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ScienceDirect
Ceramics International 36 (2010) 1017–1026
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Thermogelling behaviour of starches to be used in ceramic consolidation processes

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Received 10 September 2009; received in revised form 5 October 2009; accepted 6 November 2009
Available online 5 December 2009

Abstract

Starch is one of the agents used as both consolidator/binder of the ceramic suspension and pore former at temperature for porous ceramic processing. In this work, the thermogelling behaviour of aqueous suspensions of different starches (potato, cassava, and corn) was studied by dynamic rheological testing and optical microscopy in order to optimize the thermal consolidation of ceramic green bodies prepared by the starch consolidation method. Viscoelastic properties (G', G'', tan δ) as a function of the temperature (30–95 °C) were determined by non-isothermal rheological measurements (temperature sweep tests). In these tests, the influence of experimental variables on viscoelastic properties, such as the amount of Dolapix CE-64 as dispersant (0, 3, 4.5, and 6 wt%), the heating rate (1, 2, 5, and 10 °C/min) and the starch concentration (14 and 40 vol%) was analyzed. Swelling capacity and the analysis of volume-weighted granule size distributions (median volume granule diameters, distribution widths and arithmetic mean diameters) in aqueous suspension, as a function of the temperature, was also evaluated. In addition, the degree of disintegration of starch granules and the rheological stability of the gels were also studied by dynamic time sweep test. The obtained results are useful in order to establish the experimental variables to be used in the thermal consolidation step for the production of porous ceramics with controlled microstructures.

Keywords: Direct consolidation; Dynamic rheology; Gelatinization; Starch; Viscoelastic properties

1. Introduction

Porous ceramics exhibit several specific properties, such as low density, low specific heat, low thermal conductivity, high surface area, and high permeability. Ceramic materials with these properties are potentially used in a wide range of technological applications, such as catalyst supports, bioceramics, filters, combustion burners, and thermal or acoustic insulators, among others. Each one of these applications requires the development of a specific porosity, pore size distribution and pore morphology, besides the selection of the ceramic matrix composition. The high demand of porous ceramic materials with controlled porosity in order to meet specific properties for a determined application has driven the development of new processing methods [1,2].

It is well known that forming is a key issue in the production of ceramic materials. Among forming methods by direct consolidation, in which the ceramic suspension consolidates into non-porous moulds (e.g. metal moulds) without compaction or removal of water, a new non-contaminating technique of low cost, based on the gelling capability of starch in aqueous media at temperature (55–85 °C), has been developed for use in the manufacture of porous ceramics. It has been thus successfully employed for the production of porous bodies of alumina [3,4], cordierite [1] and mullite [5], among others. In this method, the starch acts as a consolidator/binder agent of the ceramic particles and a pore former after consolidation by burn out at high temperature [1,2]. Besides the favourable gelling properties of starches, they are environmentally friendly, easy to burn out and, not least important, they possess a low cost.

Starch is the major polysaccharide present in plants, existing in nature in the form of semi-crystalline granules. Their crystallinity is exclusively associated with the amylopectin component, while the amorphous regions mainly correspond to

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doi:10.1016/j.ceramint.2009.11.014

amylose. Amylose is a linear polymer composed of glucopyranose units linked through α-D-(1,4) glycosidic linkages, while the amylopectin is a branched polymer with high molecular weight. Depending on the botanical origin, starches contain minor components covalently linked to amylose or amylopectin, such as proteins and lipids.

When starch granules are heated in the presence of water, different changes take place in a process called gelatinization. These changes involve many physical and chemical phenomena, such as water diffusion, granule swelling, amylose leaching, disruption of crystalline structures, and realignment and formation of new intermolecular and intramolecular bonds [6]. The gelatinization process of starch granules produces an increase in the suspension viscosity, a transition to viscoelastic behaviour and the formation of a gel between 55 and 85 °C. This variation in the rheological and morphological characteristics of the starch suspension is one of the factors that affect the kinetic of ceramic body formation and their final microstructural features.

In this work, the thermogelling behaviour of aqueous suspensions of different starches (potato, cassava, and corn) was studied by dynamic rheological testing and optical microscopy in order to optimize the thermal consolidation of ceramic green bodies prepared by starch direct consolidation technique.

2. Experimental

2.1. Characteristics of starches

Potato, cassava, and corn native starches commercially available in Argentina were studied. Real densities determined by He-pycnometry (Multipycnometer, Quantachrome Co., USA) were: 1.47 g/cm^3 for potato starch and 1.49 g/cm^3 for cassava and corn starches. The particle size distributions (Mastersizer S, Malvern Instruments Ltd., UK) were determined using an aqueous suspension of starch with an ammonium polyacrylate solution (Dolapix CE-64, Zschimmer & Schwarz, Germany) as dispersant and applying ultrasound for 15 min to disperse and stabilize the starch particles. The weight percentage of moisture was determined by thermogravimetric analysis (Shimatzu, TGA-50) at 10 °C/min up to 120 °C, in air. The 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 °C/min using highly diluted aqueous starch suspensions (>70 wt% water) placed into sealed aluminium pans. The granule morphology analysis of the dry starches was carried out by scanning electronic microscopy, SEM (Jeol JSM-6460, Japan).

Table 1
Characteristics of starches studied.

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

[a] T_p, endothermic peak temperature.
[b] D_{50}, median volume granule diameter.
[c] W, width of the distribution.

The characteristics evaluated for each starch are given in Table 1 and SEM micrographs of the studied starches are shown in Fig. 1.

The pycnometric density values, moisture weight percentages and starch transition temperatures obtained for each starch studied agree with the values reported for potato, cassava, and corn starches determined in similar experimental conditions [1,2,7,8].

All starches presented bimodal granulometric distributions, with a low volume percentage (<5%) of small granules that can be associated to impurities or broken granules. The median volume diameter for potato starch (D_{50} = 47.8 μm) was notably higher than corresponding value to other starches (D_{50} = 13–15 μm). Corn and cassava starches exhibited a higher amount of small granules (0.5–4 μm) than potato starch (0.6–10 μm). 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 between the W values for different starches were determined, the corn starch presented a slightly narrower distribution (W = 1.1) than the others starches (W = 1.2–1.3).

Potato starch exhibited the largest granules, with smooth surfaces and oval or spherical forms. The rest of starches presented granules with some polyhedral morphology, with corn starch granules exhibiting the most.

The variation in the size and morphology of starch granules is attributed to their biological origin [6].

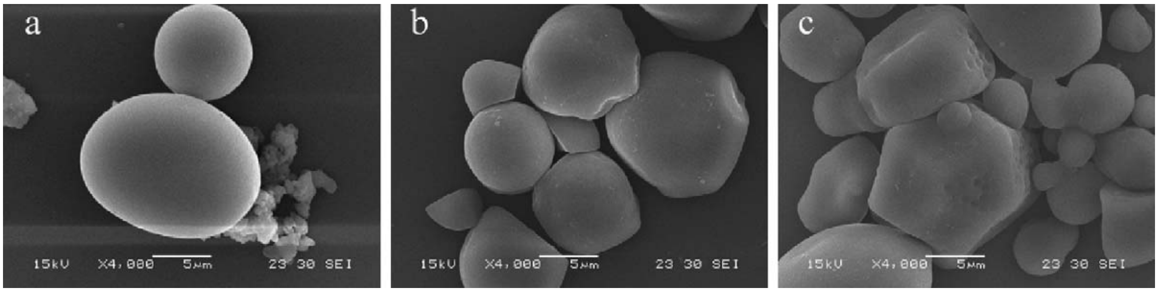


Fig. 1. Scanning electron micrographs (SEM) of starch granules at room temperature: (a) potato, (b) cassava, and (c) corn.

2.2. Dynamic rheology of starch suspensions

A rigorous approach to the gelatinization process may be provided by non-isothermal rheological measurements with small-amplitude oscillatory shear in the linear viscoelastic range. The gelatinization process can be properly analyzed in a conventional rheometer, which presents some advantages compared to a brabender visco-amylograph (BVA) or rapid visco-analyzer (RVA) if small deformations are used in a frequency range of 0.1–1 Hz. This instrument operates at considerably low shear strain or stress, thus, preventing the gel structure from breaking during tests [9].

Dynamic viscoelastic properties of aqueous starch suspensions as a function of temperature were measured using a 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). For dynamic rheological analysis, preliminary tests were conducted in order to obtain the linear viscoelastic range. A strain of 0.5% was used to ensure that all the tests were in the linear region. Variations in storage modulus (G') and loss modulus (G'') by increasing temperature from 30 °C up to 95 °C were recorded during the tests. In all the tests, a thin layer of low viscosity silicone oil was spread on the surface of the sample exposed to the atmosphere to minimize evaporation of water from the starch suspension.

Aqueous suspensions of each starch (14 vol%) with the addition of different amounts (0, 3, 4.5 and 6 wt%) of a commercial solution of ammonium polyacrylate as a deflocculant (Dolapix CE-64, Zschimmer & Schwarz, Germany) were prepared by mechanical mixing at room temperature. Temperature sweep tests were conducted (30–95 °C) at different heating rates (1, 2, 5, and 10 °C/min) using 14 vol% aqueous starch suspensions with 3 wt% of Dolapix CE-64 as deflocculant. The influence of an increase of the starch concentration on the dynamic viscoelastic properties was evaluated by temperature sweep tests carried out using 40 vol% aqueous suspensions of each starch at a heating of 10 °C/min.

The effect of isothermal heating on rheological properties was studied using a dynamic time sweep test. In this case, starch suspensions (40 vol%) were heated from 30 °C up to a given selected temperature (T_{sel}) at 10 °C/min and finally held at T_{sel} for 15 min. T_{sel} is a temperature value close to the onset temperature of gelatinization $(T_{G'_{\mathrm{o}}})$ determined at a low heating rate (2 °C/min).

A 40 vol% concentration of starch represents the minimum amount of water to ensure that complete gelatinization process takes place [10]. It is noteworthy that, with the two starch concentrations studied, it can be assumed that the tests were carried out with an excess of water so that the gelatinization temperature would be independent of the starch concentration used. Moreover, the range of the analyzed starch concentrations is sufficient to obtain porous ceramic materials by direct consolidation techniques using this gelling agent as consolidator/binder and pore former at high temperature [5].

2.3. Optical microscopy of aqueous starch suspensions

Aqueous suspensions of each studied starch (0.1 wt%) were observed at different temperatures using a transmission optical microscope (Leica DMLB, Germany) equipped with a video camera (Leica DC 100, Germany) and a hot stage (Linkam THMS 600, UK). Suspensions prepared by mechanical mixing at room temperature were placed between two glass slides sealed with a silicone adhesive and heated from 30 °C up to 85 °C at 2 °C/min. Number-weighted granule size distributions were obtained directly from the analysis of the corresponding captured images by using an image analysis software (Image-Pro Plus, Media Cybernetics). However, it is convenient to transform this type of distributions to volume-weighted size distributions in order to compare the granulometric parameters with those obtained by laser diffraction and to allow the analysis of starch swelling capacities. By considering starch granules as isometric particles, this can be done by replacing the number of objects N_{i} counted in a certain size class L_{i} by the quantity $N_{\mathrm{i}}L_{\mathrm{i}}^3$. The corresponding volume-weighted cumulative size distributions were obtained by stepwise summation of the frequency histograms [11]. For each starch, both the swelling capacity in excess of water and the characteristics of granules in aqueous suspension were evaluated as a function of the temperature taking into account the analysis of volume-weighted granule size distributions.

3. Results and discussion

3.1. Aqueous starch suspensions at temperature

3.1.1. Viscoelastic properties

The rheological properties of a material can be directly related with its structure. During the gelatinization process, starch granules swell to several times their initial volume. Moreover, the swelling process is accompanied by leaching of the granule constituents, predominantly amylose, and the formation of a three-dimensional network. These processes are responsible of the rheological characteristics exhibited by starch suspensions during heating and shearing.

The variation of storage (G') and loss (G'') modulus with the increase of temperature for aqueous suspensions of each starch type is shown in Fig. 2. The storage 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') is defined as loss tangent (tan δ), which is another parameter indicative of the physical behaviour of the material.

By increasing temperature in all the starch suspensions, G' significantly increased from a certain temperature $(T_{G'_{\mathrm{o}}})$ up to a maximum value (G'_{max}) at $T_{G'_{\mathrm{max}}}$ and then, with a further increase in the temperature beyond $T_{G'_{\mathrm{max}}}$, G' decreased, indicating that the gel structure broke down during prolonged heating. In addition, the loss modulus (G'') exhibited a pattern similar to that obtained for G' during heating, remaining below

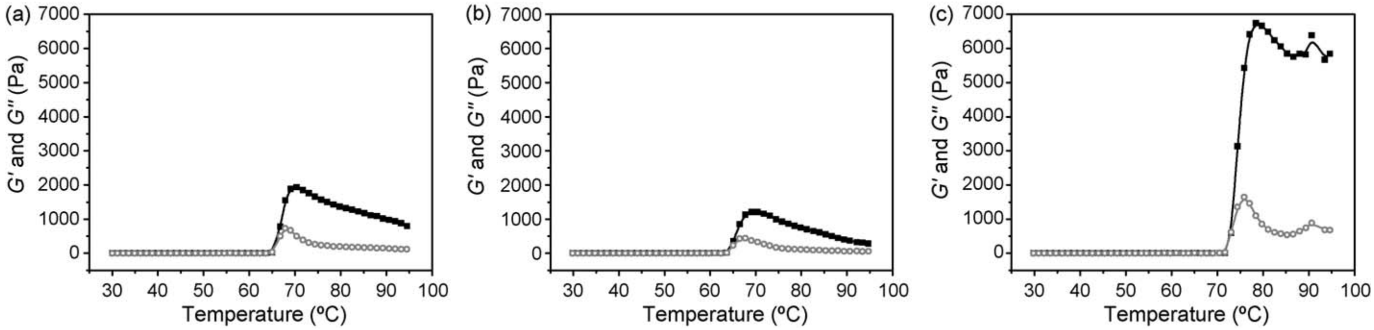


Fig. 2. Storage (G') and loss (G'') modulus as a function of temperature for aqueous suspensions (14 vol%) of starch heated at 2 °C/min: (a) potato, (b) cassava, and (c) corn. Symbols: (■) G' and (○) G''.

G' in each case. This last fact indicates that aqueous starch suspensions gelatinized behaving mainly as an elastic solid.

The initial increase in G' can be attributed to three factors: (a) the removal of water from the exuded amylose by the granules as they swell, (b) the degree of granular swelling to fill the entire available volume of the system, and (c) the formation of a three-dimensional gel network, which is developed by leached out amylose and reinforced by a strong interaction among the swollen starch granules [6]. Regarding the destruction of the formed gel structure, it could also be attributed to three factors: (a) the 'melting' of the crystalline regions remaining in the swollen starch granule; (b) the disentanglement of the amylopectin molecules present in the swollen granule that causes the softening of the granules, and (c) the loss of interaction between granules and the network matrix, mainly constituted by amylose [12].

The rheological properties of interest (onset temperature of gelatinization, $T_{G'_o}$; maximum value of G' during heating, $G'_{\max}$; temperature for $G'_{\max}$, $T_{G'_{\max}}$, and loss tangent at $T_{G'_{\max}}$, $\tan\delta_{G'_{\max}}$) obtained from temperature sweep tests are given in Table 2. From the analysis of obtained values, differences were observed between each starch type in relation to the characteristics of the gel formed ($G'_{\max}$ and $\tan\delta_{G'_{\max}}$ values) and their formation temperatures ($T_{G'_o}$) (Table 2). The rheological behaviour depends on the botanical source of each starch, which is also related to the starch composition (amylose/amylopectin content, presence of phosphates and lipids), swelling capacity, size distribution, shape, structure, rigidity, and degree of crystallinity of the starch granules [6].

The gelatinization temperatures ($T_{G'_o}$) for studied starches obtained from dynamic rheological tests (Table 2) did not correlate with those obtained by DSC (Table 1), being in some cases somewhat higher or lower than those obtained by DSC. We consider that a direct comparison of the results arising from both techniques has no real meaning since the physical parameters quantified in both cases turn out to be different. However, the results proportioned by both techniques, evaluated together, can help to explain the gelatinization mechanism. It is well known that by using the DSC technique, the thermal behaviour of a system is analyzed whereas with dynamic rheological testing, physical properties that depend on temperature and internal structure are measured using specific experimental conditions [13].

A high onset temperature of gelatinization (temperature at which G' begins to increase significantly) is indicative of a high resistance of starch granules to swelling. The corn starch suspension exhibited the highest $T_{G'_o}$ value (71.9 °C), whereas potato and cassava starches presented similar values between them that were lower than corn starch (64.6 and 63.4 °C, respectively). These results are consistent with the fact that, in general, root starch granules, as it is the case of potato and cassava starches, gelatinize more rapidly and at lower temperature than cereal starches, such as corn starch [14]. Moreover, the increase in G' up to its maximum value occurred in a temperature range ($T_{G'_{\max}} - T_{G'_o}$) that was similar for the three starches (5.4, 6.3 and 6.6 °C for potato, cassava, and corn, respectively). This result would indicate that after reaching the onset temperature of gelatinization ($T_{G'_o}$), the kinetics of gel formation is similar for all the starches studied.

The maximum values of $G'(G'_{\max})$ reached by heating during dynamic rheological tests, together with $\tan\delta_{G'_{\max}}$ values, reveal the ability of the granules to swell freely before their physical breakdown, the rigidity of the gel structure and the contribution of viscous behaviour, among others aspects. Starches with a high swelling capacity are, however, less resistant to breakdown [6]. Potato and cassava starches showed similar $G'_{\max}$ and $\tan\delta_{G'_{\max}}$ values, while corn starch exhibited the highest $G'_{\max}$ and the lowest $\tan\delta_{G'_{\max}}$ values, indicating a great resistance to granule rupture and a high gel rigidity.

Table 2
Dynamic rheological properties of starch aqueous suspensions (14 vol%) heated at 2 °C/min up to 95 °C.

Starch	$T_{G'_o}$ (°C)[a]	$T_{G'_{\max}}$ (°C)[b]	$G'_{\max}$ (Pa)[c]	$\tan\delta_{G'_{\max}}$[d]
Potato	64.6	70.0	1,943	0.28
Cassava	63.4	69.7	1,221	0.29
Corn	71.9	78.5	6,747	0.16

[a] $T_{G'_o}$: onset temperature of gelatinization.
[b] $G'_{\max}$: maximum value of G'.
[c] $T_{G'_{\max}}$: temperature at $G'_{\max}$.
[d] $\tan\delta_{G'\max}$: loss tangent at $T_{G'_{\max}}$.

3.1.2. Swelling of starch granules

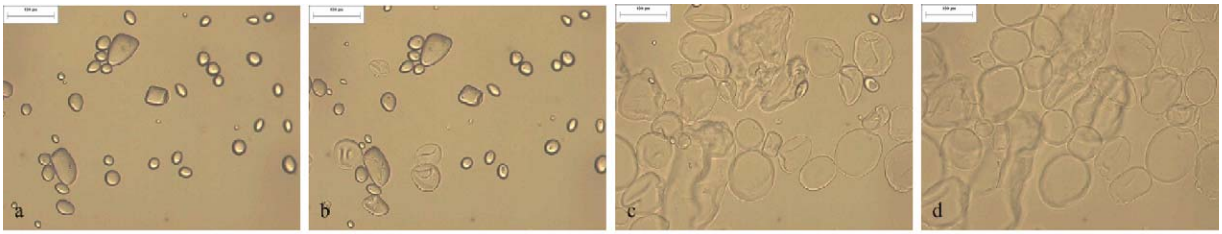
When starch granules are heated in an excess of water, their crystalline structure is disrupted and water molecules become linked by hydrogen bonding to the exposed hydroxyl groups of amylose and amylopectin, which causes an increase in granule swelling and solubility. The starch granule swelling provides evidence of the magnitude of interaction among chains within the amorphous and crystalline domains. The extent of this interaction depends on the amylose to amylopectin ratio, the characteristics of amylose and amylopectin in terms of molecular weight distribution, degree and length of branching and conformation. Therefore, the differences in the starch swelling behaviour are attributed to diversities in composition, morphology, structure and organization of starch granules [6].

Optical micrographs of starch suspensions heated at 30 °C, $T_{G'_o}$, $T_{G'_{max}}$, and 85 °C are shown in Fig. 3. In all starch suspensions, the size of granules did not increase before the onset temperatures of gelatinization $(T_{G'_o})$ is reached. However, at these temperatures $(T_{G'_o})$, a small amount of granules were slightly swollen, and at temperatures above $T_{G'_o}$, principally up to $T_{G'_{max}}$, a large amount of granules significantly increased their size in a variable range depending on starch type. At temperatures above $T_{G'_{max}}$, a certain amount of granules, depending on starch type, becomes deformed or fragmented. At higher temperatures (>85 °C), the hot starch paste became a mixture of swollen granules and granule fragments immersed into a colloidal dispersion of starch components. The characteristics of this mixture depend on the botanical source of the starch, water content and temperature. Moreover, independently of the temperature, the gelatinized granules of each starch type had a size distribution since not all granules swelled up to reach the same size.

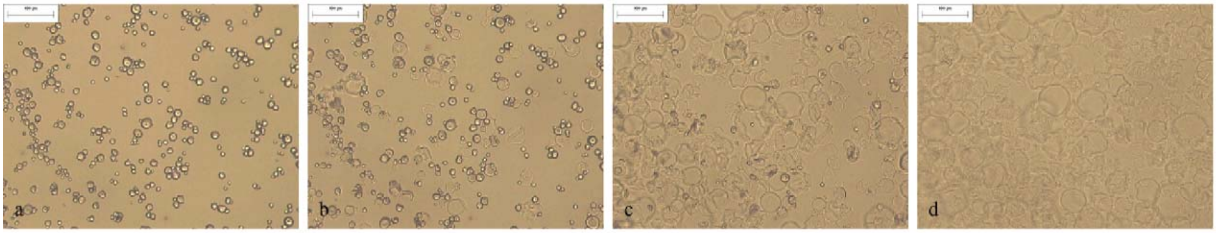
The potato starch, at all analyzed temperatures, showed notably larger diameters than the rest of the starches. However, at the highest temperature observed (85 °C) it presented a high proportion of fragmented and deformed granules.

In Table 3, swelling capacities and characteristics parameters (median volume granule diameters, D_{50}, distribution widths, $W = (D_{90} - D_{10})/D_{50}$ where D_{90} and D_{10} are the granule diameters for 90 and 10 vol% of granules, respectively, and arithmetic mean diameters (d) of the granule size distributions for each starch type as a function of the temperature are reported. The above-mentioned parameters were determined by measuring the diameter on a number considered sufficient for statistical purposes (~200 granules).

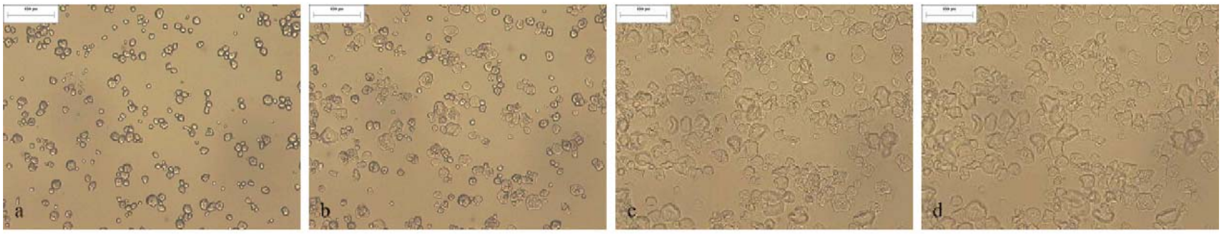
The swelling capacity of starch granules at a certain temperature T_j was estimated using relative volumetric swelling, which was defined as $(V_j - V)/V$, where V_j is the volume of the swollen starch granule at T_j, and V is the volume of the starch granule at 30 °C. The relative volumetric swelling was obtained by calculus, using a $(d_j/d)^3 - 1$ relationship, where d_j is the mean diameter of the swollen starch granule at T_j and d is the mean diameter of the granule at 30 °C. Arithmetic mean diameters of the volume-weighted size distributions were chosen for d and d_j since this parameter more adequately takes into account the polydispersity of the starch granule size [15].



Potato starch suspension at: (a) 30 °C, (b) 65 °C, (c) 70 °C, and (d) 85 °C



Cassava starch suspension at: (a) 30 °C, (b) 63 °C, (c) 70 °C, and (d) 85 °C



Corn starch suspension at: (a) 30 °C, (b) 72 °C, (c) 78 °C, and (d) 85 °C

Fig. 3. Optical micrographs (200×) of starch suspensions heated at 30 °C, $T_{G'_o}$, $T_{G'_{max}}$, and 85 °C.

Table 3
Swelling capacity and granule size distribution parameters as a function of the temperature.

Starch	T (°C)	D_{50} (μm)	W	Mean diameter (μm)	Relative volumetric swelling	Swelling rate (°C^{-1})
Potato	30	34.6	1.3	45.1	0	–
	61	35.4	1.3	45.6	0	0
	65 ($T_{G'_o}$)	48.4	0.9	50.1	0.4	0.1
	68	84.2	0.7	89.6	6.8	2.1
	70 ($T_{G'_{max}}$)	95.5	1.0	111.2	14.0	3.6
Cassava	30	13.6	1.0	16.5	0	–
	60	16.5	1.7	21.8	1.3	0
	63 ($T_{G'_o}$)	21.6	1.3	25.4	2.6	0.4
	65	29.7	1.1	31.8	6.2	1.8
	70 ($T_{G'_{max}}$)	39.7	0.8	42.4	16.0	2.0
Corn	30	14.5	0.9	17.3	0	–
	70	16.8	1.0	20.1	0.6	0
	72 ($T_{G'_o}$)	20.7	1.1	24.1	1.7	0.6
	75	27.7	0.8	30.4	4.4	0.9
	78 ($T_{G'_{max}}$)	29.5	0.7	31.7	5.1	0.2

The starch swelling rate (kinetics of starch swelling) was obtained by calculus as the ratio between the relative volumetric swelling in a determined temperature interval and the corresponding temperature interval.

For each starch, median volume granule diameters (D_{50}) determined at 30 °C (temperature $\ll T_{G'_o}$) were similar to those obtained by laser diffraction (Table 1), except for potato starch. For this last starch, a slightly higher D_{50} value was measured by laser diffraction technique (47.8 μm). This technique is based on the assumption that granules are spherical. Thus, the morphology of potato starch granules (slightly oblong, irregular, and anisometric), rather distant from the spherical form, could be one of the possible factors that affect the measurement. Also, for each starch studied, the median granule diameters increased by increasing temperature. Potato starch showed the highest median granule diameters at all temperatures while cassava and corn starches presented rather similar values along the whole temperature range analyzed. The widths of the granule size distributions of the three starches changed in a random form with the temperature, with this change being less marked in corn starch distributions. Moreover, corn starch generally presented, at all temperatures, the narrowest granule size distributions ($W < 1$), which can be considered monosized.

Regarding the swelling capacity, potato and cassava starches evidenced greater capacity for absorbing water (both showed a higher relative volumetric swelling than corn starch). Taking into account that a high value of tan $\delta_{G'_{max}}$ is associated with a high relative volumetric swelling [12] it is possible to infer that for potato and cassava starches the viscous component has a higher contribution to the overall viscoelastic behaviour (more liquid phase), in agreement with their high tan $\delta_{G'_{max}}$ values (Table 2). Thus, the swelling capacity of starch granules can be correlated to the viscoelastic properties of the aqueous starch suspension.

In addition, the evaluation of the starch swelling rate allows us to complete the analysis of the starch behaviour in aqueous suspension by increasing temperature. At temperatures above $T_{G'_o}$ up to $T_{G'_{max}}$, potato starch showed the highest swelling rates in agreement with the fact that this starch registered the most pronounced relative increase of G' in the gelatinization temperature range $(T_{G'_{max}} - T_{G'_o})$ (Fig. 2). On the other hand, corn starch exhibited the lowest swelling rate, being the swelling rate of the cassava starch intermediate between the other starches studied.

Potato and cassava starch granules swelled more at the lowest temperatures, with a higher swelling rate for potato starch. On the other hand, corn starch granules showed the slowest swelling rate and presented the lowest swelling at higher temperatures. Therefore, the swelling rate increased with the granule size and tan $\delta_{G'_{max}}$, but decreased with $T_{G'_o}$ or $T_{G'_{max}}$, according to previously reported correlations [12].

3.1.3. *Influence of experimental variables on viscoelastic properties*

The influence of different processing variables, such as the amount of dispersant (Dolapix CE-64), heating rate, and starch concentration, on viscoelastic behaviour of aqueous starch suspension was evaluated. In addition, the isothermal behaviour of aqueous starch suspensions and the properties of developed gels were also studied by dynamic rheological testing.

3.1.4. *Effect of dispersant content*

The degree of granule swelling and the amount of amylose —or possibly even amylopectin— leached out during gelatinization is governed by several factors such as amount of available water, temperature and time of heating, and the presence of others substances such as surfactants, emulsifiers, sugars, proteins, lipids and inorganic compounds that may interact with starch components and water. Therefore, the gel properties of starch can be modified by the presence of some of these substances. The influence of different amounts (0, 3, 4.5, and 6 wt%) of an ammonium polyacrylate solution (Dolapix CE-64) as a dispersant in the variation of storage modulus (G') of aqueous starch suspensions with temperature is shown in

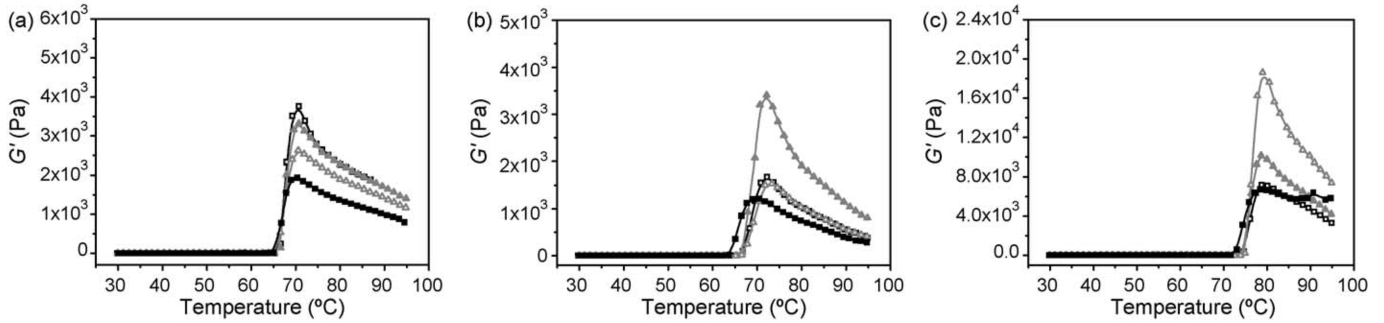


Fig. 4. Storage modulus (G') as a function of temperature for aqueous suspensions (14 vol%) of (a) potato, (b) cassava, and (c) corn starch with different amounts of dispersant (Dolapix CE-64). Symbols: (■) 0 wt%, (□) 3 wt%, (▲) 4.5 wt%, and (△) 6 wt%.

Fig. 4. A small delay in the gelatinization process, although to a lesser degree for potato starch, was observed by increasing the content of dispersant in the suspensions of studied starches. This effect involved an increase of both $T_{G'_o}$ and $T_{G'_{max}}$ but it did not produce any change in the characteristic curve of G' vs. T. The produced changes are, in many cases, attributed to the formation, inside the granule as much as on the granule surface, of insoluble helical inclusion complexes between some of the mentioned substances and both the glucosidic chains of the amylose and the longest linear branches of the amylopectin. The presence of these complexes limits the extent of amylose leaching from the granules and their swelling, thus increasing the starch gelatinization temperature and requiring more heating to develop a three-dimensional gel network [16]. Based on the obtained results, the mentioned effects can be considered irrelevant for dispersant concentrations within the range of values used for ceramic processing (usually less than 1 wt%).

On the other hand, the maximum values of G' did not correlate, in general, as the dispersant content increased. This fact suggests that, besides the above-mentioned aspects, additional considerations, such as the alteration of the conformation, principally of the amylose chains, could also influence the features of the three-dimensional network.

3.1.5. *Effect of heating rate*

The effect of heating rate on the rheological properties ($T_{G'_o}$, $T_{G'_{max}}$, and G'_{max}) of aqueous suspensions of the studied starches is shown in Table 4.

Both, the onset temperature of gelatinization ($T_{G'_o}$) and temperature for G'_{max} ($T_{G'_{max}}$) increased as the heating rate increase. The increments for $T_{G'_o}$ and $T_{G'_{max}}$ were similar for each one of the starches. These results indicate that the degree of swelling for the starch granules was affected when the starch suspension was treated at different heating rates. Furthermore, this is consistent with the fact that the gelatinization process is a kinetic phenomenon.

A possible explanation for the observed delay in the gelatinization onset could be given in the context of the time involved to reach a specific temperature. Thus, the residence time at a given temperature range is greater at slower heating rates, which allows an increase in the degree of starch swelling.

Numerous investigations have been carried out [17–19] on the determination of kinetic parameters (principally activation energy) associated with the gelatinization process. These parameters have been obtained from several assumptions related to the process mechanism as well as several mathematical approximations of the general equation below:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{Q} e^{-E/RT} dT \tag{1}$$

This relationship is derived from the Arrhenius equation, where α is the conversion degree, A the pre-exponential factor, E the activation energy, Q the heating rate, T absolute temperature, R the gas constant and $f(\alpha)$ the kinetic model. The conversion degree (α) can be calculated by using different techniques, such as rheological measurements ($\alpha \approx G'/G'_{max}$). Taking into account the high complexity of the gelatinization process, the strong dependency on experimental variables (e.g. temperature, concentration, temperature-time history) and internal factors (e.g. irregularities of polymer chains, dispersion state), we consider that kinetic parameters (A, E) obtained experimentally in this manner should be taken with precaution.

On the other hand, during rheological measurements, the temperature is assumed to be uniform within the sample.

Table 4
Dynamic rhelogical properties of starch aqueous suspensions (14 vol%) at different heating rates.

Starch	Heating rate (°C/min)	$T_{G'_o}$ (°C)	$T_{G'_{max}}$ (°C)	G'_{max} (Pa)
Potato	1	63.8	69.5	4.19×10^3
	2	65.9	70.3	3.77×10^3
	5	69.0	74.5	2.81×10^3
	10	75.2	81.6	2.74×10^3
Cassava	1	64.1	70.2	1.73×10^3
	2	66.1	71.5	1.69×10^3
	5	71.1	77.4	1.11×10^3
	10	76.8	84.7	1.06×10^3
Corn	1	71.6	77.4	8.33×10^3
	2	74.0	79.4	7.20×10^3
	5	77.5	84.8	6.97×10^3
	10	83.6	90.2	5.90×10^3

However, if the sample is heated at a high heating rate, a relatively large temperature gradient in the sample can be produced. In this manner, the registered delay could be also attributed to the temperature gradient increasing within the sample. This effect is non-linear in its nature, because the rate of the process depends on the temperature non-linearly [20].

Moreover, Table 4 shows that the values of maximum elastic modulus (G'_{max}) diminished by increasing heating rates, in a percentage that depended slightly on starch type. The higher the heating rate, the shorter the time interval over which the specific changes associated with the starch gelatinization process (e.g. swelling, amylose leaching, and granule folding) must occur. However, there is a kinetic limitation to granule swelling, and consequently to amylose leaching, and possibly other associated processes that alter the rheological behaviour. The kinetic limitation at the highest heating rates will likely influence both the extent of amylose leaching and the nature of amylose reassociation. At high heating rates, it is possible to consider that once the amylose leaches out of the granule, the reassociation on or close to the granule surface occurs quickly due to a faster phase separation between the reassociated amylose and amylopectin within the granule. At low heating rates, a more extensive amylose network could be formed due to both the slower increase in the temperature and slower phase separation. These factors could possibly explain the effect of different heating rates on G'_{max} [21].

3.1.6. Effect of starch concentration

The dynamic rheological behavior of aqueous suspensions of each starch type with 40 vol% heated at 10 °C/min is shown in Fig. 5. Values of the dynamic rheological properties of starch suspensions with 14 and 40 vol% are reported in Table 5.

For all the starches $T_{G'_o}$ and $T_{G'_{max}}$ decreased (except for the potato starch, for which the $T_{G'_{max}}$ did not change) when the concentration of the aqueous starch suspension increased. Moreover, for each starch, the maximum values of G' (G'_{max}) for concentrated suspensions (40 vol%) turned out to be notably higher than those values obtained for diluted suspensions (14 vol%).

The diminution of both temperatures by increasing starch concentration can be attributed to a combination of several factors: the increase of the volume fraction occupied by swollen granules, the decrease in the availability of free water, and the increase in the concentration of amylose forming a continuous matrix. In addition, the shifting of $T_{\acute{G}max}$ values towards lower temperatures by increasing starch concentration could be associated with a less granule swelling, and consequently, with an earlier rupture of the three-dimensional network (process that occurs overlapped with swelling). This was less marked in the concentrated suspension (40 vol%) of potato starch. For this suspension, the amount of available water for each granule is significantly greater than the other starch suspensions at the same concentration because the potato starch possesses the largest granule size (Table 1). Therefore, the potato granule swelling results less hindered (more free space among granules) by increasing the concentration.

Table 5
Dynamic rheological properties of starch suspensions 14 and 40 vol%.

Starch	Concentration (vol%)	$T_{G'_o}$ (°C)	$T_{G'_{max}}$ (°C)	G'_{max} (Pa)
Potato	14	75.2	81.6	2.74×10^3
	40	72.2	81.3	0.72×10^6
Cassava	14	76.8	84.7	1.06×10^3
	40	71.6	79.7	0.33×10^6
Corn	14	83.6	90.2	5.90×10^3
	40	78.8	85.0	1.16×10^6

On the other hand, the increase of G'_{max} observed in every starch suspension by increasing starch concentration can be explained by taking into account the following factors: the increase in the volume occupied by swollen granules, the decrease in the amount of water into the gel, the increase in the total amount of material leached out of granules (e.g. amylose), and the improvement in the integrity and rigidity of the swollen starch granules. Thus, these factors govern the rheological properties of starch gel.

Based on the obtained results, we consider that for high concentrations of starch a lower heating time is required to develop a three-dimensional network.

3.1.7. Effect of isothermal heating

The magnitude of the starch gel breakdown obtained from dynamic time sweep tests provides a measurement of the degree of disintegration of starch granules (rigidity loss of the granule) as well as the degree of rheological stability of the gel. The starch gel breakdown was determined as the difference between the G' value after an isothermal holding period of 15 min

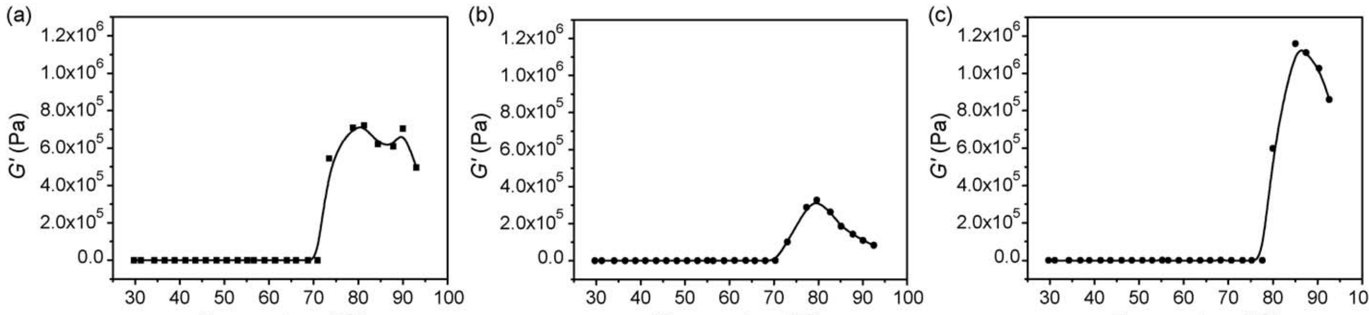


Fig. 5. Storage modulus (G') as a function of temperature for suspensions 40 vol% of (a) potato, (b) cassava, and (c) corn starch heated at 10 °C/min.

Table 6
Rheological properties of starch suspensions 40 vol% heated at 10 °C/min up to a selected temperature (T_{sel}) and held at T_{sel} for 15 min.

Starch	T_{sel} (°C)	G'_{max} (Pa)	$G'_{15\ min}$ (Pa) [a]	Breakdown (%) [b]
Potato	65	1.58×10^6	0.91×10^6	−42.4
Cassava	65	0.95×10^6	0.78×10^6	−17.9
Corn	74	2.32×10^6	1.81×10^6	−22.0

[a] $G'_{15\ min}$: value of G′ after isothermal heating at T_{sel} for 15 min.

[b] Breakdown = $100(G'_{15\ min} - G'_{max})/G'_{max}$.

($G'_{15\ min}$) at T_{sel} and the maximum value of G' (G'_{max}) obtained in the test, expressed as percentage ($100(G'_{15\ min} - G'_{max})/G'_{max}$). Breakdown values for suspensions (40 vol%) of each starch type are given in Table 6.

Potato starch showed a higher gel breakdown than corn and cassava starches (both presented similar gel breakdown values), indicating the formation of a gel with low resistance to time. This behaviour could be attributed to the fact that potato starch exhibited granules with the greatest size which swelled fastest (Table 3). Starches with both a high swelling capacity and a high swelling rate produce gels with lower resistance and show higher breakdown values. In addition, differences in the breakdown values of starches can be also attributed to differences in the composition of granules, in particular, with respect to additional constituents besides amylose and amylopectin (e.g. lipids) [6].

Moreover, G'_{max} and even $G'_{15\ min}$, were significantly higher than non-isothermal G'_{max} values. The magnitude of G'_{max} values followed the same order as those values obtained from rheological temperature sweep tests (without dwell time): corn > potato > cassava. As was mentioned, G'_{max} reflects the ability of the granules to freely swell and form a three-dimensional network. Thus, it is noteworthy to note that a gel with higher resistance to temperature increase and structural stability (less destruction of the gel) can be developed by isothermal heating at a temperature close to the onset of gelatinization temperature (T_{sel}).

4. Conclusions

The studies carried out on the thermogelling behaviour of aqueous suspensions of potato, cassava, and corn starches by dynamic rheological tests and optical microscopy are of great interest for processing porous ceramic materials. Moreover, based on these tests, it is possible to select the experimental variables to be used when forming a porous ceramic material by starch direct consolidation, allowing the development of a controlled porous microstructure.

Potato and cassava starches showed similar values for the onset temperature of gelatinization ($T_{G'_o}$), the maximum G' during heating (G'_{max}), the temperature for G'_{max}, ($T_{G'_{max}}$) and the loss tangent at $T_{G'_{max}}$ ($\tan \delta_{G'_{max}}$), while corn starch exhibited the highest $T_{G'_o}$, $T_{G'_{max}}$, and G'_{max} values and the lowest $\tan \delta_{G'_{max}}$. As a consequence, corn starch presented the greatest resistance to granule rupture and gel rigidity. For all the starches, both $T_{G'_o}$ and $T_{G'_{max}}$ increased, and G'_{max} values diminished as heating rate increased. This indicates that a low heating rate promotes the development of a stronger gel structure. In addition, the presence of a dispersant, in the range used for ceramic processing, did not significantly change the viscoelastic properties of the three starches studied.

On the other hand, potato and cassava starches possessed a swelling capacity notably greater than that of corn starch, with potato starch presenting the greatest granule size and the highest swelling rates. Corn starch, which has the lowest swelling capacity and swelling rates, presented the narrowest granule size distributions at all temperatures.

A lower granule swelling, and consequently, an earlier rupture of the three-dimensional network was observed by increasing starch concentration, an effect that was less evident for potato starch.

Starches with both high swelling capacity and high swelling rate, such as potato starch, produce gels with the lowest resistance to temperature increase. On the other hand, isothermal heating at a temperature close to the corresponding onset of gelatinization temperature promoted the development of starch gels with both a higher resistance and structural stability to time. Consequently, in the context of ceramic-forming by starch direct consolidation, a specific heating dwell time at the gelatinization temperature of the starch will provide green bodies with better properties than those obtained with treatments carried out at higher temperatures, as it is usually performed.

Acknowledgements

The authors gratefully acknowledge to Dr. M.I. Nieto and Ms. S. Benito (Instituto de Cerámica y Vidrio, CSIC, Madrid, España) for carrying out the measurements of pycnometric densities and particle size distributions by laser diffraction of starches used in this study. This study was supported by CONICET (Argentina) under project (PIP 6255, 2006–2009).

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