the set of properties more suitable to be employed as a bonding agent in the forming of mullite bodies by direct consolidation, followed by the native corn starch. In this manner, both types of porous compact are able to be green machined with a view to reducing production costs. In addition, both starches generate green compacts with pores of smaller sizes, which will contribute to the development of materials with final porous microstructures more apt for using in thermal insulating applications.

Acknowledgements

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