

Starch Consolidation Casting of Cordierite Precursor Mixtures—Rheological Behavior and Green Body Properties

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The rheology of suspensions and mechanical properties of green bodies with cordierite composition (raw materials 37 wt% kaolin, 41 wt% talc, 22 wt% alumina, resulting in 46.6 wt% SiO₂, 38.1 wt% Al₂O₃, 13.6 wt% MgO) and two types of starch (corn or potato) are investigated. Rotational viscometry of suspensions with solids loading 50, 60, and 70 wt% without starch showed that all tend to be shear-thinning with a small degree of thixotropy. Suspensions with a total solids loading of 60 wt% with 25 wt% replaced by starch exhibited higher viscosity and thixotropy, but the viscometric behavior is almost identical for the two starch types (apparent viscosities 130–50 mPa·s). Oscillatory rheometry shows that for suspensions with potato starch the onset temperature for gelatinization is 61°C–63°C, that is, lower than for corn starch (72°C–73°C). Maximum storage moduli and phase shift values after gelatinization are similar for both systems. The mechanical properties of green disks, measured via diametral compression tests, reveal clear differences between materials prepared with corn and potato starch, with the latter showing higher elastic modulus, higher strength, and higher deformation at fracture, obviously because of incompletely gelatinized starch granules in the green bodies prepared with corn starch.

I. Introduction

DURING the last decade starch consolidation casting has become a very popular method for the preparation of porous ceramics. In fact, almost simultaneously with the publication of the 1998 key paper by Lyckfeldt and Ferreira, which presented the first results for alumina ceramics,¹ this process has also been applied to cordierite ceramics.² Further applications of this processing technique, using either native or modified starches, concerned porous calcium carbonate,³ silica,⁴ gibbsite,⁵ zirconia,⁶ mullite,^{7–9} and even cermets¹⁰ and metals (porous steels) prepared by the powder metallurgy route.¹¹ Also clay-based materials,^{12,13} and, very recently, porcelain foams¹⁴ have been prepared using starch consolidation casting. At the same time, processing details as well as process optimization and material characterization issues of starch consolidation casting were further investigated for alumina^{15–24} and cordierite.^{25–29} While in the first applications of starch consolidation casting to cordierite² modified potato starch (modified by hydroxypropylation and crosslinking) has

been used, the aforementioned later research^{25–29} was primarily focused on the use of native potato starch and native and modified cassava (tapioca) starches. It is one of the aims of this study to fill this gap and to provide a complex comparison of the performance of native corn starch for this purpose with that of native potato starch.

The processing performance of starch types can be compared by rheological measurements of aqueous suspensions, both viscometric and rheometric. In particular, for assessing the castability, viscometric measurements are indispensable, and for assessing the changes in the viscoelastic behavior of aqueous starch-containing suspensions due to starch swelling and gelatinization^{30,31} rheometric measurements are necessary. Measurements of this type provide in principle a complex modulus (or complex viscosity) that contains information both on the viscosity of the system in the liquid state and the elasticity (rigidity) of the system in the solid gel state.³² In previous work such measurements have been performed for starch-containing suspensions of alumina³³ and mullite,³⁴ while the present work compares the rheology of corn- and potato starch-containing suspension of a mixture of ceramic raw materials for the preparation of cordierite ceramics and relates the rheological findings to the mechanical properties of cordierite precursor green bodies. The latter (in this work determined via diametral compression tests) is in fact a characterization of the bodies after starch swelling, gelatinization and subsequent retrogradation during cooling, that is, in the state directly corresponding to the state where the characterization by rheometry ends. It should be emphasized that these green body properties become especially important when a mature shaping technique like starch consolidation casting is to be upscaled from the laboratory scale to pilot plants and finally industry. In this case the green body mechanical properties are critical because they determine the robustness of the samples with respect to further handling before firing and may possibly restrict the degree of automation (e.g., during transport to the kiln) that may be used without destroying the samples.

The paper is organized as follows: In the Experimental part, the raw materials are characterized and details of the rheological measurement techniques, the preparation, and characterization of the green samples are given. In the Results section the viscosity of suspensions at room temperature, the temperature dependence of the viscoelastic properties are discussed, as well as the stress-strain curves of green samples during the diametral compression tests at room temperature.

II. Experimental Procedure

(1) Raw Materials and Characterization

Commercial powders of kaolin (Sedlec Ia, Sedlecký kaolin a.s., Božičany, Czech Republic), talc (EC 75; Luzenac Group, Three Springs, Australia) and alumina (CT3000 SG;

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Almatis GmbH, Ludwigshafen, Germany) were used to obtain a cordierite precursor mixture. This precursor mixture, denoted PM and composed by 37 wt% of kaolin, 41 wt% of talc and 22 wt% of alumina, was formulated based on its compositions in oxides and bears some resemblance to that of stoichiometric cordierite ($\text{SiO}_2 = 51.4 \text{ wt}\%$, $\text{Al}_2\text{O}_3 = 34.8 \text{ wt}\%$, and $\text{MgO} = 13.8 \text{ wt}\%$). However, it has a lower silica content (46.6 wt%) and a higher alumina content (38.1 wt%) than the stoichiometric composition, whereas the magnesia content is very similar (13.6 wt%). The chemical composition of the raw materials was characterized by X-ray fluorescence (XRF) analysis (ARL 9400 XP; Thermo Electron, Waltham, MA; with 4GN Rh anode).

The XRF results indicated that the kaolin has a $\text{Al}_2\text{O}_3/\text{SiO}_2$ weight ratio close to 0.8, which corresponds to the stoichiometric proportion of kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$], the main clay component of this mineral, with amounts of Fe_2O_3 , CaO , MgO , and $\text{Na}_2\text{O} < 1.9 \text{ wt}\%$ and $\sim 0.9 \text{ wt}\%$ of K_2O . Regarding the other constituents of the precursor mixture, also the talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] exhibits a SiO_2/MgO weight ratio ($64.4/33.1 = 1.9$) close to the stoichiometric composition, with contents of Fe_2O_3 (0.9 wt%) and CaO (0.4 wt%) as impurities. The alumina powder (Al_2O_3) showed a high purity (99.85 wt%), with an alkaline and alkaline-earth impurity level lower than 0.2 wt% and a very small amount of silica and iron oxides (0.05 wt%).

Qualitative phase analysis of the raw materials was performed by X-ray diffraction (XRD; X'Pert PRO, PANalytical, Almelo, the Netherlands; $\text{CuK}\alpha$ radiation at 40 mA and 40 kV, and $1^\circ 2\theta/\text{min}$). Kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$; PDF 06-0221] was determined as the main crystalline phase in the kaolin powder, with small amounts of quartz (SiO_2 ; PDF 01-083-2465) and halloysite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$; PDF 013-0375] as secondary phases. Talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$; PDF 19-0770] was the main phase in the respective raw material (a very small peak of hematite was also determined in the diffractogram), and corundum (Al_2O_3 ; PDF 01-82-1399) was the only phase identified in the alumina powder. For each raw material, the phases detected by XRD were consistent with the results obtained via XRF analysis.

Particle size distributions of raw materials were measured by laser diffraction (Analysette 22 NanoTec, FRITSCH GmbH, Idar-Oberstein, Germany). The D_{50} (median particle diameter) values were 3.2, 9.0, and $0.8 \mu\text{m}$ for kaolin, talc, and alumina powders, respectively.

Concerning starches, commercially available powders of potato (Solamyl, Natura a.s., Havlíčkův Brod, Czech Republic) and corn (Gustin, Dr. Oetker, Kladno, Czech Republic) starches were used as consolidator/binder and pore forming agent. Densities (ρ) were determined by He-pycnometry (Multipycnometer, Quantachrome Instruments, Boynton Beach, FL). The values obtained (1.47 and 1.49 g/cm^3 for potato and corn starches, respectively) were in the range of the values reported for these types of starch.^{4,35} Based on XRD peak positions, the corn starch was classified as A-type (15.2 , 17.1 , 18.0 , and $22.9^\circ 2\theta$), whereas the potato starch was designed as B-type (5.4 , 15.0 , 17.2 , 21.8 , and $24.0^\circ 2\theta$).³⁶

The volume-weighted particle size distributions (Analysette 22 NanoTec, FRITSCH GmbH, Idar-Oberstein, Germany) were determined by using an aqueous suspension of starch with a polyacrylic acid solution (Dolapix CE-64; Zschimmer & Schwarz, Lahnstein, Germany) as dispersant and applying ultrasound for 15 min to disperse and stabilize the starch particles. Each starch presented a bimodal distribution with low volume percentage of small particles, which are associated with impurities or broken granules. The median particle diameter for potato starch ($D_{50} = 45 \mu\text{m}$) was notably higher than the corresponding to the corn starch ($D_{50} = 15 \mu\text{m}$). Both starches have $\sim 5 \text{ vol}\%$ of small granules ($0.5\text{--}5.0 \mu\text{m}$). The parameter $W = (D_{90} - D_{10})/D_{50}$ (where D_{90} and D_{10} are the granule diameters for 90 and 10 vol% of granules, respectively) was chosen for estimating the width of particle

size distributions. The corn starch presented a slightly narrower distribution ($W = 0.8$) than the potato starch ($W = 1.1$).

The weight percentage of humidity was determined by thermogravimetric analysis (TGA-50, Shimadzu, Kyoto, Japan) at $10^\circ\text{C}/\text{min}$ up to 120°C , in air, being the determined values (13.1 and 10.6 wt% for potato and corn starches, respectively) in the range of those usually reported for each type of starch.^{4,35}

The granule morphology analysis of the dry starches was carried out by scanning electronic microscopy (SEM; JSM-6460, JEOL, Tokyo, Japan). Potato starch exhibited the largest granules, with smooth surfaces and oval or spherical forms, while corn starch showed granules with some faceted isometric edges.

(2) Forming of Green Bodies

(A) Rheological Behavior of Aqueous Suspensions:

First, with the aim to select the solid loading to be used in the preparation of precursor mixture suspensions, aqueous suspensions with inorganic solid contents of 50, 60, and 70 wt% were prepared by: (a) mixing (impeller mixer) ceramic powders in distilled water (70.4 vol%) with 1 wt% of Dolapix CE-64 (Zschimmer & Schwarz) and 0.5 wt% of sodium naphthalene-sulfonate (Nutrimer Argentina S.A., Buenos Aires, Argentina), both amounts with respect to the ceramic solid content, added in a sequential manner (the kaolin suspension first, with a pause of 24 h, then the talc and finally the alumina); (b) homogenizing in a ball mill for 4 h; and (c) degassing for 20 min. Rheological measurements of these suspensions at room temperature were performed by rotational viscometry using a rheometer (Physica MCR 301, Anton Paar GmbH, Ostfildern, Germany) and a coaxial cylinder (DIN 53019, Anton Paar GmbH). Flow curves were obtained with a three-stage program: (1) a linear increase in shear rate from 0 to 1000 s^{-1} in 300 s, (2) 60 s at 1000 s^{-1} , and (3) a further decreasing to zero shear rate in 300 s. Based on the obtained results, the ceramic loading was selected in order to prepare the precursor mixture suspensions with starch. The used starch amount, 25 wt%, was selected in order to obtain ceramic materials with porosities higher than 35% by starch consolidation casting, taking into account the result of a previous work³⁷ and data reported in the literature.³⁸

The aqueous ceramic-starch suspensions were prepared using the aforementioned procedure for the preparation of the ceramic suspensions. After homogenizing the inorganic solids in water, starch was added together with extra water in order to obtain the desired concentration of 25 wt% of starch and 35 wt% of ceramic powders, that is, to retain the total solids loading of 60 wt%. Considering a value of $2.40 \pm 0.05 \text{ g/cm}^3$ for the pycnometric density of the precursor mixture with starch determined by He-pycnometry (Multipycnometer, Quantachrome Instruments), the volume fraction of starch related to suspension volume was 15 vol%. The starch was homogenized into the ceramic suspension by mixing at a low rate for 1–2 min to avoid the rupture of starch granules, and thus, in consequence, to avoid the possible occurrence of an incipient gelatinization process at room temperature.³⁹ Subsequently, the ceramic-starch suspension was degassed under vacuum for 20 min.

The influence of the starch on the rheological behavior of the ceramic suspension was also evaluated. The rheological tests were performed using the same instrument and experimental conditions than those employed for starch-free suspensions.

Moreover, viscoelastic properties (storage and loss moduli, G' and G'' , respectively, and the phase shift, $\delta = \arctan G''/G'$) of aqueous starch and ceramic-starch suspensions as a function of temperature ($30^\circ\text{C}\text{--}95^\circ\text{C}$) were determined by temperature sweep tests at a heating rate of $5^\circ\text{C}/\text{min}$. All the dynamic measurements were carried out using the aforementioned rheometer in the oscillatory mode, operated with a 25-mm diameter parallel-plate geometry, a gap of 1 mm and a

frequency of 1 Hz. Preliminary measurements were conducted in order to obtain the linear viscoelastic range. A strain of 0.5% was used to ensure that all the temperature sweep tests were within the linear region. In all the measurements, a thin layer of low viscosity silicone oil was spread on the surface of the sample exposed to the atmosphere to minimize the evaporation of water from the starch suspension. Moreover, the viscoelastic behavior of aqueous starch suspensions was evaluated employing 10 vol% of starch with 1 wt% of Dolapix CE-64 (Zschimmer & Schwarz) as dispersant to ensure the occurrence of the gelatinization process even when the evaporation of a certain water volume is produced.

(B) Preparation and Characterization of Green Compacts: Green disks (diameter = 18 mm, thickness = 4–5 mm) were prepared by thermal consolidation of aqueous suspensions of the cordierite precursor mixture with starch. The suspensions were poured into cylindrical stainless steel molds (diameter = 20 mm; thickness = 10 mm), which were covered with Teflon tape to reduce water evaporation, heated in air in an electric stove with circulation of forced air (UFP 400; Memmert, Schwabach, Germany) at 80°C for 4 h and dried at 40°C for 12 h. Once the consolidation was completed, the samples were taken out of their molds. Experimental conditions (temperature and dwell time) used for the consolidation of suspensions were established on the basis of results previously reported by the authors,^{25,26} other data reported in the literature² and the rheological testing. The consolidation temperature was selected to ensure the occurrence of a complete gelatinization process in the majority of granules, which also minimizes segregation of the ceramic particles and starch granules during the consolidation. The dwell time at that temperature made possible the consolidation of disks, and thus ensured successful demolding.

Green densities (ρ) were determined by immersion in Hg (Archimedes method). Porosities of green disks (% P) were calculated via the relation $100 \cdot (1 - \rho/\rho_p)$, where ρ_p is the pycnometric density of the powdered green sample, namely of the precursor mixture with starch (2.4 g/cm³). The microstructural analysis of the prepared green disks was carried out by SEM (JSM-6460; JEOL) on fracture surfaces.

Finally, the evaluation of the mechanical behavior was performed by diametral compression testing. An INSTRON 8501 (Instron Ltd., High Wycombe, Bucks, UK) high stiffness servohydraulic machine and steel platens (HRc 65) were used. MoS₂ 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).⁴⁰ Tests were carried out at room temperature, in displacement (of the actuator) control, with a rate of 0.6 mm/min, which was previously adjusted in order to avoid temporal effects and to achieve an adequate arrangement of the sample in the load system. Three to five disks of each set of compacts were mechanically tested. The duration of each test was approximately 1 min.

The thickness-diameter ratio (t/D) of the tested disks varied between 0.2 and 0.3 in order to ensure a plane stress state during the nonmechanical testing, and also to reduce the generation of a nonuniform distribution of the axial applied load.⁴¹ The assumption of a plane stress state is implicit in the theoretical treatment of the diametral compression loading case [Eq. (1)].^{40,41} The apparent stress (σ) versus strain (ε) curves were obtained by employing the following relationships:

$$\sigma = \frac{2P}{\pi Dt} \quad (1)$$

$$\varepsilon = \frac{d}{D} \quad (2)$$

where P is the applied load when the specimen failed and d is the actuator displacement.

From σ vs ε curves, the following parameters were determined: the mechanical strength (σ_F) using the maximum load; the fracture strain (ε_F) considered as the strain corresponding to the maximal stress; 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 curve deviates from linearity. The σ_Y/σ_F ratio, considered as the degree of deviation from the linear behavior caused by any irreversible strain mechanism (such as global plasticity and/or localized plasticity, compacting and microcracking) was also calculated.

It should be noted that the word “apparent” has to be added when the elastic modulus is determined as the slope of the linear part of the stress-strain curve, due to the following reasons. At first, the stress component calculated by Eq. (1) and the deformation obtained from Eq. (2) do not correspond to the same space directions, but to directions that are mutually perpendicular. The Poisson’s modulus (ν) relates the magnitudes of deformations (strains) in orthogonal directions, e.g., x and y :

$$\nu = \frac{-\varepsilon_x}{\varepsilon_y} \quad (3)$$

Since the Young’s modulus (E) is defined by Hooke’s law for tensile loading

$$\sigma_x = E\varepsilon_x \quad (4)$$

which combined with the Poisson’s modulus gives the relationship

$$\sigma_x = -E\nu\varepsilon_y = -E_a\varepsilon_y \quad (5)$$

it is evident that the apparent elastic modulus, as used and defined in this paper (E_a), is the product of the Poisson’s ratio and the Young’s modulus. Considering that the disk is compressed during the test, the ε_y magnitude is negative thereby the negative sign of Eq. (5) is canceled.

On the other hand, the actuator displacement d is not strictly equivalent to the disk displacement, although is a very good estimation if high stiff loading system and testing machine are used, as is the case here. Furthermore, d value includes all the contributions to the deformation, independently of the type (reversible or irreversible) and location, besides the purely linear elastic deformation from which the Young’s modulus is defined. This point is relevant for the diametral compression test due to the existence of effects in the contact zone with the compression platens.^{40–43} In this sense the apparent elastic modulus used in this work could be interpreted more precisely as an elastoplastic tangent modulus.

Finally, crack patterns and fracture surfaces of the tested disks were analyzed by ocular inspection and SEM (JSM-6460, JEOL).

III. Results and Discussion

(1) Rheological Behavior of Aqueous Ceramic-Starch Suspensions

(A) Shear Flow Properties: Apparent viscosity as a function of shear rate at room temperature for the aqueous cordierite precursor mixture suspensions with 50, 60, and 70 wt% of solid content is plotted in Fig. 1(a). Similar curves for the aqueous precursor mixture suspensions with 60 wt% of solid content, containing 25 wt% of corn or potato starches are shown in Fig. 1(b). Apparent viscosity values at a shear rate of 1000 s⁻¹ (η_{1000}) for aqueous ceramic-starch suspensions are reported in Table I.

As expected, the rheological behavior exhibited by aqueous ceramic suspensions changed by increasing the solid

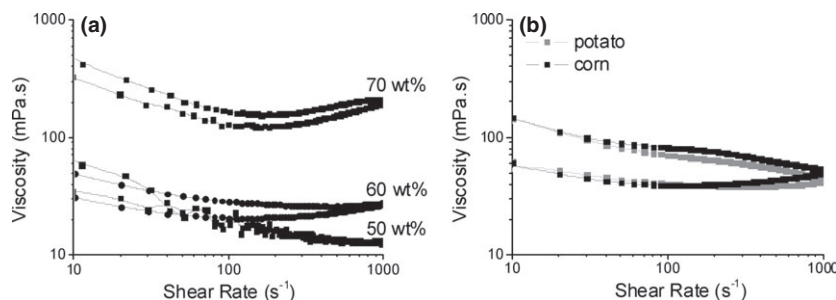


Fig. 1. Viscosity curves of (a) aqueous precursor mixture suspensions with 50, 60, and 70 wt% of solid content and (b) aqueous precursor mixture-starch suspensions with 60 wt% of solid content and 25 wt% of starch content at room temperature.

loading. The suspension with the lowest solid loading (50 wt%) showed a clearly shear-thinning behavior over the whole range of shear rates, possibly with a certain degree of thixotropy. With a solid content of 60 wt%, the suspension exhibited shear-thinning behavior in almost the entire range of shear rates, but showed a very slight dilatancy for shear rates higher than 700 s^{-1} . Regarding the suspension with the highest solid content (70 wt%), the rheological behavior was more complex, exhibiting a transition from shear thinning to shear thickening at shear rates as low as 200 s^{-1} (similarly complex rheological behavior was also reported in a previous work of the authors³⁴ and by others authors,³⁸ for mullite and mullite-starch suspensions with similar properties). With increasing solids content the hysteresis of the viscosity versus shear rate curves increases. Usually this is interpreted in terms of thixotropy, a type of time-dependent behavior that is characteristic of clay-containing suspensions. In this case, this rheological behavior is usually explained by the fact that in stagnant suspensions the oblate (platelet-shaped) clay particles, which exhibit opposite electrostatic surface charges on the faces than along the edges, build up a three-dimensional voluminous “card-house” structure, which is gradually destroyed with increasing shear rate (or even with the action of a constant shear rate for a longer time).⁴⁴

Although it has to be admitted that sedimentation effects may in some cases interfere with thixotropy effects, so that the “apparent” thixotropy measured in viscometric measurements can be both due to the aforementioned intrinsic structural reasons and due to a slow demixing of the suspension with time, no indication of the latter was found here on the time scale of the viscometric measurement.

Even though all the suspensions presented an apparent viscosity range (Table I) suitable for casting ($<2000 \text{ mPa}\cdot\text{s}$)⁴⁵ in the shear rate range investigated, the suspension with the highest solid content (70 wt%) exhibited the highest viscosity ($\eta_{1000} = 210 \text{ mPa}\cdot\text{s}$), as expected. For 50 and 60 wt% of solid loading, similar viscosity values were registered up to 50 s^{-1} , whereas from this shear rate, the suspension with 60 wt% presented higher viscosities, reaching a value twice that of the suspension with the lowest solid content (η_{1000} was 27 and 13 mPa·s for suspensions with 60 and 50 wt% of solids, respectively). Based on these results and considering the convenience of using concentrated suspensions with shear-thinning behavior and low thixotropy for casting and colloidal ceramic processing in general, a solid loading of 60 wt% was selected for preparing the aqueous mixture precursor cordierite suspensions with starch.

When starch is added to the as-prepared and homogenized ceramic suspensions [Fig. 1(b)], the apparent viscosities are higher than those of the starch-free ceramic suspensions (with 60 wt% of solid loading). Also the degree of thixotropy is higher in this case, obviously as a consequence of the presence of starch that assists structure formation. It has to be noted that, despite the fact that the solid loading (in weight percentage) was not modified by adding the starches, the viscosity of both ceramic-starch suspensions is higher

Table I. Apparent (η_{1000}) Viscosity of Aqueous Precursor Mixture Suspensions (PM) and Aqueous Precursor Mixture-Starch Suspensions

Aqueous suspension	Solid content (wt%)	Starch content (wt%)	η_{1000} (mPa·s)
PM	50	0	13
PM	60	0	27
PM	70	0	210
PM-Potato	60	25	45
PM-Corn	60	25	52

than that of the pure ceramic precursor suspension and that the viscosity increase is essentially independent of the starch type (corn starch or potato starch). Of course, the viscosity increase is not very surprising, because the starch granules have much lower density than all the ceramic phases present and therefore the volume of the starch fraction is much larger than that of the fraction of ceramic phases they replace. Note that it is the volume fraction and not the weight or mass fraction that determines the rheological behavior of the suspensions.

However, when going into detail, the incidence of the following factors on the rheological behavior, which may slightly modify the aforementioned principal effect, may be considered as well: (a) the presence of starch granules larger than the ceramic particles and with smaller surface area, (b) the increase in the width of particle size distributions that implies improved particle packing, (c) the contribution of starch granules to avoid the formation of agglomerates of ceramic particles (the mechanism of this effect is not clarified but it might be related to the preferential adsorption of smallest mineral particles on the surface of starch granules) and (d) the immobilization of water by adsorption due to specific interactions of water molecules with starch granules (such as hydrogen bonds, for instance), which add to the already existing interaction between water and ceramic particles, mainly clay particles. The first three factors would reduce the viscosity of the ceramic-starch suspension compared to the starch-free ceramic suspension, while the last factor could lead to an increase in the system viscosity. On the other hand, although the water uptake related to the swelling process by some starch granules would significantly decrease the free water available for flow and consequently, lead to a viscosity increase, this effect can be neglected here, since the viscometric measurements were carried out at room temperature, that is, far below the temperature required for the onset of swelling. However, whatever the nature of the interactions may be, it is clear that any attractive interaction between the surfaces of solid particles (both ceramic raw material powders and starch granules) and water molecules leads to a decrease in free water available for flow (immobilization of water by adsorption).

(B) *Viscoelastic Properties:* The variations in G' (storage modulus) and G'' (loss modulus) with increasing

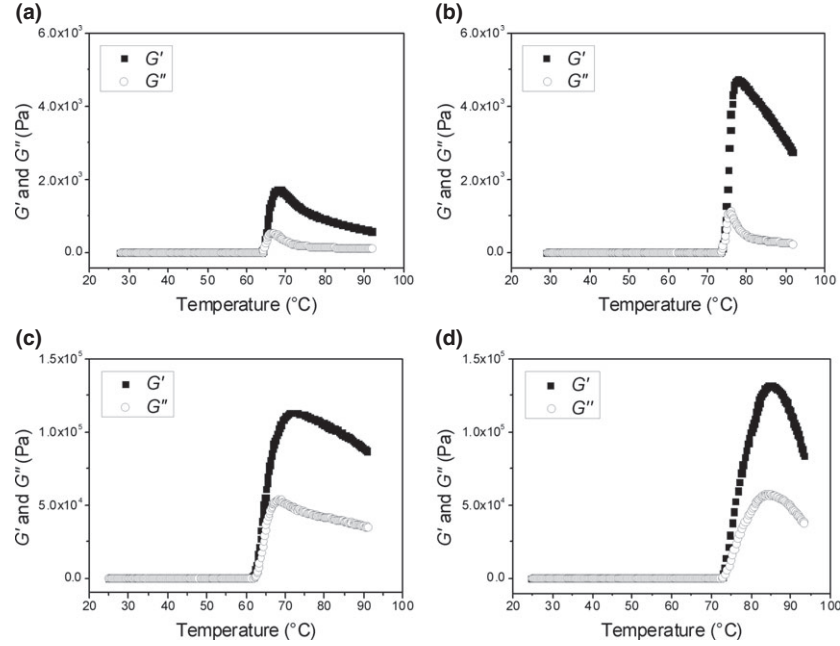


Fig. 2. G' , G'' versus temperature curves for (a) potato and (b) corn starch suspensions, and the precursor mixture suspensions with (c) potato and (d) corn starches.

temperature are shown in Fig. 2 for aqueous precursor mixture suspensions with corn or potato starch, along with G' and G'' versus temperature curves for aqueous suspensions of each starch alone (i.e., without the ceramic precursor mixture). In Table II, selected characteristic temperatures and viscoelastic parameters are presented.

In all the suspensions, G' showed a significant increase when a certain temperature was reached, namely the “onset temperature of gelatinization” $T_{G'0}$. The maximum value of the storage modulus G'_{max} was attained at a higher temperature $T_{G'max}$, and then, with a further increase in the temperature, G' decreased due to a partial gel structure breakdown during further heating under oscillation. On the other hand, G'' exhibited a pattern similar to that obtained for G' during heating, remaining below the latter value in the whole temperature range analyzed, the phase angle (δ) is below 45° for the gelatinized starch systems, or in other words, these materials are more elastic than viscous after gelatinization. In fact, after gelatinization the loss modulus is several orders of magnitude smaller than the storage modulus, so that the phase angle is close to zero and the starch gels behave essentially as elastic solids.

The behavior of the storage modulus with increasing temperature reflects (a) the removal of free water by the swelling starch granules, (b) the degree of granular swelling relative to the free volume of the system, (c) the exudation of linear amylose molecules by the swelling starch granules and the viscosity-increasing effect of the amylose in the surrounding aqueous medium, (d) the release of some amylopectin molecules into the surrounding aqueous medium and (e) the formation of a three-dimensional gel network by the leached-out amylose reinforced by a strong interaction among the swollen starch granules and the agglomerates of amylopectin molecules.⁴⁶ On the other hand, the rupture of the gel structure can be attributed to other three factors: (a) the “melting” of the crystalline regions remaining in the swollen starch granules, (b) the softening of the swollen granules due to the disentanglement of the amylopectin molecules present in them, and (c) the loss of interaction between granules and the network matrix which is mainly constituted by amylose.⁴⁷

According to the analysis of the viscoelastic parameters (Table II), differences between the two starch types in rela-

Table II. Characteristic Temperatures and Viscoelastic Parameters of Starch-Water Suspensions and Aqueous Starch-Containing Precursor Mixture (PM) Suspensions

Aqueous suspension	$T_{G'0}$ (°C)	$T_{G'max}$ (°C)	G'_{max} (Pa)	δ_{ag} (°)
Potato	63	68	1710	10
PM-Potato	61	72	115 000	22
Corn	73	78	4740	5
PM-Corn	72	83	132 000	24

δ_{ag} , phase shift after gelatinization.

tion to G'_{max} and phase shift after gelatinization (δ_{ag}) values, which control the features of the formed gel and its onset temperature of gelatinization ($T_{G'0}$), were determined. A high onset temperature of gelatinization indicates a high resistance of starch granules to swelling. The corn starch suspension exhibited a higher $T_{G'0}$ value (73°C) than the potato starch suspension (63°C). This result is consistent with the fact that, in general, the granules of tuber starch gelatinize more readily and at a lower temperature than the granules of cereal starch such as corn starch. The increase in the storage modulus G' up to its maximum value occurred in a temperature range ($T_{G'max} - T_{G'0}$) that was similar for both type of starches (5°C). This result indicates that, after reaching the onset temperature for gelatinization ($T_{G'0}$), the kinetics of gel formation is fairly similar for both starches studied. Regarding the G'_{max} values, the corn starch exhibited a higher G'_{max} indicating higher gel rigidity.

For the aqueous ceramic-starch suspensions, the increase in the storage modulus as a function of temperature can be attributed to starch gelatinization and the formation of a three-dimensional gel network that includes ceramic particles. Some water loss by evaporation may also contribute to the increase in the storage modulus. The presence of ceramic particles in the aqueous starch suspensions did not change significantly the onset temperature for gelatinization, but caused a marked increase in the G'_{max} values and $T_{G'max}$. While increased storage moduli are expected simply because of the mixture rules (since ceramic particles are inherently much stiffer than the starch gel), the latter fact seems to indicate that the kinetics of the gelatinization process is delayed.

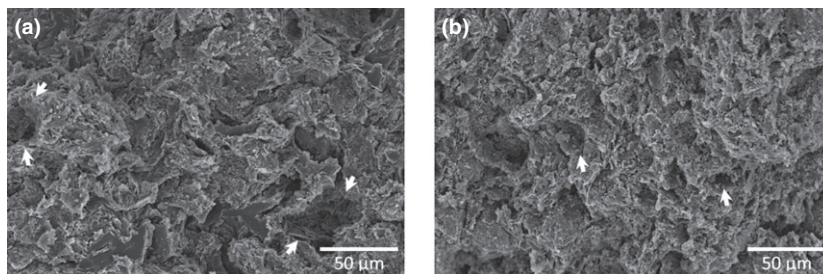


Fig. 3. SEM micrographs on fracture surface of green disks: (a) PM-potato and (b) PM-corn.

The reason for this apparent delay, however, may be the simple fact that it takes longer time for the storage moduli to attain their (much higher) maximum values. It is clear that the viscoelastic behavior of the gel structure formed with ceramic particles is essentially controlled by the starch gel network, while the ceramic particles only increase the final storage moduli. Note that after gelatinization the starch gels have smaller phase shifts (Table II) than the gels from suspensions containing both starch and ceramic particles. From the viewpoint of viscoelasticity that means that, although their absolute stiffness (rigidity) is definitely lower, pure starch gels behave more like an elastic solid than the systems with ceramic particles, where the viscous component is more pronounced. This fact seems to indicate that the ceramic particles, especially the clay particles, can modify the starch gel network by steric hindrance or the introduction of points of discontinuity.

(2) Characterization of Green Disks

After the drying process, green disks obtained attained 18.6 ± 0.9 mm in diameter and 3.7 ± 0.7 mm in height. The shrinkage in diameter during the consolidation and drying processes was 7%. The disks did not exhibit cracks or deformations.

Both types of green disks presented similar densities of 1.5 ± 0.2 g/cm³ and 1.6 ± 0.1 g/cm³ for PM-potato and PM-corn, respectively. The total porosity was also similar between them: $38\% \pm 6\%$ for PM-potato and $36\% \pm 5\%$ for PM-corn, respectively. Typical SEM micrographs of green compacts obtained with potato and corn starches are shown in Fig. 3.

The values of total porosity of green disks (<40%) were not so high when they are compared to ~50% of porosity attained for others green ceramic materials formed by consolidation casting of native starches and similar processing conditions.⁴⁸ A possible explanation for this result could be found taking into account the features of the developed microstructures. In SEM images of PM-potato and PM-corn microstructures, only a very small amount of cavities with starch-granule-specific morphology (i.e., originating from the loosening of starch granules, indicated by arrows in the Fig. 3), was observed. Moreover, no interconnected channels

(windows) were identified in the cavity walls, as was usually reported in previous works.^{48,49} The scarce amount of cavities developed in both materials, in particular for that prepared with potato starch, could be attributed to the combined effect of: (a) the occurrence of an advanced gelatinization process in the majority of granules that consequently lead to the complete loss of granular integrity and (b) the fine distribution of the leached-out granule components (mainly amylose) throughout the matrix interstices, which transformed the original discrete starch granules into a continuous and amorphous gel mass. In the microstructure of the material prepared with corn starch, where several discrete starch granule-shaped cavities could be identified, an average cavity size of 17 ± 4 μm was determined. This value is similar to the D_{10} value (19 ± 3 μm) of corn starch granules suspended in water, after their swelling and gelatinization at a temperature ~80°C, determined by analyzing of images captured by optical microscopy. This finding supports the interpretation that the gelatinization process occurs more readily or more rapidly for the larger granules. These granules might deform and burst into fragments, and only the granules of smaller sizes retained their integrity. The slight microstructural differences between both PM-corn and PM-potato green materials, in particular with respect to the presence of cavities, could be associated with different characteristics of the formed gel and the evolution of this structure at the consolidation temperature (80°C). For the potato starch, the consolidation temperature was higher than $T_{G,max}$, and therefore it is expected, that almost all the potato starch granules are completely gelatinized during the consolidation step and lose their granule identity. In the case of PM-corn materials, the consolidation temperature was lower than $T_{G,max}$, and thus the starch is less prone to complete gelatinization.

(3) Mechanical Behavior of Green Disks

In Fig. 4, typical stress–strain (σ – ϵ) curves are shown for green bodies prepared by thermal consolidation of potato and corn starches. In Table III, mean and standard deviation values of the mechanical parameters are given.

Stress–strain relationships of both types of disks were linear at the beginning but they deviated relatively soon from

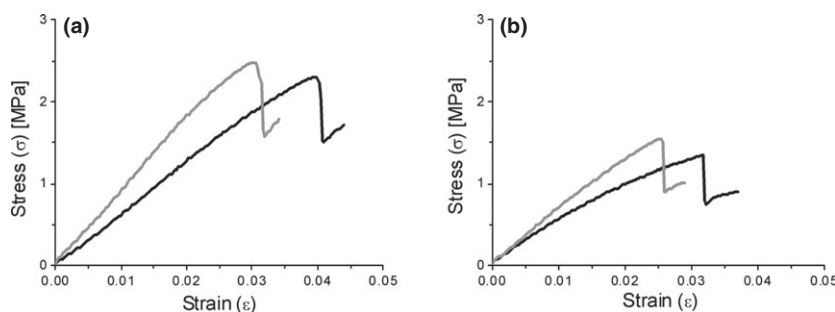


Fig. 4. Typical stress–strain curves for green bodies (a) PM-potato and (b) PM-corn.

Table III. Mechanical Parameters of Green Disks

Disk	E_a (MPa)	σ_F (MPa)	ϵ_F	σ_Y/σ_F (%)
PM-potato	72 ± 18	2.3 ± 0.2	0.039 ± 0.008	64 ± 7
PM-corn	57 ± 12	1.6 ± 0.4	0.029 ± 0.004	33 ± 19

linear behavior, as is manifest by their low σ_Y/σ_F ratio (Table III). This behavior could be attributed to the occurrence of certain degree of irreversible deformation, due to the contribution of the plasticity of the starches and the microcracking of the green compact. The latter mechanism could take place mainly in the contact between the disk and the compression platens, considering the typical low load-bearing capacity of a green body. The nonlinearity was more expressed when corn starch was used in the consolidation step, thus a mean value of σ_Y/σ_F as low as 33% was calculated. Bearing in mind the mechanisms contributing to nonlinearity of the σ - ϵ curve, PM-corn disks could be more susceptible to microcracking because they were the less mechanically resistant (lower values of σ_F , Table III).

Green disks broke by one diametral crack in every case, this being the fracture pattern expected for this loading configuration. This type of fracture led to a sudden drop of the stress after its maximum value in the stress-strain curves (Fig. 4), when the diametral crack propagated.

Disks prepared with potato starch showed higher mechanical strength and stiffness than those obtained using corn starch. The reason for this is the fact that the fully gelatinized potato starch just glues the ceramic particles efficiently together, whereas the (not fully gelatinized) corn starch contains a significant amount of intact granules that may act as stress-concentrating defects. Of course, these differences are closely related to the aforementioned relation between the consolidation temperature and the value of $T_{G'_{max}}$. The consolidation of the aqueous suspension at a temperature lower than that corresponding to $T_{G'_{max}}$ leads to the formation of a poorly developed gel. This was the case when corn starch was used. In contrast, when the consolidation process occurs at a temperature higher than $T_{G'_{max}}$, as in the case of the suspension with potato starch, the gelatinization process proceeds further and, therefore, a stiffer three-dimensional gel network is developed. This difference in the characteristics of the developed gels, which affect their capacity as binder of ceramic particles, certainly contributes to the lower mechanical strength of the PM-corn disks and can be a major reason for its lower apparent Young modulus.

On the other hand, it should be taken into account that during the cooling step after completing the consolidation process at 80°C, the called "retrogradation process", which involves the formation of chain entanglements, short-range molecular order and crystallization of double helical aggregates, can be produced and to lead to further stiffening. The increase in the shear modulus (storage modulus) during this period is consistent with the tendency of the starch constituents to associate or retrograde as the temperature decreases. The amylose content of the starch has been reported to be one of the influential factors for this process.³⁹ A higher amount of amylose has traditionally been linked to a greater retrogradation but amylopectin and intermediate materials also play an important role.⁵⁰ Other factors which affect this complex phenomenon are the source of starch, starch concentration, as well as heating and cooling temperatures, among others.

Due to the kind of changes occurring in the system when retrogradation takes place, it is expected that the stiffness of the green compact and probably also the mechanical strength increase. Moreover, the occurrence of a consolidation process at a temperature higher than $T_{G'_{max}}$ (i.e., here for the system with potato starch) may be expected to produce a higher degree of retrogradation. Furthermore, potato starch gel has

a higher inherent tendency toward retrogradation associated with the more fragile nature of the granules^{51,52}. Thus, a higher effect of retrogradation on stiffness and strength could be expected in the system MP-potato, compared to the system MP-corn.

Considering Eq. (5), an estimation of ϵ_F can be obtained from σ_F/E_a ratio. The larger deformation displayed by PM-potato disks when comparing with those prepared with corn starch (Table III) indicates that the effect of the higher mechanical strength of the former was higher than the stiffness increase.

Finally, considering the above-mentioned results and taking into account the results of mechanical properties analyzed together with the remaining information discussed in this work, it can be inferred that potato starch performs as a better binder than corn starch in the studied ceramic system and the used experimental conditions, as was observed in a previous work for other silicate ceramics.⁷

IV. Conclusions

The study of the steady-state rheological behavior of suspensions with solids loading 50, 60, and 70 wt% without starch showed that for sufficiently low shear rates all tend to be shear thinning with a small degree of thixotropy, although with increasing concentration the behavior can change to slightly shear thickening at higher shear rates. Suspensions with a total solids loading of 60 wt% with 25 wt% replaced by starch exhibited higher viscosities and also a higher degree of thixotropy, but the viscometric behavior has been found to be almost identical for the two starch types. The apparent viscosities of the starch-containing suspensions were rather low (range 130–50 mPa·s) so that there is a certain room for process optimization by increasing the solids loading without losing castability.

Oscillatory rheometry was used to characterize the viscoelastic behavior of starch suspensions and starch-ceramic suspensions as a function of temperature. It has been found that for suspensions with potato starch (with or without ceramic particles) the onset temperature for gelatinization is 61°C–63°C, which is by about 10°C lower than that of suspensions with corn starch (72°C–73°C). Maximum storage moduli and phase shift values after gelatinization were similar for systems with corn and potato starch. Interestingly, although the presence of ceramic particles enhanced the respective storage moduli by much more than an order of magnitude (compared to pure starch-water systems), from the viewpoint of viscoelasticity these systems retained a significant viscous component with a phase shift greater (i.e., a loss tangent higher) than pure starch gels immediately after gelatinization.

The mechanical properties of green disks, measured via diametral compression tests, revealed clear differences between materials prepared with corn and potato starch, with the latter showing higher apparent elastic modulus, higher strength, and higher deformation at fracture. Relics of incompletely gelatinized starch granules have been identified by microscopic studies as the main reason for the lower mechanical properties of cordierite precursor green bodies prepared with corn starch. Considering these results, in combination with the previous rheological analysis, the potato starch showed a better performance as a binder agent than corn starch.

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