

Rheology of aqueous mullite–starch suspensions

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Abstract

One of the forming methods developed for the manufacture of porous materials by direct consolidation, in which a ceramic suspension consolidates into non-porous molds (e.g. metal molds) by thermogelation of an organic agent, uses starch as both consolidator/binder of the ceramic suspension and pore former at high temperature. Changes in the rheological behavior of the aqueous suspensions are produced by starch gelatinization thermal process. This process as well as the presence of both the ceramic particles and added processing additives, influences the kinetics of green ceramic body formation and its microstructural features.

In this work, the thermogelling behavior of mullite aqueous suspensions (40 vol.%; 0.45 wt.% of a polyacrylic polyelectrolyte as dispersant) containing 10 vol.% of different native starches (potato, cassava, and corn) was studied by dynamic rheology in order to determine the experimental conditions that must be used for forming mullite green bodies by thermal consolidation. Viscoelastic properties (G' and G'') as a function of temperature (30–95 °C) and deformation (0.1–625.0% at 40 °C) were determined by temperature sweep tests and dynamic strain sweep tests, respectively. From these tests, and considering previous results of the rheological behavior of starch suspensions, we analyzed the influence of ceramic particles on the starch gelatinization process and the strength of the developed gels. On the other hand, shear flow properties of aqueous mullite–starch suspensions were also analyzed to obtain information on the rheological behavior of the suspensions at room temperature.

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1. Introduction

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is an important ceramic material due to its good mechanical properties at high temperature as well as its low thermal conductivity, low thermal expansion coefficient and good chemical stability. These properties make the development of mullite materials useful in several applications, such as dense bodies (e.g. structural components, microelectronic industry devices, among others) or highly porous bodies (e.g. thermal insulators, catalyst supports, combustion burners).^{1–5}

In recent years, several new processing methods with low environmental impact have been developed to satisfy the high demand for materials possessing controlled porous microstructure.^{6,7} Among these, one of the most promising methods is direct consolidation, in which a ceramic suspen-

sion consolidates inside non-porous molds (e.g. metal molds) without compaction or removal of water. Direct consolidation can be produced through the formation of a physical gel as a consequence of the creation of a network structure among particles or through the formation of a chemical gel by chemical polymerization of monomers or thermal gelation of polysaccharides. Polysaccharides can form a gel either on cooling (as in the case of agar, agarose and carrageenan) or on heating (as for methylcellulose derivatives, dextrans and starches). Cooling of agaroids has been widely used for obtaining dense bodies,⁸ although porous materials can be easily obtained also.^{9,10} The ability to form strong gels on heating is the basis of the so-called “starch consolidation process”, a new non-contaminating low-cost consolidation technique based on the gelling capability of starch in aqueous media at temperatures between 55 and 85 °C. In this method, starch acts as a consolidator/binder agent of the ceramic particles as well as a pore former after consolidation by burnout at high-temperature.^{11–15} This technique takes advantage of the insolubility of starch granules in water below 50 °C,

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which allows handling and processing at room temperature without affecting the structure. When starch granules are heated in the presence of water, various changes take place in a process called gelatinization. These changes involve physical and chemical phenomena, such as water diffusion, granule swelling, amylose leaching, the disruption of crystalline structures, and the realignment and formation of new intermolecular and intramolecular bonds.¹⁶ Starch gelatinization process increases the suspension viscosity and then induces the formation of a gel between 55 and 85 °C. Consequently, when this process occurs in an aqueous ceramic-starch suspension, the rapid and irreversible swelling of the starch granules by water absorption¹⁷ causes the ceramic particles to stick together, thus consolidating into a solid body.

For colloidal forming methods, the study of the rheological behavior provides relevant information regarding the stability of the suspension. Solid type and content, amount of organic additives, the way they are added and their interactions play relevant roles in the features of the final structure.

In addition, the presence of mullite in the aqueous starch suspension modifies the behavior of the starch granules as a function of temperature as well as the characteristics of the developed gel. Therefore, the change of rheological properties in the ceramic-starch suspension and their morphological characteristics, determined by both the inherent gelatinization process and the incidence of the ceramic powder and added processing additives, affects the kinetics of ceramic body formation and its final micro-structural features.

In this work, the rheological behavior of concentrated aqueous mullite suspensions with different native starches (potato, cassava, and corn) was studied by dynamic rheology as a function of temperature and strain. From these tests, and considering previous results of rheological behavior of aqueous suspensions of the employed starches, the influence of ceramic particles on the starch gelatinization process and the strength of developed gels were also studied. Furthermore, shear flow properties of aqueous mullite–starch suspensions were analyzed in order to obtain information about the rheological behavior of the suspensions at room temperature.

2. Experimental

2.1. Starting materials

A high-purity mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) powder (MULS, Baikowski, France) was used as the ceramic raw material. The impurity level determined by wet chemical analysis was less than 0.2 wt.%. The weight percentages of the elements (expressed in oxides) were also determined from this analysis. Thus, an excess of alumina (3.0 wt.%) with respect to the stoichiometric composition ($\text{Al}_2\text{O}_3 = 71.8$ wt.%, $\text{SiO}_2 = 28.2$ wt.%) was calculated, 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 forms solid solution with mullite¹⁸). This result is in agreement with the crystalline phases (mullite as primary phase and α -alumina and cristobalite as secondary phases) identified by X-ray diffraction analysis (XRD) (Philips PW1830, $\text{CoK}\alpha$, at 30 mA and 40 kV, and at 1° $2\theta/\text{min}$), and with the pycnometric

Table 1
Characteristics of starches studied.

Starch	Density (g/cm^3)	Moisture content (wt.%)	T_p (°C) ^a	Particle size distribution	
				D_{50} (μm) ^b	W ^c
Cassava	1.49	11.5	67.5	13.6	1.2
Corn	1.49	10.9	66.8	14.8	1.1
Potato	1.47	14.4	65.0	47.8	1.3

^a T_p , endothermic peak temperature.

^b D_{50} , median volume granule diameter.

^c W , width of the distribution.

density value measured in kerosene at 37 °C ($3.35 \text{ g}/\text{cm}^3$) which was discovered to fall midway between the theoretical densities of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($3.16 \text{ g}/\text{cm}^3$) and $\alpha\text{-Al}_2\text{O}_3$ ($3.98 \text{ g}/\text{cm}^3$). The powder presented a bimodal particle size distribution (Mastersizer S, Malvern Instruments Ltd., UK) with a low mean volume diameter ($D_{50} = 1.5 \mu\text{m}$), a high volume percentage of fine particles $<1 \mu\text{m}$, and containing agglomerates up to $50 \mu\text{m}$ associated with the presence of the very fine particles. These results are consistent with the high value of specific surface area ($13.5 \text{ m}^2/\text{g}$) determined by the BET method (Monosorb, Quantachrome Co., USA). A scanning electron microscopy (SEM) micrograph of mullite powder is shown in Fig. 1.

Native potato, cassava, and corn starches (Avebe S.A., Argentina) were also employed. Real densities determined by He-pycnometry (Multipycnometer, Quantachrome Co., USA) were: $1.47 \text{ g}/\text{cm}^3$ for potato starch and $1.49 \text{ g}/\text{cm}^3$ 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 applying ultrasound for 15 min to disperse and stabilize the starch particles. The weight percentage of moisture was determined by thermogravimetric analysis (Shimadzu TGA-50, Japan) at $10^\circ\text{C}/\text{min}$ up to 120°C , in air. Starch transition temperatures (T_p : endothermic peak temperature) were determined by differential scanning calorimetry (DSC) (Shimadzu DSC-50, Japan) up to 120°C at $5^\circ\text{C}/\text{min}$ using highly diluted aqueous starch suspensions (>70 wt.% water) placed into sealed aluminum pans. The granule morphology analysis of the dry starches was carried out by SEM (Jeol JSM-6460, Japan).

The characteristic properties for each starch are given in Table 1 and SEM micrographs of the dry native starches are also shown in Fig. 1.

The pycnometric density values, moisture weight percentages, starch transition temperatures, and particle size distributions obtained for each starch studied are in good agreement with values reported for cassava, corn, and potato starches in similar experimental conditions.^{11,12,19–21}

All the starches presented bimodal granulometric distributions, with a low volume percentage ($<5\%$) of small granules, which can be linked to impurities or broken granules. The median volume diameter for potato starch ($D_{50} = 47.8 \mu\text{m}$) was notably higher than the corresponding values of the other

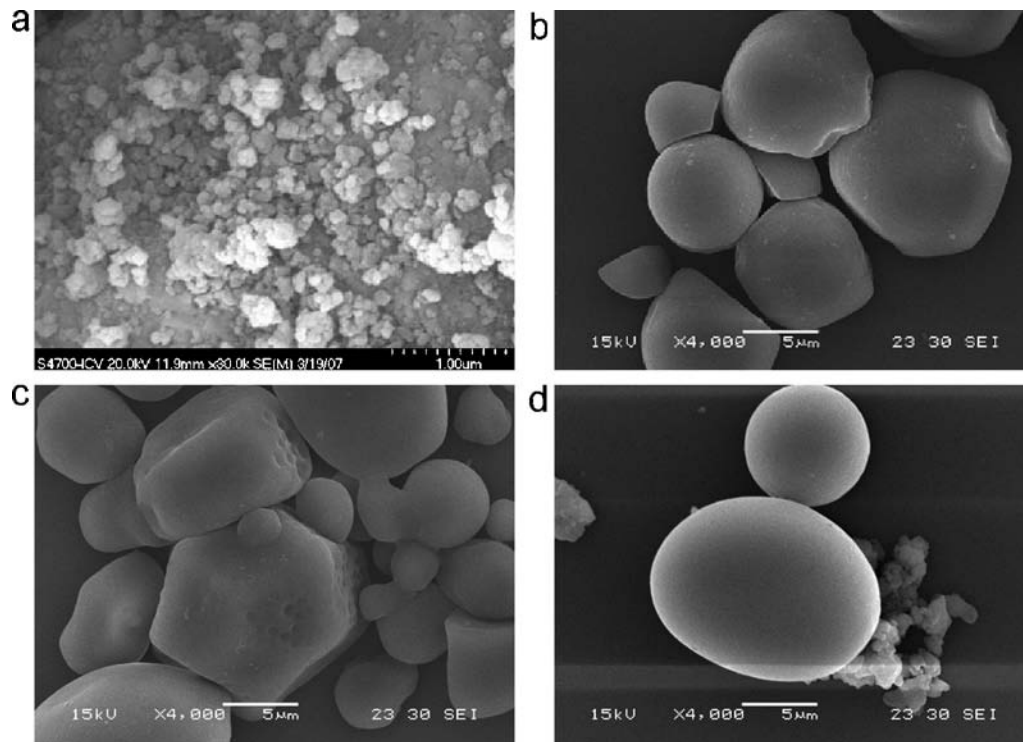


Fig. 1. SEM micrographs of mullite powder (a) and granules of cassava (b), corn (c), and potato (d) starch.

starches ($D_{50} = 13\text{--}15\ \mu\text{m}$). Corn and cassava starches exhibited a higher amount of small granules ($0.5\text{--}4\ \mu\text{m}$) than potato starch ($0.6\text{--}10\ \mu\text{m}$). 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. Although, no significant differences were determined among the W values for the different starches, corn starch presented a slightly narrower distribution ($W = 1.1$) than the others ($W = 1.2\text{--}1.3$).

Potato starch exhibited the largest granules, with smooth surfaces and oval or spherical forms. Corn and cassava starches presented granules with polyhedral form, being corn starch granules most representative of this kind.

2.2. Rheological behavior of aqueous mullite–starch suspensions

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 solid content, (b) homogenization in a ball mill for 6 h to stabilize the suspension, and (c) adding aqueous starch suspension (40 vol.%) and mixing (impeller mixer) for 5 min.

The optimum stability conditions for preparing the aqueous mullite suspensions were previously determined²² by measuring zeta potential (Zetasizer Nano ZS, Malvern Instruments, UK) and shear flow properties. Viscosity measurements at room temperature were performed using a rotational rheometer (Haake RS50, Thermo Electron Corp., Germany) under controlled stress

or controlled rate operating modes with a double-cone/plate sensor configuration (DC60/2°, Haake, Germany). Flow curves of the mullite suspension were obtained with a three-stage measuring program with a linear increase of shear rate from 0 to $1000\ \text{s}^{-1}$ in 300 s, 60 s at $1000\ \text{s}^{-1}$, and a further decreasing to zero shear rate in 300 s.

Dynamic viscoelastic properties, such as storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta = G''/G'$) of aqueous mullite–starch suspensions (0.25 starch volume fraction of 40 vol.% total solid loading) as a function of temperature ($30\text{--}95\ ^\circ\text{C}$) and deformation (0.1–625.0%) were determined by temperature sweep tests at a heating rate of $10\ ^\circ\text{C}/\text{min}$ and by dynamic strain sweep tests at $40\ ^\circ\text{C}$, respectively. Dynamic strain sweep tests were carried out on mullite–starch suspensions after heating at $10\ ^\circ\text{C}/\text{min}$ up to $95\ ^\circ\text{C}$ and quickly cooling down to $40\ ^\circ\text{C}$ in order to analyze the strength of the developed gels. All the dynamic measurements were carried out in rotational rheometer (RDA-II, Rheometric Scientific, USA) operated with a 50 mm-diameter parallel-plate geometry, a gap of 1 mm and a frequency of 1 rad/s (0.16 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. Additionally, shear flow properties of aqueous mullite–starch suspensions were also studied. These tests were done using the same rotational rheometer (Haake RS50, Thermo Electron Corp., Germany) and the same experimental conditions reported for mullite suspensions.

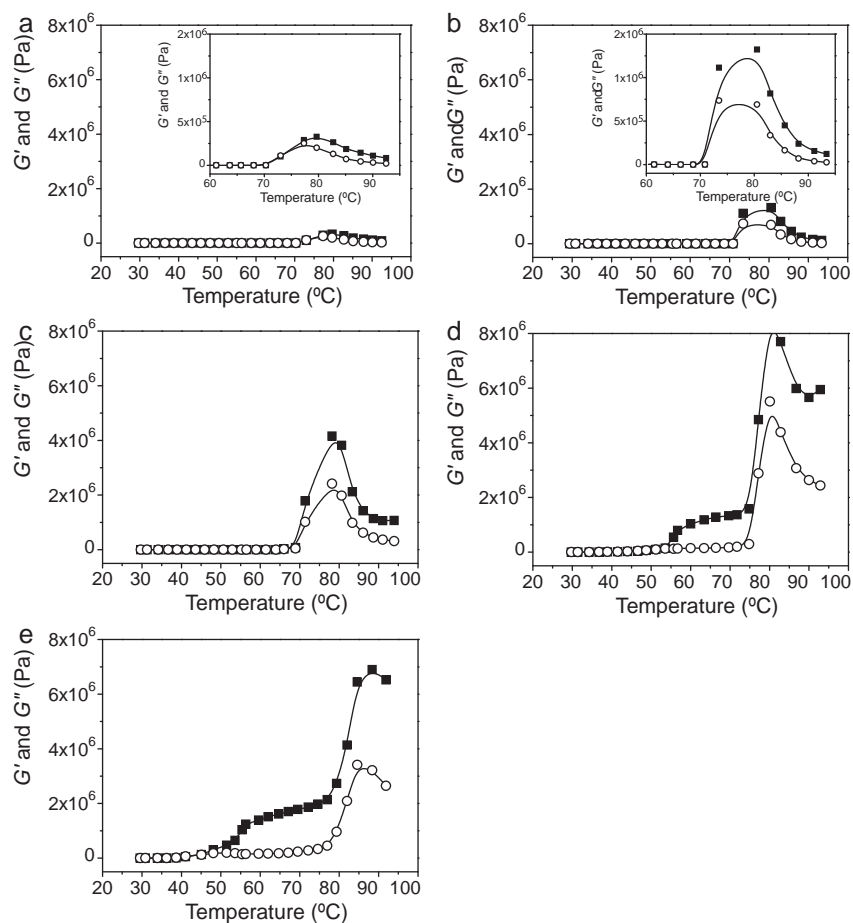


Fig. 2. G' and G'' vs. temperature for aqueous mullite-cassava starch suspensions (40 vol.%) with the following volume fractions: (a) 0/1.0; (b) 0.15/0.85; (c) 0.30/0.70; (d) 0.50/0.50, and (e) 0.75/0.25. (■) G' and (○) G'' .

The proportion of starch used in the aqueous mullite–starch suspensions was selected taking into account: (a) the content of starch usually used to produce porous ceramic, with porosities higher than 35 vol.%, by the starch consolidation technique^{13,14} and (b) the results obtained from sweep temperature tests of aqueous mullite suspensions with the addition of different amounts of cassava starch. Viscoelastic properties (G' and G'') of aqueous mullite suspensions with 0.85, 0.70, 0.50, and 0.25 volume of cassava starch and a constant solid content of 40 vol.% were analyzed by dynamic rheology as a function of temperature in the range of 30–95 °C.

3. Results and discussion

3.1. Effect of starch concentration on the dynamic rheological behavior of aqueous mullite-cassava starch suspensions

The influence of starch concentration on the dynamic rheological behavior of mullite–starch suspensions was evaluated by using cassava starch. The volume fraction of starch in the aqueous suspensions was varied from 1.0 to 0.25 for a constant total solid loading of 40 vol.%. For comparative purposes, the dynamic rheological

behavior of aqueous cassava starch suspensions was also considered.²³

Fig. 2 shows viscoelastic properties (G' and G'') of aqueous mullite–starch suspensions as a function of temperature (30–95 °C) for different volumes of cassava starch (1.0, 0.85, 0.70, 0.50 and 0.25).

The storage or dynamic modulus (G') is a measure of the energy stored in the material and recovered from it per cycle, while the loss modulus (G'') is a measure of the energy dissipated or lost per cycle of sinusoidal deformation. The ratio of the energy lost to the energy stored for each cycle (G''/G') defined as loss tangent ($\tan \delta$) is another parameter indicative of the physical behavior of the material.

Starch gelatinization process occurs by heating the granules in the presence of an excess of water. In this process, granules swell to several times their initial volume, amylose is leached out, and a three-dimensional network is formed. Then the rheological properties exhibited by starch suspensions during heating and shearing are characteristics of the changes in starch structure. Furthermore, ceramic particles in the aqueous starch suspensions influence the gelatinization process modifying the rheological properties of the suspension.

The typical rheological behavior exhibited by aqueous starch suspensions as a function of the temperature was observed in

the aqueous cassava suspension (Fig. 2a). G' increased from a certain temperature (onset temperature of gelatinization, $T_{G'_0} = 71.6^\circ\text{C}$) up to a maximum value ($G'_{\text{max}} = 330\text{ kPa}$) at $T_{G'_{\text{max}}} = 79.7^\circ\text{C}$) and then decreased beyond $T_{G'_{\text{max}}}$, G' with a further increase in the temperature, indicating that gel structure had broken down. The loss modulus (G'') exhibited a pattern similar to that obtained for G' during heating, remaining below G' . This last fact indicates that aqueous cassava suspensions behave mainly as a viscoelastic material. The removal of water from the exuded amylose as the granules swell and the formation of a three-dimensional gel network¹⁶ are some of the responsible factors for the initial increase of G' , while the breakdown of the formed gel structure can be attributed to the disentanglement of the amylopectin molecules present in the swollen granule, and the loss of interaction between the granules and the network matrix (mainly composed of amylose),²⁴ among others factors.

The behavior of G' in the aqueous mullite–starch suspensions (Fig. 2b–e), as the temperature increased, can be related to the starch gelatinization and the formation of a three-dimensional gel network which includes ceramic particles. It must be remarked that heating induces swelling of starch granules, thus leading to a volume exclusion effect, so that particles have to rearrange in a lower available volume. The bridging of electrosterically stabilized ceramic particles that occurs above 60°C when adding a polyelectrolyte dispersant (e.g. Dolapix CE-64) can have also an influence.^{25,26} In these cases, moreover, minimum water loss due to evaporation during heating (typical experimental problem for rheological tests at temperature associated with heating using dry air) of small suspension volumes, such as those used in these rheological tests, contributed to the instability of mullite concentrated suspension, which furthermore increased the value of elastic modulus.

The above-mentioned factors explains the continuous increase of G'_{max} by increasing the nominal mullite content up to 50 vol.% (Fig. 3a). The slight decrease in this parameter for mullite contents higher than 50 vol.% was associated with an incomplete gelatinization process due to the high amount of ceramic particles. The values of the onset temperature of gelatinization, $T_{G'_0}$ and the temperature for which G' reached the maximum value during heating, $T_{G'_{\text{max}}}$ (Fig. 3b and c) increased 9°C when the nominal mullite content was increased from 0 to 75 vol.%. This fact indicates that the presence of mullite particles causes a delay in the thermogelation process of the cassava starch suspension, since both the onset of the process (swelling and gel network formation) as well as the breakdown of the formed gel structure is modified. The existence of a physico-chemical interaction between water molecules and the surface of ceramic particles and the decrease of the water diffusion rate on the surface of the granules reduce the amount of free water available for their complete gelatinization.

Based on the results obtained, and considering the starch proportions conventionally used in ceramic suspensions to obtain porous ceramics (porosity > 35%) by direct consolidation techniques,^{12–14} the chosen starch proportion to be used in the aqueous mullite–starch suspensions was 0.25 from a total solid loading of 40 vol.%.

3.2. Rheological behavior of aqueous mullite–starch suspensions according to starch type

3.2.1. Shear flow properties

Shear stress and apparent viscosity as a function of shear rate curves at room temperature for the aqueous mullite suspension and aqueous mullite suspensions containing the selected amount (25 vol.%) of cassava, corn, or potato starch are shown in Fig. 4a and b, respectively. Apparent and relative viscosity values of these suspensions are given in Table 2. The relative viscosity was defined as the ratio of the apparent viscosity of the mullite–starch suspension and the apparent viscosity of the starch-free mullite suspension (both suspensions with 40 vol.% of total solid loading).

The aqueous mullite suspension exhibited a slight transition from shear-thinning (pseudoplastic) to shear-thickening (dilatant) behavior for shear rates higher than 300 s^{-1} (Fig. 4b), thus behaving as a complex-fluid,²⁷ in which the viscosity progressively decreased while maintained at the highest shear rate, 1000 s^{-1} for 60 s.

When one part of the total volume of mullite particles was replaced by starch, the rheological behavior was similar to that observed for the mullite suspension but with a quite lower viscosity and very small shear thickening behavior. However, the thixotropic thickening was higher than observed for the mullite suspension, which can be associated with the presence of starch acting as a binder for the concentrated ceramic suspension.

The mechanisms behind the pseudoplastic to dilatant transition are not clear, although it can be associated to the arrangement of particles in the flow direction when shearing until the shear force becomes too high to maintain the linear flow and the interactions among the particles in suspension strongly increases and shear-thickening occurs.²⁷ At low shear rates, the repulsion forces dominate the structure of the suspension; however, at high shear rates viscous forces predominate over repulsion forces. Developed models assume that ceramic particles form a two dimensional structure from an equilibrium position for low shear rates and a disordered three dimensional structure for high shear rates.²⁸ On the other hand, when the disordered structure is maintained at a constant shear rate during a certain time, particles are rearranged in a more stable two dimensional structure. The observed rheological behavior was also reported by others authors^{14,28} for mullite and mullite–starch suspensions with similar properties.

Additionally, when one part of the total volume of mullite particles was replaced by either of the native starches, the viscosity decreased throughout the entire shear rate range (Fig. 4 and Table 2). This behavior, which is opposite to that reported using modified starches,^{12,14} was more evident when potato starch was used. Mullite suspensions with cassava or corn starch presented viscosity values between those for mullite and mullite–potato starch suspensions. The increase in viscosity observed for ceramic suspensions when modified starches were added has been related to the effects caused by the chemical modification and faster water uptake allowed by the more open starch–granule structure.¹² Taking into account that total solid loading was maintained constant (40 vol.%), the behavior observed with

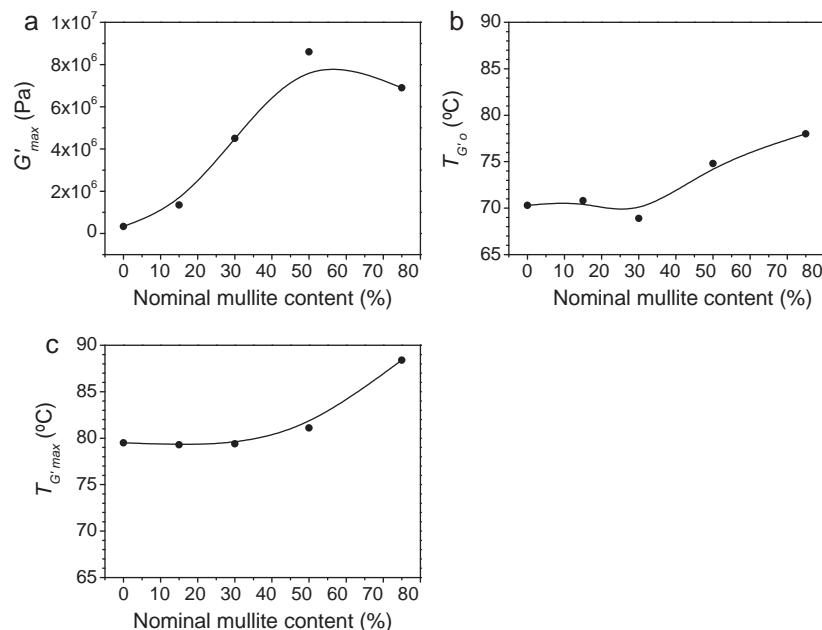


Fig. 3. G'_{\max} (a), $T_{G'_0}$ (b) and $T_{G'_{\max}}$ (c) variations as a function of nominal mullite content in the total solid loading (40 vol.%) for aqueous mullite-cassava starch suspensions.

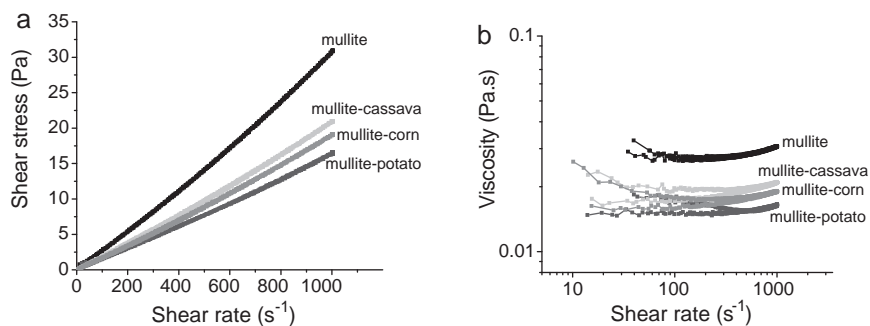


Fig. 4. Shear stress (a) and viscosity (b) curves of aqueous mullite–starch suspensions with 0 and 25 vol.% of starch nominal content at room temperature.

the native starches can be mainly attributed to the fact that starch granules are larger (the potato starch had the largest size, $D_{50} = 47.8 \mu\text{m}$) than mullite particles (Table 1, $D_{50} = 1.46 \mu\text{m}$) and presents smaller surface area, which decreases the viscosity. In addition, the width of particle size distribution increased as the starch was added and it should be considered as another effect influencing the viscosity. Thus, the possibility of a better particle packing could also be a contribution to a decrease in viscosity. On the other hand, although the water uptake by some starch granules decrease the free water (volume exclusion effect)

which can increase the viscosity, this effect was not significant since the measurements were carried out at room temperature (below the temperature required for the onset of swelling).

In spite of the viscosity of aqueous mullite suspension resulted similar to that reported by Barea et al.¹⁴, whose employed a similar mullite powder (SASM, Baikowski, France) and suspensions prepared in alike conditions, the apparent viscosities (Table 2) obtained for all the aqueous mullite suspensions with the native starches were one order of magnitude lower than values reported by these authors for mullite

Table 2

Apparent (η_{1000}) and relative (η_r) viscosity of aqueous mullite–starch suspensions.

Aqueous suspensions	Nominal starch content in suspension (vol.%)	Starch content in suspension (vol.%)	η_{1000} (m Pa s)	η_r (at 1000 s^{-1})
Mullite	0	0	30.8	1
Mullite-cassava	25	10	20.9	0.68
Mullite-corn	25	10	19.0	0.62
Mullite-potato	25	10	16.5	0.53

Table 3
Viscoelastic parameters of starch and mullite–starch suspensions.

Aqueous suspensions	$T_{G'_0}$ (°C)	$T_{G'_{\max}}$ (°C)	G'_{\max} (Pa) $\times 10^{-6}$	$\tan \delta_{G'_{\max}}$
Cassava	71.6	79.7	0.33	0.61
Mullite-cassava	78.0	88.4	6.90	0.56
Corn	78.8	85.0	1.16	0.32
Mullite-corn	84.7	91.5	6.87	0.38
Potato	72.2	81.3	0.72	0.45
Mullite-potato	76.0	88.7	19.5	0.89

suspensions with modified starches (with a constant total solid fraction). On the other hand, Gregorová et al.²⁹ reported an increase of the apparent viscosity of ceramic aqueous suspensions by adding native corn starch due to the increase of the total solid volume fraction.

It is well known that in colloidal ceramic processing, such as starch consolidation processing, the viscosity of the suspension should be low enough to allow an adequate mould filling without entrapping air and, at the same time, high enough to avoid critical segregation phenomena before the consolidation process takes place. Thus, the relatively low viscosity obtained, along with the presence of solid particles (mullite and starch) with very different sizes and densities, contributes to the increase of segregation during the consolidation step. Therefore, the use of native starch in the ceramic forming process by the direct consolidation method represents a modification of the conventional process proposed in a previous work.¹⁵

3.2.2. Viscoelastic properties

The variations of G' , as the temperature increase, for aqueous mullite suspensions with cassava, corn, or potato starch, are shown in Fig. 5 along with G' vs. temperature curves for aqueous suspensions of each starch.

A detailed study on the thermogelling behavior of the studied starches was reported in a previous work.²² Viscoelastic properties of aqueous starch suspensions depend on the botanical source of each starch, which is also related to the intrinsic composition (amylose/amylopectin content, presence of phosphates and lipids), swelling capacity, granule size distribution, shape, structure, rigidity, and degree of crystallinity.¹⁶ A high onset temperature for gelatinization indicates that starch granules have a high resistance to swelling. The maximum values of G' (G'_{\max}) obtained by heating during dynamic rheology, together with loss tangent values calculated at the maximum values of G' ($\tan \delta_{G'_{\max}}$), reveals the ability of granules to swell freely before their physical breakdown, the rigidity of the gel structure and the contribution of viscous behavior, among others aspects. Starches with a high swelling capacity are, however, less resistant to breakdown.¹⁶

Corn starch suspension exhibited the highest $T_{G'_0}$, $T_{G'_{\max}}$, G'_{\max} and the lowest $\tan \delta_{G'_{\max}}$ values (Table 3), indicating a great resistance to granule rupture and high gel rigidity, while cassava starch presented the lowest $T_{G'_0}$, $T_{G'_{\max}}$, G'_{\max} and the highest $\tan \delta_{G'_{\max}}$ values (Table 3). Moreover, the increase of

G' up to its maximum value occurred in a temperature range ($T_{G'_{\max}} - T_{G'_0}$) that was similar for potato and cassava starches (9.1 and 8.1 °C, respectively) and lower for corn starch (6.2 °C). This result would indicate that after reaching the onset temperature for gelatinization ($T_{G'_0}$), the kinetics of gel formation is faster for corn starch suspensions.

The presence of ceramic particles delayed the entire gelatinization process for all the aqueous starch suspensions (Table 3), with an increasing in G' values as mentioned before. In particular, the addition of mullite particles to corn starch suspension caused G'_{\max} to have a lower value than with other starches despite the fact that suspension of this starch without mullite achieved the highest value. Based on this result and taking into account the fact that mullite-corn starch suspension presented the highest gelatinization temperature ($T_{G'_0} = 84.7$ °C), an incomplete gelatinization process was inferred. On the other hand, the addition of mullite to cassava and corn starch suspensions did not strongly modify the corresponding $\tan \delta_{G'_{\max}}$ values (Table 3), which indicated that viscoelastic behavior of the formed structure with mullite particles was controlled by the starch gel network. However, the presence of mullite in the aqueous potato starch suspension caused an unexpected viscoelastic behavior. The notable increase of G' and $\tan \delta_{G'_{\max}}$, can be attributed to the strong destabilization of the suspension generated due to a high and fast segregation of the components; therefore, a heterogeneous system with high inhomogeneity should have developed. This fact can be explained taking into account that aqueous mullite-potato starch suspension presented the lowest apparent viscosity (Fig. 4) since potato starch granules were the largest. In this case, the developed network should consist of a gelled starch suspension with a small amount of mullite particles included, as well as aggregates of ceramic particles bonded by weak interactions. Moreover, the intrinsic nature of each starch type, which also determines a different interaction between ceramic particles and starch granules, can also affect the viscoelastic behavior.

The properties of gels developed from aqueous mullite–starch suspensions were obtained by dynamic strain sweep tests carried out at 40 °C. Experimental curves are shown in Fig. 6, from which the ‘gel strength’ may be obtained. The strain where G' equals G'' was considered an indicator of gel strength. All the gels showed elastic modulus values higher than viscous modulus, which indicates that in a defined range of strain, depending on the starch type, the gel behaves as an elastic solid. In general, as strain increased and the magnitude of G'' overcame G' , the gel structure broke down and the system behave as a viscous fluid.

Mullite-cassava gel showed the highest value of gel strength (% strain = 157.5) while the gel with corn starch showed the lowest value (% strain = 15.7), at least ten times lower than the value obtained with cassava starch. This result is consistent with the development of a stiffer gel (lower value of $\tan \delta_{G'_{\max}}$) with less susceptibility to deformation. The non-typical behavior of the gel obtained from the mullite-potato starch suspension (a continuous decrease of the viscoelastic modulus was observed over the entire strain range studied) agrees with the formation of a hetero-

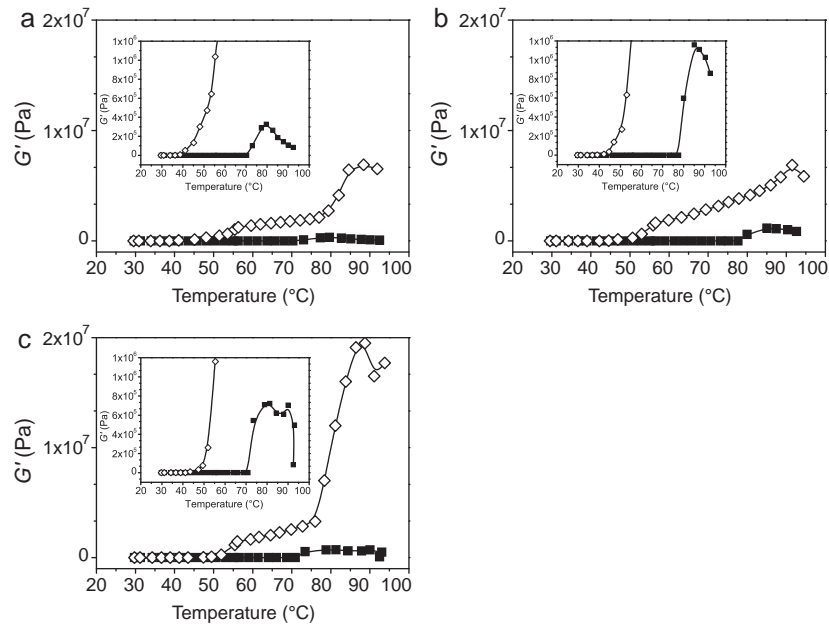


Fig. 5. G' vs. temperature for aqueous starch and mullite–starch suspensions (25 vol.% of starch nominal content): (a) cassava; (b) corn, and (c) potato. (■) Starch suspension and (◇) mullite–starch suspension.

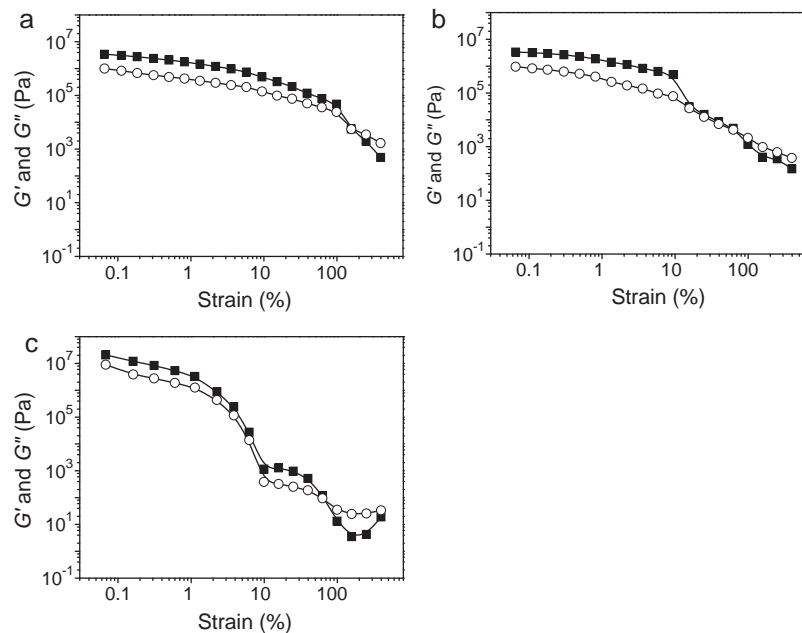


Fig. 6. Dynamic strain sweep curves for mullite–starch gels (25 vol.% of starch nominal content): (a) mullite–cassava starch, (b) mullite–corn starch, and (c) mullite–potato starch. (■) G' and (○) G'' .

geneous and unstable structure, as it was already mentioned. This fact hindered the ability to determine the “gel strength” value for the gel formed using the mullite–potato starch suspension.

4. Conclusions

The influence of starch type (potato, cassava, and corn) on the rheological behavior of concentrated aqueous mullite suspensions was studied by steady state and dynamic tests demonstrating that mullite particles modify starch gelatinization process.

The replacement of one part of the total volume of mullite particles by starch granules did not modify the rheological behavior of the mullite suspension, i.e. a transition from a shear-thinning to a shear-thickening behavior, even though the dilatancy slightly decreased and the thixotropic thickening increased, in agreement with the behavior of starch as a binder in concentrated ceramic suspensions. However, the viscosity decreased over the entire shear rate range, opposite to results reported for chemically modified starches. Aqueous mullite–potato starch suspensions presented the lowest values of apparent viscosity, while the suspensions with cassava or corn starches showed

viscosity values between mullite and mullite-potato starch suspensions.

The presence of mullite particles in aqueous starch suspensions delayed the overall thermogelation process of starch suspensions due to the reduction of the amount of available free water. The increase in viscoelastic properties as temperature increased was attributed to starch gelatinization and the formation of a three-dimensional gel network in which ceramic particles are forced to occupy a lower volume as starch granules swell, the bridging of electrosterically stabilized ceramic particles and minimum water loss by evaporation. For mullite-cassava and mullite-corn starch suspensions, the viscoelastic properties were controlled by starch gel network. Mullite-corn starch gel was the stiffest and less susceptible to deformation. On the other hand, for mullite-potato starch suspensions, the developed network consisted of a starch gel with the addition of a small amount of mullite particles and aggregates of ceramic particles bonded by weak interactions. A strong destabilization of the suspension, generated by a high and fast segregation of the components due to a low apparent viscosity, explains this behavior.

Results obtained with native starches are useful in order to establish experimental modifications to the conventional starch direct consolidation technique and the adequate experimental conditions, for developing homogeneous mullite green microstructures with good mechanical properties.

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