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Mechanical evaluation of cordierite precursor green bodies obtained by starch thermogelling

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Abstract

The mechanical behavior of green bodies (porous cordierite precursors) obtained from suspensions of kaolin, talc and alumina powders consolidated by starch thermogelling was studied. Different starches were employed as consolidator/binders: potato, cassava, corn or modified cassava.

Aqueous suspensions of the powders (29.6 vol.%) with 11.7 vol.% of starches were prepared by intensive mechanical mixing, homogenization and vacuum degasification. Disks were prepared by thermogelling the suspensions for 4 h at 75–85 °C and additional drying. Green bodies were characterized by bulk density and apparent porosity measurements and microstructural analysis by SEM/EDAX.

The mechanical evaluation was carried out by diametral compression in displacement control. Apparent stress–strain relations were obtained from load–displacement curves and several mechanical parameters were determined: mechanical strength, apparent Young modulus and yield stress. Crack patterns were analyzed together with fractographic analysis by SEM. Mechanical results were related to the behavior of the starches in aqueous suspension and the properties of the formed gels.

Keywords: Starch consolidation; Mechanical properties; Diametral compression test; Cordierite inorganic precursors

1. Introduction

Among forming methods by direct consolidation, in which the ceramic suspension consolidates into non-porous molds (e.g. metal molds), a new group of low-cost and non-contamination forming techniques exist in which the gelling agent acts as both consolidator/binder of the ceramic suspension and a pore former at temperature. This is the case with starch that is added to a ceramic suspension that gels between 50 and 80 °C and acts as a consolidator/binder of the ceramic particles and a pore former after consolidation by burn-out at high temperature.[1–3] This method has been successfully employed for the production of porous bodies of alumina,[4,5] cordierite[1] and mullite,[6] among others.

When a ceramic suspension with starch is heated, the intermolecular bonds holding granules together are weakened. During this process the granules undergo a rapid and irreversible swelling by water absorption (gelatinization process).[7] This process causes an increase in the suspension viscosity, a transition to viscoelastic behavior and the formation of an elastic gel between 55 and 85 °C, depending on the type of starch and other various factors. In this manner, the amount of water available gradually diminishes, causing the ceramic particles to stick together and, consequently, to consolidate into a solid body. The amylose molecules leached from starch granules due to the gelatinization process adsorb at the surface of the ceramic particles. This process is the main factor responsible for bonding the ceramic particles and improving the mechanical strength of the green body.[8,9] Moreover, the amount of the starches used, their characteristics (morphology and size of the granules) and their behavior in suspension at temperature (swelling capacity, distribution of sizes and morphology of swollen granules, retrogradation degree)[10,11] will determine the final porous microstructure.

Due to the high degree of hardness that ceramics possess, green machining of ceramic parts is preferred in the industry over the machining of sintered parts. This alternative reduces costs, but can also increase the number of pieces rejected due to the low mechanical strength of the green bodies. Consequently, the improvement of the green compacts' mechanical proper-

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ties is one of the keys for optimizing the complete production cycle. The use of gelling agents improves these properties with respect to those materials prepared by conventional forming methods.[12,13] However, the machining of the green parts can be hindered if extensive plastic deformation occurs due to the high plasticity of the organic additives (e.g. binder). The addition of gelling agents must therefore be controlled in order to achieve a compromise between the improvement in strength and the degree of plasticity.[14,15]

The evaluation of mechanical properties of green porous ceramic bodies provides information for optimizing not only the forming process but also the machining step. The diametral compression test has usually been employed in the mechanical evaluation of green compacts[16,17] due to several advantages: simpler piece preparation, simple geometry and quickness of testing, independent data with regard to surface finish and no edge effects. However, this test requires rigorous analysis in order to validate the obtained data.

In this work the mechanical behavior of green disks prepared by thermal consolidation of aqueous suspensions of kaolin, talc and alumina with different starch types as consolidator/binder agent is studied. To achieve this, diametral compression tests were carried out and the validated results obtained were linked to starches' behavior in aqueous suspension and the properties of the formed gels.

2. Experimental

2.1. Raw materials and characterization

A mixture of commercially available powders of kaolin (kaolin C-80, Stone Big CORP., Arg.), talc (Talc 40, China) and alumina (A2G Alcoa, USA), with particle sizes <5 μm, were used as a cordierite precursor. From qualitative analysis by X ray-diffraction (Philips PW3710, Cu Kα radiation, at 20 mA and 40 kW) of raw materials, kaolinite (File 06-0221) was determined to be the main crystalline phase, with vestiges of quartz (File 5-0490) and orthoclase (File 31-0996) in the kaolin powder; talc was the main phase (File 19-0770), with vestiges of dolomite (File 34-0517) and tremolite (File 02-0455) in the mineral of talc, and corundum (File 42-1468) was the only identified phase in alumina powder. The cordierite precursor mixture was formulated based on its compositions in oxides and bears a resemblance to that of stoichiometric cordierite ($SiO_2 = 51.4$ wt.%; $Al_2O_3 = 34.8$ wt.% and $MgO = 13.8$ wt.%), but with less silica content and higher alumina and magnesia proportions: 37 wt.% of kaolin, 41 wt.% of talc and 22 wt.% of alumina.

Potato, cassava, modified cassava and corn starches commercially available in Argentina were used as consolidator/binder agents. Real densities determined by He-pycnometry (QuantaChrome, USA) were: 1.47 g/cm^3 for potato starch and 1.49 g/cm^3 for the remaining starches. The particle size distributions (Malvern Instruments Ltd., UK) were determined by using an aqueous suspension of starch with a polyacrylic acid (Dolapix CE-64, Zschimmer & Schwarz, Germany) as dispersant and applying ultrasound for 15 min to disperse and stabilize the starch particles. Each starch presented bimodal distributions, with a low percentage volume of small granules that can be associated to impurities or broken granules. The mean particle diameter for potato starch ($D_{50} = 48$ μm) was notably higher than those of the others starches ($D_{50} = 12$–15 μm). Corn, cassava and modified cassava starches showed a higher amount of small granules (0.5–3 μm) than potato starch (1–10 μm). The parameter $W = D_{90} - D_{10}/D_{50}$ (where D_{90} and D_{10} are the diameters of granules for 90 and 10 vol.% of granules) was chosen for estimating the width of particle size distributions. The corn starch presented a more narrow distribution ($W = 0.9$) than the other starches ($W = 1.3$–1.5). The weight percentage of humidity was determined by thermogravimetric analysis (Shimatzu, TGA-50) at 10 °C/min up to 120 °C, in air, and the following values were obtained: 14.4 wt.% for potato starch; 11.5 wt.% for cassava; 12.4 wt.% for corn and 10.9 wt.% for modified cassava starch. The granule morphology analysis of the dry starches was carried out by scanning electronic microscopy (Jeol JSM-6460). Potato starch exhibited the largest granules, with smooth surfaces and oval or spherical forms. The rest of starches exhibited granules with some polyhedral morphology, with corn starch granules exhibiting the most.

2.2. Preparation and characterization of green compacts

Green disks (diameter = 15 mm; thickness = 4.2–2.3 mm) were prepared by thermal consolidation (75–85 °C) of aqueous suspensions of the cordierite precursor mixture (29.6 vol.%) and 11.5 vol.% of each starch. The suspensions were prepared by: (a) mixing (impeller mixer) ceramic powders in water (70.4 vol.%) with 1 wt.% of Dolapix CE-64 (Zschimmer & Schwarz, Germany) and 0.5 wt.% of sodium napthalenesulfonate (both with respect to the content of ceramic solids), added in a sequential manner (kaolin first, with a pause of 24 h, then the talc and finally the alumina; (b) homogenization in a ball mill, 2 h; (c) the addition of starch and mixing (impeller mixer) for 2 min and (d) degassing, 20 min. The suspensions were poured into cylindrical stainless steel molds (which were covered with Teflon tape to reduce water evaporation) heated in air for 4 h to the following temperatures: 85 °C for potato and cassava starches and 75 °C for corn and modified cassava (Memmert, electric stove with circulation of forced air) and dried at 50 °C for 12 h. The disks were machined using 600-grit SiC paper to obtain flat and parallel surfaces.

The labels for the prepared disks were selected according to the starch type used: P for potato starch; T for cassava starch; C for corn starch and MT for modified cassava starch. For comparative purposes, disks without starch (labeled WS) were made by slip casting in plaster molds using an aqueous suspension of the cordierite precursor mixture prepared in the above described conditions. The green densities (δ_v) were determined by immersion in Hg (Archimedes method) and the disk porosities ($\%P_v$) were calculated by taking the pycnometric density of the solid (δ_{pic}) as $100(1 - \delta_v/\delta_{pic})$. By pycnometry in kerosene at 37 °C, the following δ_{pic} values for the precursor mixture with and without starch were determined to be 2.44 ± 0.06 and 2.95 ± 0.02 g/cm^3, respectively. The microstructural analysis of the prepared green disks was carried out by SEM (Jeol JSM-6460)/EDAX (Genesis XM-2-Sys).

2.3. Mechanical testing

In the diametral compression tests, a uniaxial compressive load is applied diametrally on a disk until failure.[16–18] An INSTRON model 8501 servohydraulic machine was used, with a load cell of 5 kN maximum load and steel platens (R_c 65). MoS_2 lubricant paste was used in order to reduce the effect of friction between the specimen and the platens. We considered that the plasticity of green compacts associated with the ceramic matrix (clay and talc powders) and starches was sufficient to distribute the applied load without requiring the use of pads.[16,18] In some cases, both white and carbon papers were placed between each platen and the specimen in order to estimate the contact width (w). Tests were carried out at room temperature, in displacement (of the actuator) control, with a rate of 0.1 mm/min and on a number of disks considered sufficient for statistical purposes.

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 in the analysis ($t/D \leq 0.25$).[19] This assumption is implicit in the theoretical treatment of the diametral compression loading case (Eq. (1)).[18–20]

From experimental load vs. displacement curves, the apparent ratio stress (σ)–strain (ε) was obtained by calculus, using the following relationships[16–20]:

$$\sigma = \frac{2P}{Dt} \tag{1}$$

$$\varepsilon = \frac{d}{D} \tag{2}$$

where P is the fracture load, D and t are the diameter and the thickness of the disk, respectively, and d is the actuator displacement. From σ vs. ε curves, the following parameters were determined: mechanical strength (σ_F) using the peak load, the apparent Young modulus (Ea) as the slope of the linear part of the curves, the elastic limit (σ_Y) defined as the value of stress that corresponds to a deviation of deformation of 1% with respect to the linear behavior[16] and the ratio σ_Y/σ_F expressed as a percentage. This last parameter was considered indicative of the deviation from the linear behavior, i.e., the degree of plasticity.

Fracture features of tested disks (with and without starch) were analyzed by ocular inspection, and fractographic analysis was performed by SEM (Jeol JSM-6460).

3. Results and discussion

3.1. Characterization of green disks

The values of density (δ_v) and porosity ($\%P_v$) of the green compacts are shown in Table 1.

The relative order of green porosities was: P ∼ C > T ∼ MT. The porosity of the disks without starch also fell within this range of values.

Table 1
Density (δ_v) and porosity ($\%P_v$) of green disks.

	δ_v [g/cm^3]	$\%P_V$
P	1.20 ± 0.04	51 ± 2
T	1.30 ± 0.05	47 ± 2
C	1.22 ± 0.04	50 ± 2
MT	1.34 ± 0.04	45 ± 2
WS	1.54 ± 0.02	48 ± 1

The differences in the porosity values can be explained by taking into account that the microstructures are influenced by the starch characteristics, in particular, its behavior in aqueous suspension at temperature (swelling capacity and the characteristics of the swollen granules).[21] Potato starch exhibited the highest swelling capacity measured using relative volumetric swelling,[22] and at consolidation temperature a high proportion of gelatinized granules preserved their integrity. With regards to the corn starch, it possessed the lowest swelling capacity as well as a large proportion of integral gelatinized granules at consolidation temperature. These facts are consistent with having a high onset gelatinization temperature, which is close to consolidation temperature. On the other hand, cassava and modified cassava starches showed intermediate swelling capacity, and the amount of broken granules at consolidation temperature was rather high in both starches. We considered that the presence of broken granules favors the packing of particles, thus diminishing the porosity of green bodies, which thereby accounts for the values of $\%P_V$ (Table 1).[21]

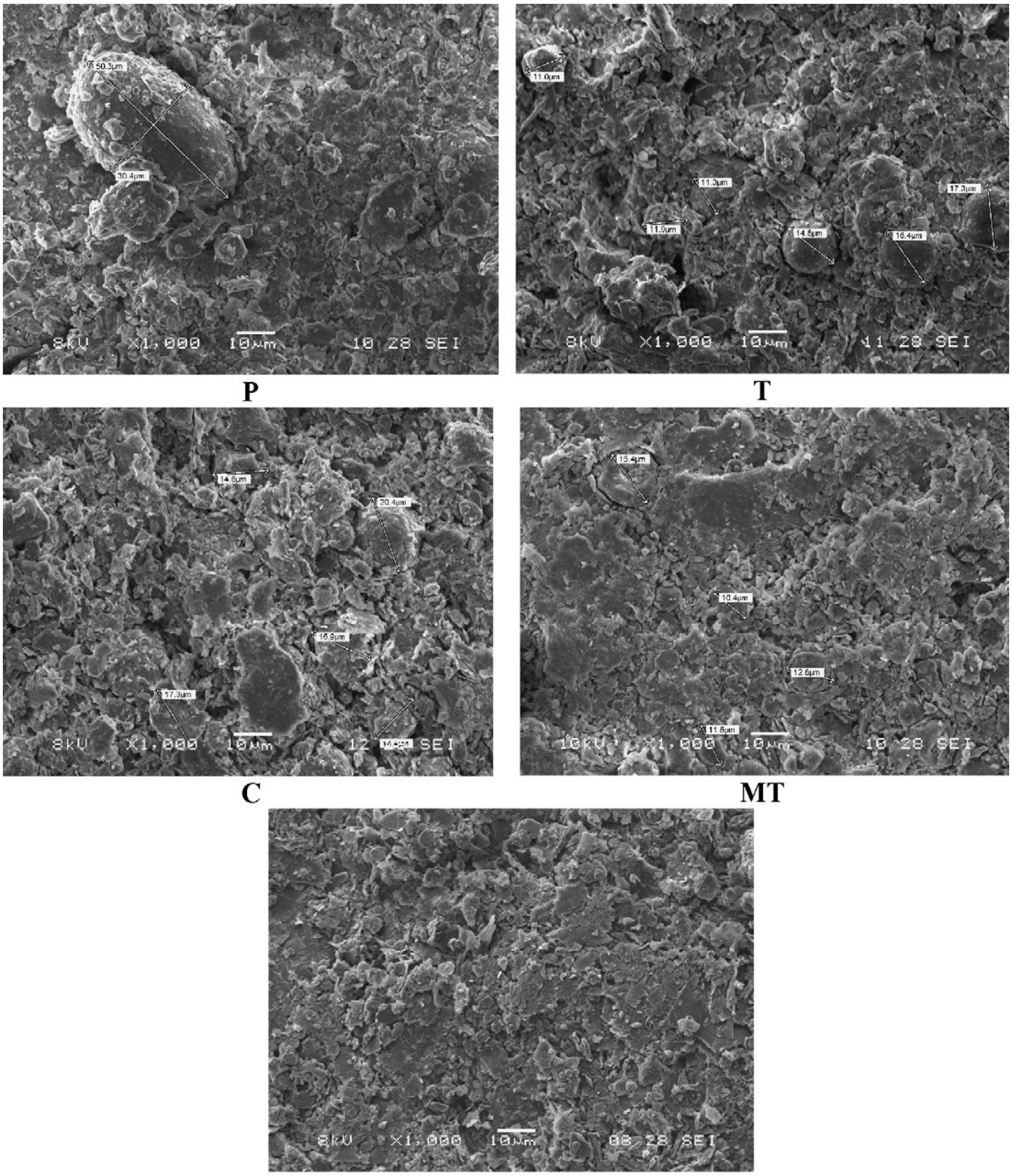
SEM micrographs of green compacts both with and without starch are presented in Fig. 1. The most significant difference between the microstructures of these materials is the presence of starch granules that form the gel structure in the green compacts with starch. This fact was confirmed by elementary analysis of carbon (EDAX). In Fig. 2, C mapping for P, T and WS disks are shown. The low percentage of carbon in the last samples is mainly attributed to the presence of organic additives used for processing. The sizes and morphology of the granules observed by SEM are within the range of the values determined for dry and in gelatinized starches.[21] The porosity differences determined from density measurements (Table 1) is not clearly seen in SEM micrographs.

3.2. Analysis of mechanical behavior

3.2.1. Mechanical parameters

In Fig. 3, stress–strain curves are shown for green bodies without starch and for disks prepared by thermal consolidation of different starches. In Table 2, average and standard deviation values of mechanical parameters and w/D are given.

The theoretical basis from which Eq. (1) arises considers, among other things, the condition of point load.[18–20] However, in practice the load is distributed over an area of thickness w. As a consequence, stress distribution in the disk[19] is modified by a magnitude that depends, although not exclusively, on w/D value. Therefore, the validity of Eq. (1) employed to calculate the mechanical resistance depends on the value of this relationship.



P **T**

C **MT**

WS

Fig. 1. Microstructures of the green disks.

There is no agreement concerning the range of w/D values that should be used to validate the calculation. The error in the calculation of σ_F using Eq. (1) for the flat load distributed condition has been estimated to be small (∼4%) when $w/D < 0.2$.[19] Keeping in mind the experimental results that reveal a flattening of the contact zone of the disks, and the magnitudes of w/D (Table 2), we considered that only the mechanical strength obtained for MT disks would be affected by an error slightly higher than 4%.

Taking into account that one of the functions of the starch is to act as a binder, an increase of mechanical strength in the compact consolidated from the different starches is expected. The values of Table 2 show, except for C disks, that the green compacts consolidated with the rest of the starches exhibited notably higher mechanical strength than that of WS disks (labeled σ_0). The bonding effectiveness thus follows the order: modified cassava > cassava > potato. The possibility that the porosity of the green disks (Table 1) also influences the magnitudes of σ_F cannot be ruled out, although it is believed that its contribution is much smaller than the bonding effect of each type of starch. In light of this, the corn starch did not exhibit bonding power at all.

Corn starch behavior, as well as the relative order of mechanical strength of green bodies obtained from the other starches, can be explained keeping in mind the results of dynamic strain sweep tests (RDA-II, Rheometrics Inc., parallel plates geometry: Ø = 50 mm and gap = 1 mm, testing temperature: 40 °C, deformation: 0.1–625.0%) carried out on gels obtained from these starches at 95 °C. Experimental curves are displayed in Fig. 4, from which a measure of the ‘gel strength’ may be obtained.

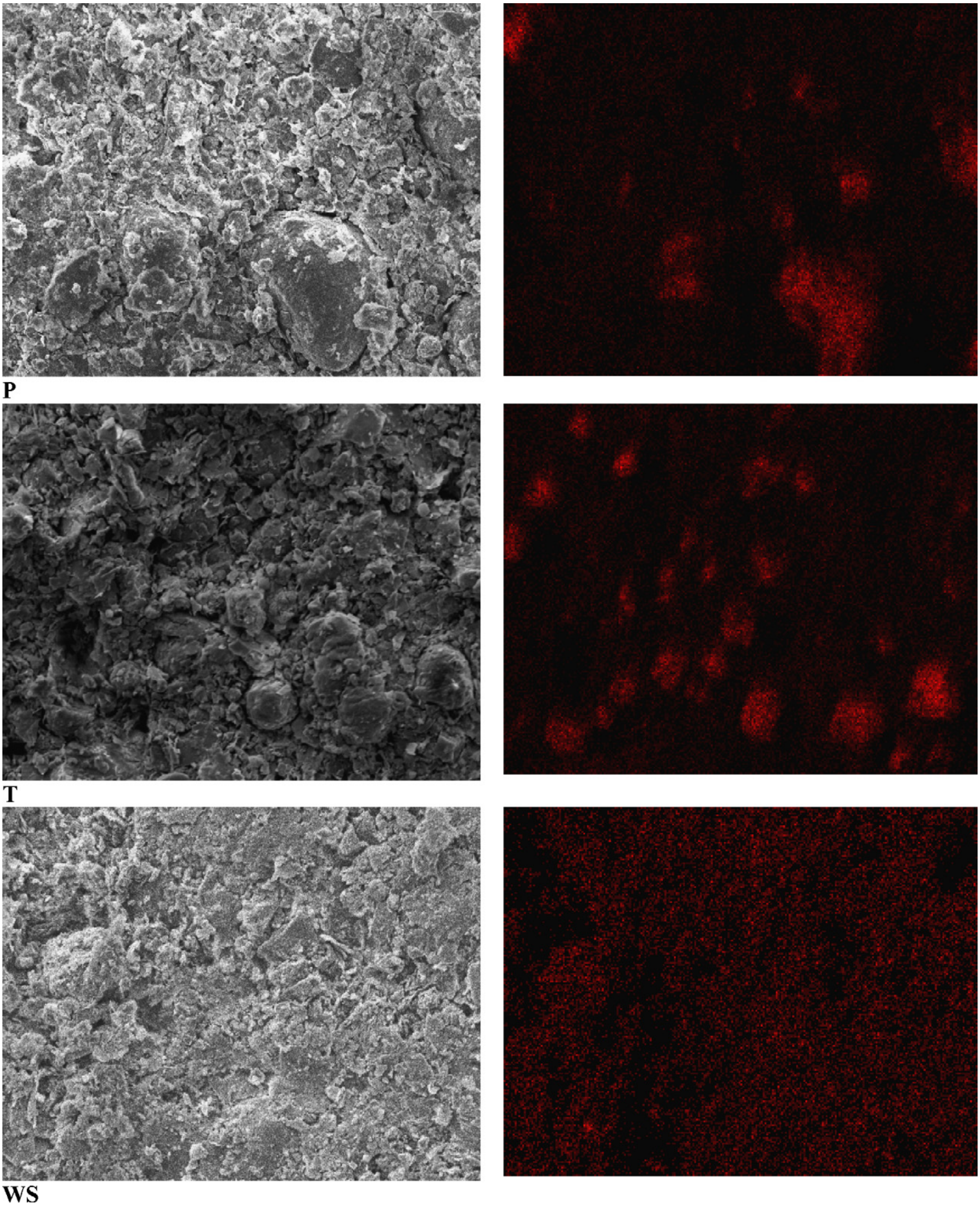


Fig. 2. SEM-EDAX micrographs of green surfaces and C mapping (100×).

Every gel showed elastic modulus (G') values higher than the viscous modulus (G''), indicating that in a variable range of deformation depending on the starch type, the material behaves as an elastic solid. The percentage deformation value where G' equals G'' is considered an indicator of the gel strength. In general, as deformation increases the magnitude of G'' overcomes G' as the gel structure ruptures and takes on the behavior of a fluid or viscous solid.

Corn starch exhibited the lowest value of gel strength, at least six times lower than the values of the others starches. Moreover, after the intersection of the G' and G'' curves, a very steep fall in G' with the deformation was observed,

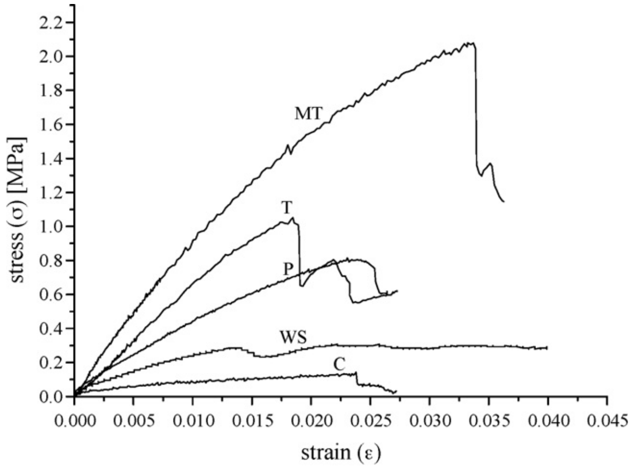


Fig. 3. Stress–strain curves for green bodies.

Table 2
Average values of mechanical parameters and w/D.

	σ_F [MPa]	Ea [MPa]	$\%\sigma_y/\sigma_F$	w/D
P	0.80 ± 0.20	43 ± 11	62 ± 11	0.22 ± 0.02
T	1.30 ± 0.50	71 ± 24	66 ± 19	0.21 ± 0.03
C	0.14 ± 0.01	7 ± 1	61 ± 3	0.23 ± 0.03
MT	2.10 ± 0.60	115 ± 69	24 ± 12	0.28 ± 0.04
WS	0.28 ± 0.03	15 ± 7	64 ± 19	0.23 ± 0.05

which indicates a rapid breakdown of the corn starch gel structure. These facts are related to the low mechanical strength of the disks obtained from this starch and its null bonding power.

On the other hand, the starches that evidenced a bonding effect ($\sigma_F > \sigma_0$) exhibited a similar value of gel strength, with the following relative order: potato ∼ cassava > modified cassava. After the intersection of G' and G'' curves, these starches showed a less marked fall in G' with respect to what was observed in corn starch gel, with the following order of magnitude: potato ∼ modified cassava > cassava. This shows that not only do the gels have a larger ability to deformation, but also the degradation of the structure with increasing deformation is less severe to that of corn starch. However, the influence of ceramic particles on the dynamic rheological behavior of different starches cannot be ruled out. These gel characteristics evaluated together explain the tendency observed in the mechanical strength of disks obtained by consolidation with different starches: MT > T > P.

With regard to the values of Ea, they follow the same relative order as that of mechanical strength: MT > T > P ≫ C. In turn, the presence of the different starches in green compacts, except in the case of C disks, produced a significant increase in stiffness (Table 2). Young modulus values may also be affected by the porosity of the green compact since experimental ranking of Ea can be explained by its effect only. However, the increment in the magnitude of the elasticity modulus of disks prepared from starches with respect to Ea_0 (compact without starch), except for C disks, indicates that the presence of gels mainly determines the Ea values.

As with the results obtained in the analysis of mechanical strength values, the Young modulus of compacts with corn starch did not exhibit a significant change with respect to Ea_0. Thus, besides the lack of bonding power, the nature of the corn starch–ceramic particle interaction is very similar to the union

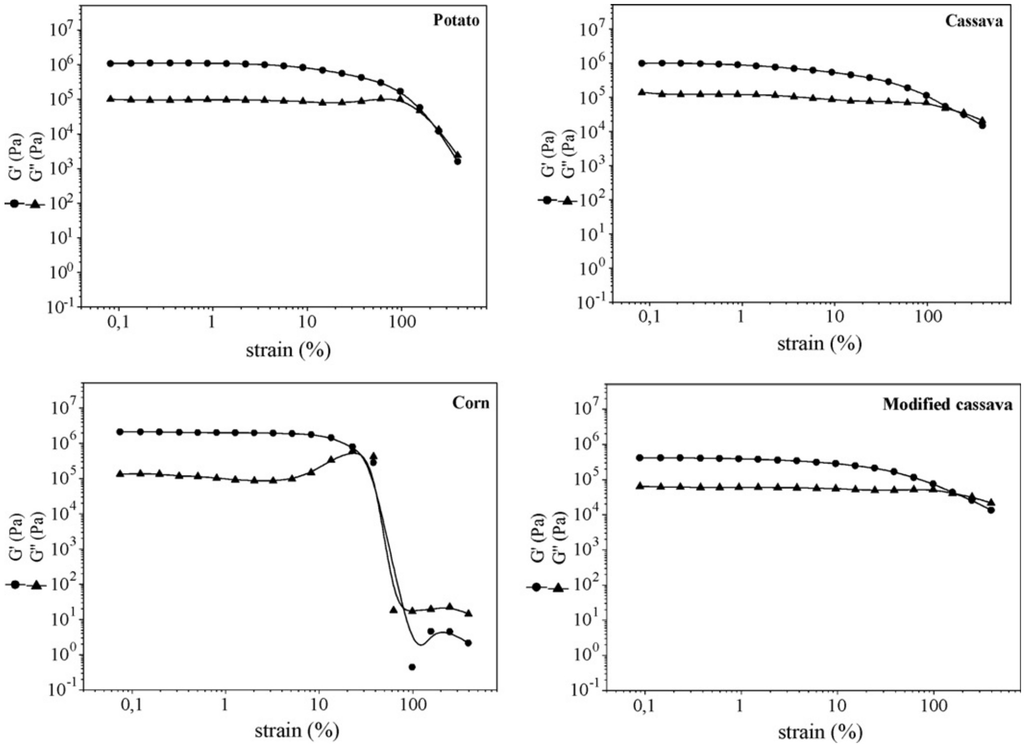


Fig. 4. Dynamic strain sweep test curves for starches.

between the ceramic particles themselves. Therefore, either of these interactions may equally determine the mechanical behavior of the disk. In dynamic rheological testing for determining G' (indicator of gel elastic modulus) in function of temperature, it was established that the incorporation of ceramic particles to a corn starch suspension (at a constant volume) inhibited its gelatinization in a significant way.[22] This was mainly attributed to the smaller availability of water due to both its interaction with ceramic particles in suspension and its loss by evaporation. The effect of both factors is intensified by the high temperature of gelatinization (72 °C, determined by dynamic temperature ramp test at 2 °C/min) of the corn starch and its low swelling capacity in function of temperature.[22] Therefore, in the conditions used to prepare disks, the presence of a poorly developed gel as revealed by the rheological testing would account for the mechanical behavior exhibited by C compacts.

The increase in the modulus of elasticity with respect to Ea_0 in the case of P, T and MT green compacts shows that developed gels provide a stiffer structure than with just the ceramic particles alone. A conservative estimation of Young modulus of gels using the results in Table 2 provides values in the 150–400 MPa range, which are consistent with those reported for similar polysaccharide binders.[23]

Elastic moduli G' obtained for potato, cassava and modified cassava starches at their respective consolidation temperatures (85, 85 and 75 °C, respectively) did not correlate with the values of Young modulus obtained by diametral compression tests. We consider that the differences between both rheological and mechanical tests—deformation ranges, for instance—are possible causes for the lack of correlation between G' and Ea. Also, the effects caused by the retrogradation process[24] (especially in a short range due to amylose crystallization) should be not discarded. This process depends on the type of starch (amylose/amylopectin ratio) and modifies the gel's mechanical properties due to an increase in stiffness caused by the polymeric chains alignment. From the dynamic rheological studies, the tendency towards retrogradation experienced by the used starches was established[22]: cassava and modified cassava $\gg$ potato and corn. The possibility that the presence of ceramic particles, whose interaction with each starch is different, affects the advance degree of the retrogradation process cannot be ruled out. These results explain (in conjunction with porosity) the tendency observed in the values of Young moduli for the green bodies prepared with each starch.

Stress–strain curves of green compacts (Fig. 3) show an evident deviation from the linear behavior attributed to the occurrence of irreversible deformation (plasticity) that occurs with or without the presence of starch. This behavior is attributed to several factors: the presence of raw materials with laminar morphology (clay and talc), the contribution of the ductile behavior of the starch,[25] the microcracking and the densification by compaction. It is believed that these last two mechanisms will occur predominantly at the points of contact with platens.

With regard to $\%\sigma_y/\sigma_F$ values, a moderate and similar plasticity degree was observed (60–65%) for WS, P, T and C disks. Those compacts obtained from modified cassava (MT) registered a significant higher plasticity (24%). These results are consistent with the estimated values of w/D, keeping in mind that this parameter provides a measure of the permanent deformation degree in the contact zone. The difference registered between modified cassava and the remaining starches that did not modify the plasticity degree of the compact in a significant way is attributed to both the higher capacity to retain water or 'hygroscopicity' (this property was determined by visual inspection of the gels after the dynamic rheological tests) and the higher loss tangent G''/G' (Fig. 4) of modified cassava starch.

3.2.2. *Fracture patterns*

Fig. 5 shows the typical fracture patterns for each type of compact.

Three fracture types were detected:

(1) *Diametral fracture (DF)*: Characterized by a fissure that runs along the diametral axis of load. This fracture type is derived from the stress distribution for point and distributed load conditions. In addition, the theoretical treatment predicts the fracture beginning at the central point of the disk where the maximum principal stress takes place.[20] Although some authors consider this one of the valid fracture patterns, along with the 'triple-cleft',[18,26] there is not general agreement in this aspect.[18]

In some cases, besides the diametral crack, secondary fissures were observed in the contact zone (SF, Fig. 5) that propagated almost parallel to the diametral fissure, but did not go through the entire specimen. Secondary cracks were located in one or both sides of the diametrical fissure and in one or both contact regions. The presence of these fissures is consistent with the distribution of principal stresses calculated by FEM simulations of disks under diametral uniaxial compression using both elastic and elasto-plastics models.[20] It has been determined that tensile stresses are developed at the edge of the specimen on a small material volume near the region of platen contact that can reach up to 50% of the maximum tensile stress.[20]

(2) *Load region fracture (LRF)*: Occurs in the region of contact between the disk and the compression platens and consists of the presence of a clearly defined shear prism at generator, which in some cases culminates with small flakes of material becoming detached from the face of the cylinder adjacent to the platen contact (spalling). In extreme cases, a complete fragment of the disk can become separated as observed in Fig. 5c, e, f and i. The fracture in the contact zone occurs due to compressive and shear stresses in this region despite being attenuated by the effects of load distribution. Some authors conclude that this fracture type is invalid for the calculation of the mechanical strength using Eq. (1)[18] although others consider that the test is still indicative of the bearing capacity of the material under the test condition.

(3) DF plus LRF

Table 3 shows the frequency of appearance of the different fracture types for each type of compact. The cases in which only LRFs occurred were not considered valid for calculation

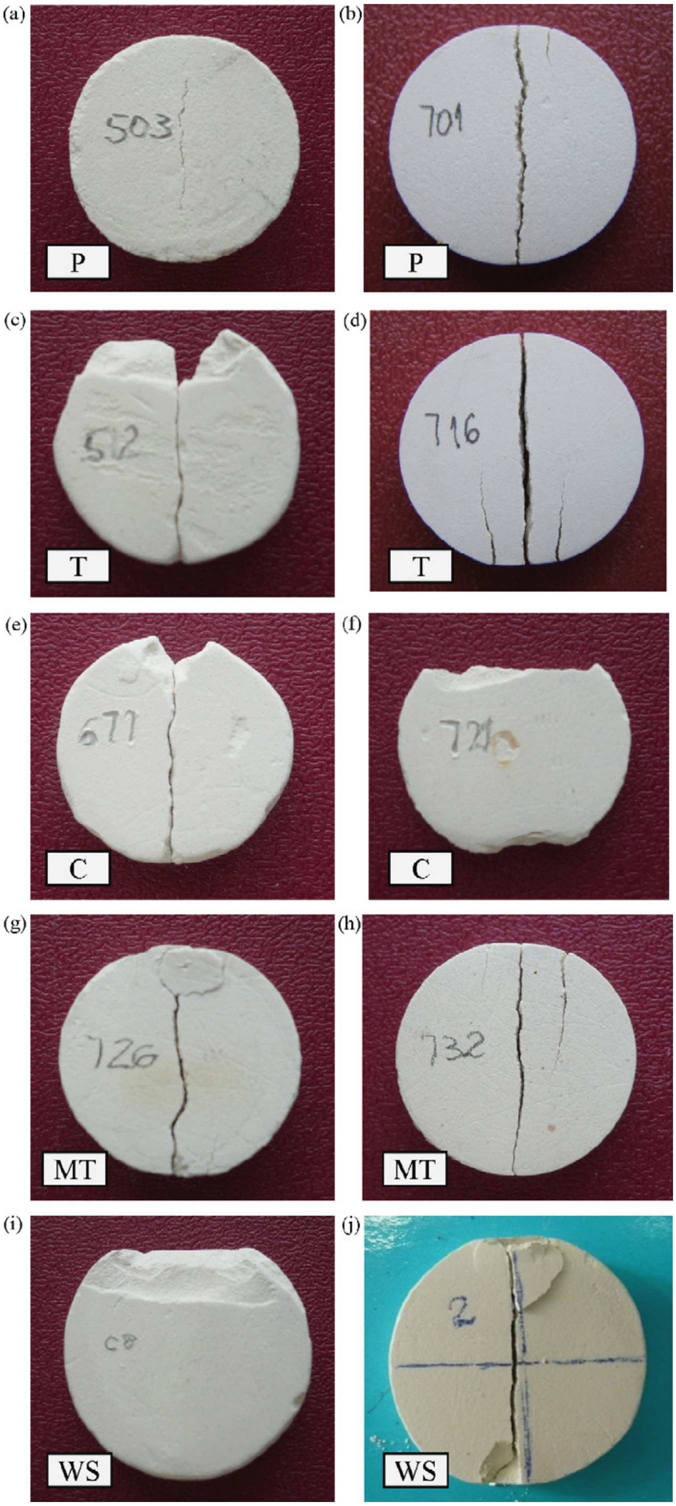


Fig. 5. Fracture patterns of disks broken in diametral compression tests.

of mechanical strength values reported in Table 2. As seen in Table 3, this fracture type occurred very frequently in C and WS disks, which exhibited the smallest cohesion degree. This is associated with the finite rate of load transmission during the test that produces a quicker rise of stresses in the contact region (with respect to what happens in the disk centre, for instance). Therefore, the critical condition is satisfied before in this region where shear stresses prevail. In general, the mechanical behavior revealed by the fracture characteristics of C and WS disks was quite poor and similar between both types of compacts.

Table 3
Frequency of appearance of the different fracture types.

	DF	LRF	DF + LRF	SF
P	100%	–	–	11%
T	67%	–	33%	55%
C	–	50%	50%	–
MT	40%	–	60%	25%
WS	–	40%	60%	–

On the other hand, differences were observed in the frequency in which the different fracture types were seen between disks consolidated with the rest of starches. The P disks only failed diametrically while T and MT specimens also exhibited, in some cases, LRFs. The highest frequency of LRFs was registered in MT disks. Also, the three types of disks exhibited secondary fissures, which occurred more frequently in T compacts.

In MT disks, diametrical cracks were observed that frequently propagated with marked deviations from the central axis (Fig. 5g). In the case of P and T compacts, path deviations are much less marked. In summary, MT disk fractures were more irregular than those of the others disks even though they possessed the highest mechanical resistance. P compacts, in turn, failed in the most regular and uniform manner. The characteristics of T disk fractures fell between the two previously mentioned cases.

3.2.3. *Fractographic analysis*

Figs. 6 and 7 show SEM micrographs of fracture surfaces of the compacts, both with and without starch, corresponding to the central region of the disk.

Given the microstructural heterogeneity of all the observed surfaces and the stress distribution, according to which the maximum stress values are almost uniform along of the disk thickness (plane stress), it was not possible to identify the critical flaw that originated the fracture in none of the specimens.

The aspect of the C disk surfaces observed with low magnification (Fig. 6) was similar to that of the WS disk surfaces. Both exhibited a greater flatness in their texture than the other surfaces, which could be associated with a smaller contribution of plastic deformation mechanism in C and WS specimens.[13] However, the plasticity degree measured by the $\%\sigma_{\mathrm{Y}}/\sigma_{\mathrm{F}}$ parameter was similar in all the materials except in those disks prepared with modified cassava.

In order to establish the fracture mode, the surfaces were observed with higher magnification (Fig. 7). In WS disks, it is expected that the fracture will propagate through the weakly linked ceramic particles. In those specimens consolidated with starch, the failure of the ceramic particle–starch interfaces may be the major contribution to fracturing. Taking into account the mechanical parameters discussed above, this interaction dominated the mechanical behavior of the material. In the specific case of C disks, the previously discussed results indicate

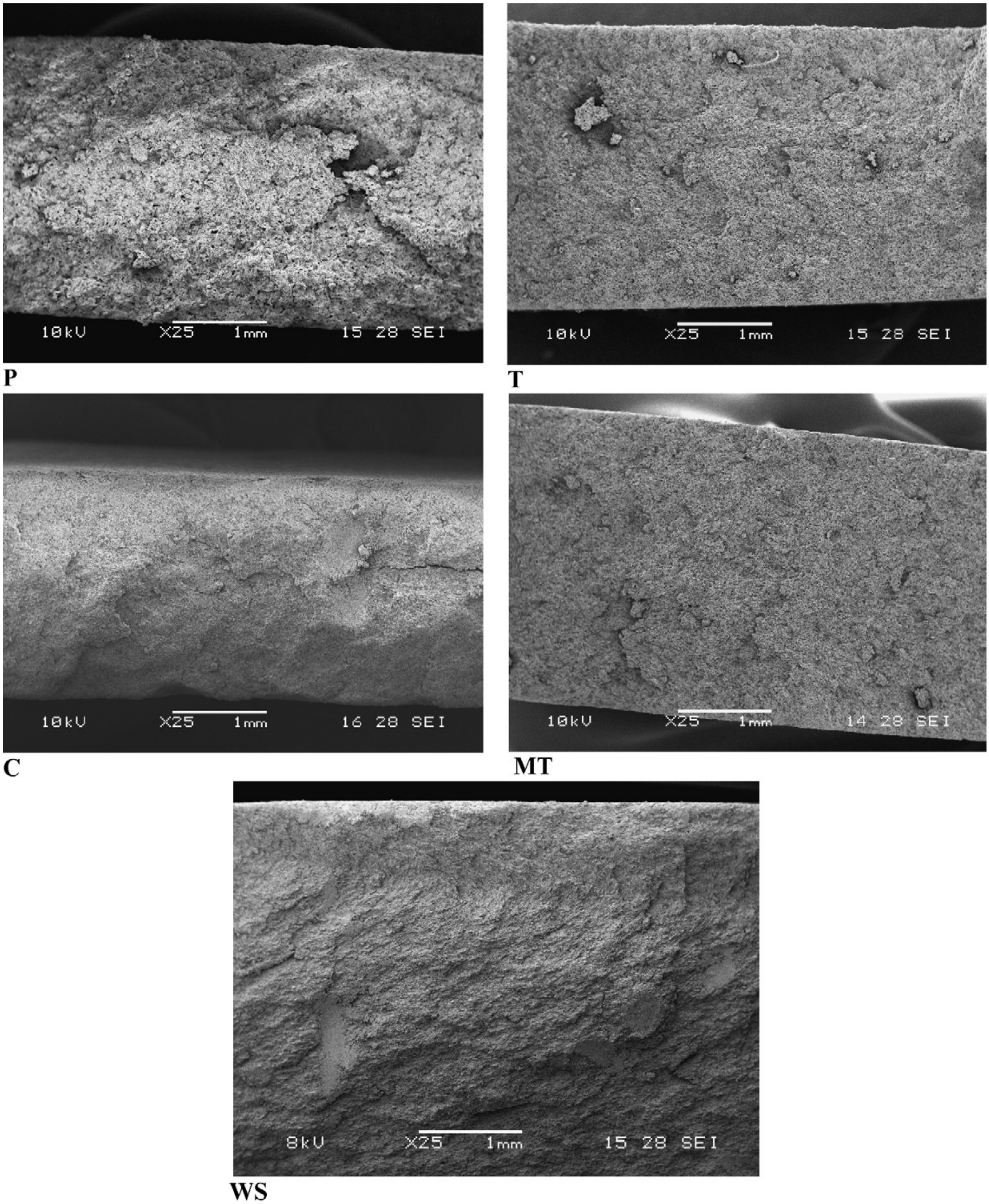


Fig. 6. Low magnification SEM micrographs of fracture surfaces of green disks.

that the ceramic particle–starch interface was as weak (null bonding power) as the union of the ceramic particles to each other.

At higher magnification (Fig. 7), differences in the microtextural characteristics of the surfaces of disks without starch with respect to those obtained from starch confirmed the fracture modes. In the latter specimens, more clearly in P disks, the presence of starch granules and cavities with sizes and morphology similar to each other sustain the fracture path through the ceramic particle–starch interface. Unfortunately, the high irregularity of the surfaces impeded the elementary analysis of carbon by EDAX that would quantify the contribution of this mechanism with respect to the failure through the unions of ceramic particles.

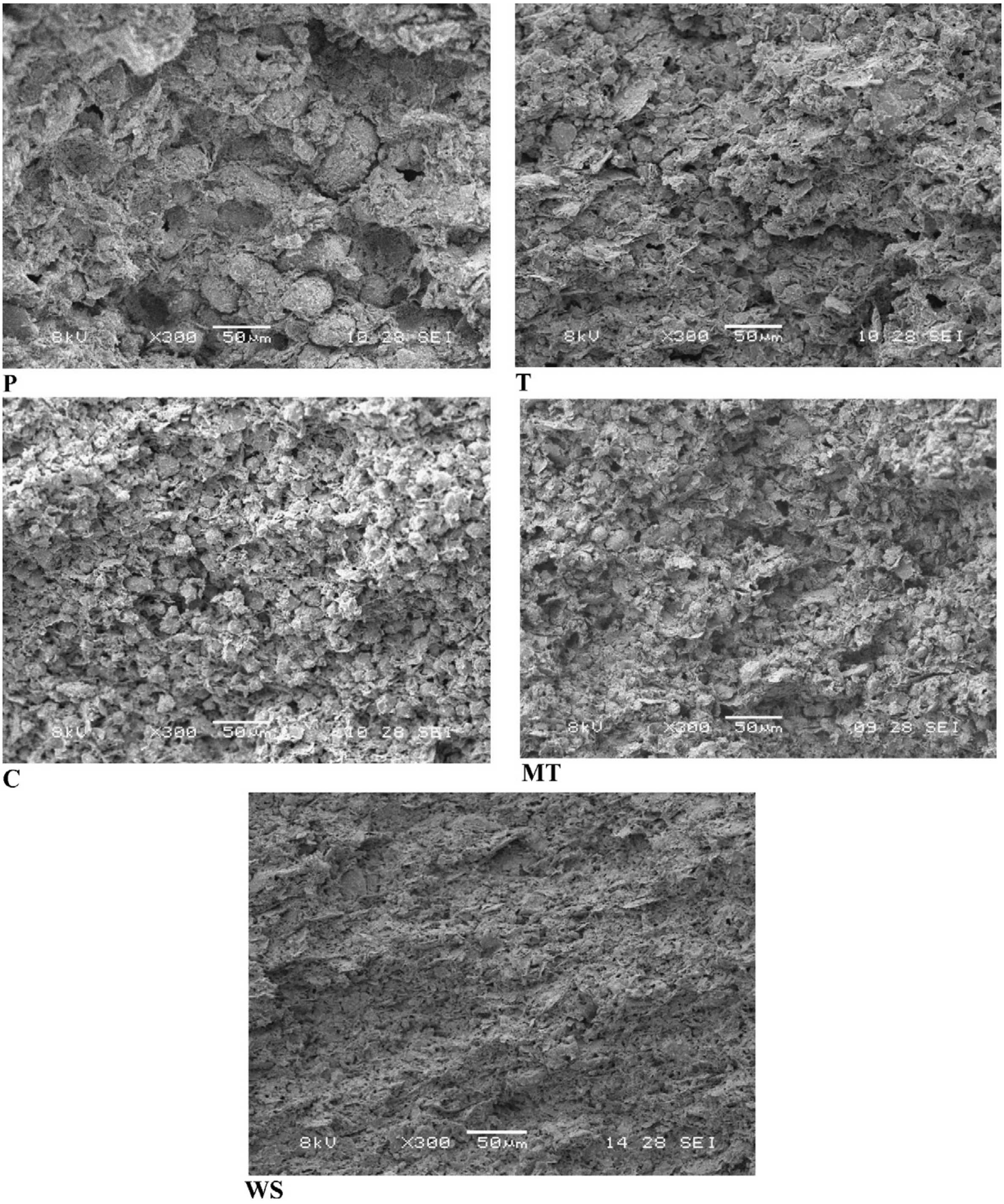


Fig. 7. SEM micrographs of fracture surfaces of green disks.

4. Conclusions

With the exception of corn starch, the starches used in the consolidation of disks act properly as a binder producing an increase in the mechanical strength with respect to that of the green compact without starch. The incorporation of potato, cassava and modified cassava starches also increases compact stiffness as well as the degree of plasticity in the case of modified cassava. The effect of starches in the mechanical behavior of the green disks was related to their behavior in aqueous suspension at temperature evaluated by rheological dynamic tests.

With regard to the fracture characteristics, disks obtained from potato starch exhibited more regular failure characteristics, which was also more frequently in agreement with what is considered valid for the mechanical test employed (diametral compression), compared to the specimens containing the cassava and modified cassava starches. On the other hand, the fracture surface of compacts fabricated with potato starch was coarser than the others two types of disks at microstructural level.

Keeping in mind that the recommendations for an appropriate machining of ceramic green pieces requires high mechanical strength but low plastic deformation, modified cassava starch is a good candidate to be employed as a binder, although its plastic deformation could be a disadvantage. If this is the case, cassava starch would also be effective and even potato starch could be used in spite of its lower mechanical performance. On the other hand, corn starch was found to be completely inefficient as a binder in the prepared compacts used in this study.

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