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RHEOLOGICAL CHARACTERIZATION OF ALUMINA – NANOZIRCONIA SUSPENSIONS DURING *IN-SITU* COAGULATION CASTING

Isabel Santacruz^{*†}, Jon Binner[‡]

IPTME, Loughborough University, Loughborough, LE11 3TU Leicestershire, UK

Abstract

The rheological behavior of electrosterically dispersed aqueous suspensions composed of submicron alumina and nano zirconia particles in different ratios and solids contents has been studied during *in-situ* coagulation casting. Glucono- δ -lactone was used as the coagulant to achieve destabilization of the ceramic suspensions by acidifying the suspension so that the pH became close to the isoelectric point (IEP) for both powders. The effect of the lactone content and the solids loading were studied on the rheological parameters during the coagulation process and the conditions optimized to yield homogeneous green samples with a uniform nano zirconia distribution and densities between 58 and 60% of theoretical. These were subsequently sintered to yield composites with a final density of 97%.

^{*} Author to whom correspondence should be addressed. Dr. Santacruz, e-mail: cruz@icv.csic.es

[†] Currently of Instituto de Cerámica y Vidrio (CSIC), Madrid, Spain.

[‡] Member, American Ceramic Society.

I. Introduction

Alumina-based composites containing dispersions of zirconia generally display superior strength, toughness and wear resistance compared to monolithic alumina and consequently there has been considerable interest in them,¹⁻³ with a wide range of different processing routes being used for their preparation.^{1,4-6} Applications include cutting tool tips and abrasion wheels amongst others; the latter can outperform monolithic alumina wheels by up to a factor of 8.⁷

In recent years there has been significant interest in the potential offered by nanocrystalline materials since they can provide unusual physical and mechanical properties, including superplasticity in ceramics, transparency for usually opaque materials and higher hardness and strength in both metals and ceramics.^{8,9} The concept of nanocomposites as materials in which the dispersed second phase exhibits a submicron and/or nanometric scale was initially proposed by Niihara,¹⁰ and supposed a revolutionary approach in the field of ceramic-ceramic composites. The most relevant results presented by this author refer to materials containing a small addition (~5 vol%) of nanometric SiC particles, both intra- and intergranular, within a matrix of either alumina or silicon nitride (Si_3N_4), whose strength and toughness were found to be significantly higher than those of the materials without any second phase. In the case of zirconia-alumina composites, the fracture toughness is in part controlled and optimized by the amount of ZrO_2 content and its grain size. A reduction in grain size to the nanoscale level is advantageous over the coarse grained materials since it leads to improved strength and hardness.¹¹

One of the main problems associated with ceramic processing is the production of defect-free green bodies, particularly by dry forming routes. Colloidal techniques, however, offer significant potential for controlling the nature and number of defects present as a result of the ability to control the homogeneity of the precursor suspension or paste. This can lead to

ceramics with a decreased number and size of agglomerates and pores and so higher reliability.¹² An inherent factor in colloidal systems is that there is a well-defined separation surface between the dispersed phase and dispersing medium, so the interface has a key role in controlling the surface properties such as adsorption, surface charge and electric double layer.¹³ Since nanopowders have very much larger surface areas than their conventional submicron counterparts, the development of green nanostructured ceramics by wet forming routes requires very strict control of the colloidal forces involved in order to overcome the strong tendency to agglomeration.

Tremendous effort has been devoted to developing new forming methods, providing the possibility to manufacture complex-shaped ceramic products with minimal number of detrimental defects.¹⁴⁻¹⁶ A wide variety of methods have been proposed recently, such as direct coagulation casting (DCC), gel casting with acrylamides⁴ or polysaccharides,¹⁷ freeze casting,¹⁸ clay-like forming/vibraforming,^{19,20} solid free-form (SFF),²¹ temperature induced forming (TIF),²²⁻²⁴ binder coagulation casting (BCC),²⁵ hydrolysis assisted solidification (HAS),²⁶ etc.

Direct coagulation casting (DCC)²⁷⁻³² has been investigated and patented as a method for the production of complex-shaped, high strength, high reliability ceramic components. This procedure is based on the destabilization of a high solids loading, electrostatically stabilized suspension, produced mainly by any one of the following methods:³¹ (a) changing the pH of the suspensions from a pH regime with high surface potential towards the IEP of the powder through the addition of urea with catalyzers or lactones;³³⁻³⁵ or (b) increasing the ionic strength in order to compress the electrostatic double layer of the powder particles.³¹ It has also been shown to be possible to destabilize ceramic suspensions by increasing the salt concentration by the direct addition of salts,³⁶ although mixing problems arose because the suspensions became highly viscous too quickly.

In order to obtain coagulated bodies swiftly, without requiring the addition of catalyzers, the use of carboxylic acid derivatives, viz. lactones, as coagulants has been successfully applied to aqueous alumina suspensions^{33,37-39} and subsequently patented.⁴⁰ Although a wide range of different lactones can be used to achieve in-situ coagulation³⁹ via their hydrolysis to gluconic acid, which causes a pH shift towards the system's isoelectric point where the net surface charge is zero, Glucono- δ -lactone has been determined to be one of the most effective in terms of the efficiency of the process and lower price.

Since the rheological properties of a suspension are influenced on the one hand by the quantity, shape, and size of particles and on the other by the nature and strength of the interparticle forces, it is important to correlate the rheology with the green body characteristics being formed as the slurry is processed.⁴¹ When three-dimensional structures are created, as in coagulation casting,^{42,43} it is useful to follow the viscoelastic behavior of the sample during processing by means of forced oscillation methods, also known as dynamic measurements, in which the response of the sample to a small amplitude oscillatory shear is measured. This allows the correlation of the elastic response to the suspension's structure, i.e., the particle pair potentials.^{13,41} One practical aspect of such an analysis, however, is that a good dynamic measurement requires long characterization times, which can cause problems when dealing with low volumes of suspension in a rheometer due to effects such as drying of the sample.

It is customary to write:

$$G^* = G' + iG'' \quad \text{(equation 1)}$$

$$\text{where} \quad G' = G^* \cos \delta \quad \text{(equation 2)}$$

$$\text{and} \quad G'' = G^* \sin \delta \quad \text{(equation 3)}$$

where a viscoelastic fluid is characterized by a phase angle $0 < \delta < 90^\circ$. G' is referred to as the elastic or storage modulus, which is a measure of the energy stored during the test but which it recovers immediately afterwards whilst G'' is the viscous or loss modulus, which is used to determine the energy for flow to start and which is irreversibly lost as heat on shearing. In an ideal solid $G^*=G'$, whereas in an ideal liquid $G^*=G''$.

The aim of this work is the preparation of homogeneous ceramic bodies through the in-situ coagulation casting of suspensions with a submicrometer sized alumina matrix and nanosized dispersed phases of zirconia. The effect of the initial solids loading and the coagulant content were studied through the rheological behavior of the suspensions before and during coagulation, and these results have been compared with the properties of the samples. In-situ coagulation of the suspensions was achieved as result of the acidification of the suspension close to the IEP of both powders through the hydrolysis of a lactone.

II. Experimental Procedure

The source of nano zirconia particles was a commercial aqueous suspension of 2.7 mol% yttria stabilized nano zirconia with a solids loading of 24.0 wt% (MEL Chemicals Ltd., Manchester, UK) with an average particle size of 15-20 nm.⁴⁴ The pH of the as-received nanosuspension was adjusted from ~ 2.7 to 11.5 ± 0.1 using 6.7 wt% tetramethylammonia hydroxide,^{45,46} TMAH (Aldrich Chemicals Ltd, Dorset, UK), and then 4.5 wt% of Dispex A40, an ammonium salt of carboxylic acid (Allied Colloids, Bradford, UK), was added as a dispersant.^{44,46} Both TMAH and Dispex A40 amounts were calculated by weight of the zirconia present.

Suspensions with different ratios of alumina to zirconia and also different solids loadings were prepared by adding alumina powder to the basic dispersed zirconia nano-suspension. The alumina powder, Alcoa CT3000SG, (Alcoa Chemie GmbH, Ludwigshafen, Germany)

had a mean particle size of 0.4 μm as measured by an AcoustoSizer II (Colloidal Dynamics, Sydney, Australia), and a specific surface area of 7.5 m^2/g (measured by N_2 adsorption, BET, Monosorb, Quantachrome, Fleet, UK).⁴⁷ It was added to three aliquots of the dispersed zirconia nanosuspensions, the characteristics of the initial Al_2O_3 / Y- ZrO_2 suspensions, S_1 , S_2 and S_3 , being described in table I. All the slurries had a characteristic pH value of 9.5 ± 0.1 at room temperature and were easily pourable. In order to break any agglomerates present, the suspensions were subjected to ultrasonic agitation produced by a KS 150 ultrasound probe (Kerry Ultrasonics Ltd, Skipton, UK) for 3 minutes. The vibrational output was at a frequency of 20 kHz and a power level of 75 W (amplitude 14 μm).

In order to promote coagulation, 0.5 to 6.7 wt% additions, by reference to the solids loading, of Glucono- δ -lactone (Jungbunzlauer, Basel, Switzerland) were introduced to the suspensions, followed by stirring for 1 minute, in line with previous studies^{34,37,38} before the suspensions were cast in non porous plastic moulds measuring 60 \times 60 \times 25 mm that had been coated by a thin layer of lubricant (multipurpose grease, RS Components, Corby, Northamptonshire, UK) in order to avoid cracks forming due to sticking during drying of the green bodies.

The rheological behavior of the alumina-zirconia suspensions was studied before and after the addition of the lactone. A Visco 88 BV viscometer (Bohlin Instruments, Cirencester, UK) with a C14 concentric cylinder sensor was used, varying the shear rate from 0 to 1000 s^{-1} in 8 minutes in controlled rate mode. Control rate measurements were also performed on the suspensions with lactone in order to study the viscosity and thixotropy of the suspensions just after the lactone additions. This experiment was useful for comparing the viscosity of the suspension with different lactone contents at the same shear rates, and, also, the effect of the shear rate on the suspensions. Oscillatory measurements were performed using a CS-10 rheometer (Bohlin Instruments, Cirencester, UK) with parallel plate geometry (PP40, 40 mm

in diameter). The linear viscoelastic zone was found by performing: (a) a stress sweep, from 0.01 to 10 Pa, and fixing 1 Hz as the frequency, and (b) a frequency sweep, from 100 to 0.01 Hz, fixing the applied strain value depending on the linear viscoelastic region obtained from the stress sweep curve. The strain selected was 5.0×10^{-3} (0.5%) for suspensions without lactone. Once the stress-strain and frequency parameters were selected in the linear region, the effect of time on the viscoelastic properties of the suspensions with lactone present were investigated with the samples subjected to continuous oscillation at a frequency of 1 Hz and the strain was kept constant at 0.01 (1%).

A solvent trap was used to allow the rheology of the coagulating suspension to be measured continuously without the sample drying out.

The applied stress and the resulting oscillatory strain were automatically measured and analyzed to yield the dynamic storage modulus, G' , and the dynamic loss modulus, G'' . The viscoelastic data were collected every 30 or 60 seconds depending on the duration of the experiment since the software was inherently limited to a maximum number of 950 readings.

The suspensions containing lactone were cast into non-porous moulds and left at room temperature to coagulate. The resulting green densities of the bodies formed were measured by the Archimedes' method using Hg and then the samples were sintered at 1540°C/1h, with an initial hold at 500°C for 0.5 h to allow the organics to burn out. The sintered bodies were polished and thermally etched for microstructural observations and their densities were measured by immersion in water. Electron microscopy of both the green and sintered samples was performed using a FEG-SEM, (LEO 1530VP, LEO Elektronenmikroskopie GmbH, Oberkochen, Germany).

III. Results

The addition of Dispex to zirconia and alumina suspensions shifted down the IEP of those powders, to values between 3 and 4. The IEP values of both powders dispersed with Dispex were close enough to avoid any problems with heteroaggregation and so were considered to be appropriate for the purpose of the study.

Flow curves of the three initial suspensions, S_1 , S_2 and S_3 , without lactone are shown in figure 1, where the effect of solids loading can be observed. The stress and frequency sweep curves of the suspension with the highest solid content, S_3 , are shown in figures 2 (a) and (b), respectively, whilst those for S_3 with 0.5 wt% addition of coagulant are plotted in figures 3 (a) and (b), respectively. The effect of solids loading on suspensions with the same lactone content of 4.0 wt% is shown in figures 4 (a) and 5 (a) through the flow curves and oscillatory measurements, respectively, whilst the effect of the lactone content on S_3 is shown in figures 4 (b) and 5 (b) through static and dynamic measurements.

Suspension S_3 was selected for further studies since it had the highest solids loading and this was expected to yield the highest green density samples. No attempt was made in the present work to increase the solids loading further beyond S_3 due to the presence of the nanosized zirconia, which would have resulted in a rapid increase in viscosity as a function of the solids loading, risking the introduction of heterogeneities in the green bodies.

As has already been indicated, the *in-situ* coagulation casting process utilized in this work is based on the pH change that occurs as a result of the hydrolysis of the lactone; figure 6 shows the change in pH to more acidic values as a function of time for suspension S_3 with 4.0 and 6.7 wt% lactone additions at room temperature.

Figure 7 shows the FEG-SEM micrographs of the green samples prepared from the suspensions at different solids content and containing 4.0 wt% lactone, whilst figure 8 shows the effect of the lactone content on the microstructure of the green samples. Finally, figure 9

shows the microstructures of the sintered, polished and thermal etched samples prepared from S_3 suspensions with different lactone contents.

IV. Discussion

From figure 1, which depicts the flow curves of the three suspensions, S_1 , S_2 , and S_3 , without lactone, it can be observed that the viscosity and thixotropy increase with solids loading and shear thinning behavior is present in all the suspensions.

Figure 2 shows the results of the stress and frequency sweep measurements that were performed on the most concentrated suspension, S_3 , in order to detect the linear viscoelastic region. It is fundamental to start the viscoelastic study with a stress sweep measurement in order to select the linear viscoelastic region where the response is independent of the strain. This is important because the theory of linear viscoelasticity provides linear differential equations that can be solved for constants related to materials parameters. Changing the test conditions can lead to non-proportionality between stress and strain and no absolute data were then measured. When plotting the data obtained from the stress sweep experiment, there is a point where the parameters lose the linearity that defines the limit of the linear viscoelastic region.⁴¹ In the present case, for suspension S_3 with no lactone, a loss of linearity was observed at an oscillatory stress ≥ 3.4 Pa, as marked in the figure, and which consequently defined the limit of the linear viscoelastic region. After this test, the viscoelastic behavior was measured by a frequency sweep in order to select the frequency value of the linear viscoelastic region; for this measurement, a value of strain of 5.0×10^{-3} (0.5%), i.e. an oscillatory stress of 2.3 Pa, was selected from the stress sweep for performing the measurement. The frequency curve is shown in the figure 2 (b), from which a value of 1 Hz was chosen. For the selected parameters, the elastic modulus, G' , was higher than the viscous modulus, G'' , showing that some solid structure was present even without lactone.

Figure 3 shows similar data for suspension 3 with the minimum lactone content used in the present work, viz. 0.5 wt%. In this case, the linear viscoelastic region was observed to extend up to a value of 2.3 Pa for the oscillatory stress as marked in the figure, so a value of 0.8 Pa of oscillatory stress, 1% strain, was chosen at 1 Hz of frequency. Since higher strain values are obtained in the linear viscoelastic region after the addition of a small amount of lactone, it was expected that a strain value of 0.01 (1%) would be in the linear viscoelastic region for the suspensions with larger amounts of lactone.

The frequency sweep was performed using this parameter and the results may be observed in figure 3 (b), where $G' > G''$ is observed at frequency values higher than 0.7 Hz, the opposite being found at lower frequency values. This meant that under the conditions used in the present work, 1% strain and 1 Hz frequency, the lactone-containing suspensions displayed a value of G' that was higher than G'' . Similar results have been observed by other authors for alumina suspensions when using similar parameters.³² In the present work, $G' > G''$ was expected under all the conditions studied due to the oscillatory parameters selected and the sharp increase in G' during coagulation.

From figure 4 it may be seen that both the viscosity and thixotropy increased with the solids loading and lactone content of the suspensions whilst figure 4 (b) reveals for suspension S₃ that the thixotropy increased significantly at high lactone contents such as 4.0 and 6.7 wt%. This is believed to be because the suspension was beginning to coagulate. These suspensions also suffered a viscosity reduction at shear rates between 400 and 500 s⁻¹, suggesting that the formation of the physical structures was sensitive to high shear rates.

Oscillatory studies are the best method for correlating the elastic response to the structure of the suspension during the coagulation process, since in dynamic tests the response of the sample to a small amplitude oscillatory shear is measured and hence the sample structure is

slightly perturbed with respect to that at rest, but not completely destroyed. Strain and frequency were fixed according to the results shown in figure 3.

Figure 5 (a) shows the evolution of G' for the three suspensions containing 4.0 wt% lactone. In all three cases G' increases with time as would be expected due to the coagulation reaction. As expected, slightly higher G' values were obtained when the solids content was increased, since a stronger solid structure was obtained. In contrast, figure 5 (b) highlights very clearly the large effect of different lactone concentrations on the value of G' as a function of time. It suggests that stronger green bodies should be formed more readily at higher lactone concentrations, a value of 180 kPa being achieved for G' after 40 min, rising to 340 kPa after an hour when 6.7 wt% of lactone was used. Even for the lowest lactone content studied, 0.5 wt% or $2.92 \times 10^{-5} \text{ mol g}^{-1}$, a value of 57.3 kPa was achieved after 1 hour, which compared very favorably with that obtained using other lactones such as D-gulonic- γ -lactone³⁴ under the same conditions, where a value of 4.4 kPa was achieved for G' after 1 hour.

The significant increase in the magnitude of the effect with lactone concentration is very clearly marked and can be related directly to the change in pH as a function of time at room temperature that is shown in figure 6. The more lactone that is present, the more acid that will have been formed, resulting in both a faster coagulation process and also a greater degree of coagulation. In all the cases, shorter coagulation times are expected at higher temperatures.³⁴

However, it is also important to consider the homogeneity of the green bodies formed since excessively fast coagulation could potentially result in lower density structures whilst the high lactone contents involved could also yield problems at the binder burn out stage, leading to higher final porosities. Figures 7 and 8 show the effect of the solids loading and lactone contents on the green microstructures produced. Little difference can be observed from them, confirmed by the similarity in the densities obtained, table II, though Figure 8

suggests that the 2 wt% lactone sample might have a more uniform nano zirconia distribution compared to the other two samples.

Figure 9 shows the microstructure of the sintered, polished and thermal etched samples. Two trends are apparent. First, that, again, the sample with 2 wt% lactone has the most uniform zirconia distribution and second, that the degree of porosity increases with increasing lactone content. The latter result is supported by the sample densities, table II. Whilst the majority of the zirconia was present as agglomerates up to ~300 nm in size located at the grain boundaries in the alumina, some zirconia grains <100 nm in size may be observed inside the alumina grains.

Although densities up to 97% of theoretical were obtained, in general the densities were disappointingly low suggesting that optimization of the sintering cycle is still required. Moreno et al. studied the sintering of different aluminas and the relative density obtained for the Alcoa CT3000SG following the same sintering cycle was 96%.⁴⁸ Optimization was not performed in the present work because the focus was on the in-situ coagulation molding stage.

V. Conclusions

The rheological behavior of electrosterically dispersed aqueous suspensions composed of submicron alumina and nano zirconia particles in different ratios and solids contents has been studied during *in-situ* coagulation casting. The macroscopically determined moduli, G' and G'' , obtained during oscillatory investigations were found to be sensitive rheological parameters that describe the structural changes occurring at a microscopic level within the material. The *in-situ* coagulation process resulted in the formation of a solid-like network that exhibited strongly elastic behavior. The ability of this technique to monitor these changes over a much wider consistency range was of considerable advantage, allowing the precursor suspension composition to be optimized.

It was observed that whilst higher lactone contents and solids loadings produced faster coagulation and stronger green bodies, excessive coagulation agent reduced the homogeneity of the second phase distribution and increased the degree of porosity after sintering. Whilst the sintering schedule was not optimized in the current work, a useful, relatively rapid route to the production of homogeneous bodies was developed. Further work will focus on optimizing the sintering of the 2 wt% lactone-based suspension S₃ and then evaluating the mechanical properties obtained.

VI. Acknowledgements

Authors would like to acknowledge MEL Chemicals Ltd. for provision of the nanosuspension free of charge, CERAM and Dr. Giuliano Tari for the use of the rheometer, and Prof. Rodrigo Moreno for helpful discussions.

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Captions

Fig. 1. Flow curves of suspensions S_1 , S_2 and S_3 .

Fig. 2. Stress (a) and frequency sweep (b) curves of suspension S_3 .

Fig. 3. Stress (a) and frequency sweep (b) curves of suspension S_3 with 0.5 wt% lactone.

Fig. 4. Flow curves of S_1 , S_2 and S_3 suspensions with 4.0 wt% lactone (a) and S_3 with different lactone contents (b).

Fig. 5. Evolution with time of the elastic modulus of S_1 , S_2 and S_3 suspensions with 4.0 wt% lactone (a) and S_3 with different lactone contents (b).

Fig. 6. Evolution of the pH with time during coagulation of S_3 with 4.0 and 6.7 wt% lactone.

Fig. 7. FEG-SEM micrographs of the green samples prepared from suspensions S_1 (a), S_2 (b) and S_3 (c) with 4.0 wt% lactone.

Fig. 8. FEG-SEM micrographs of the green samples prepared from suspension S_3 with (a) 0.5, (b) 2.0 and (c) 6.7 wt% lactone.

Fig. 9. FEG-SEM micrographs of the sintered samples prepared from suspensions S_3 with (a) 0.5, (b) 2.0, (c) 4.0 and (d) 6.7 wt% lactone.

Table I. Properties of the initial suspensions

Suspension	Name	Solids loading/ wt%	Solids loading/ vol%	Theoretical		
				Powder density/ g cm ⁻³	Al ₂ O ₃ / ZrO ₂ v / v	Al ₂ O ₃ / ZrO ₂ w / w
1	S ₁	68.5	34.3	4.17	90.4 / 9.6	86.2 / 13.8
2	S ₂	70	36.0	4.15	91.2 / 8.8	87.2 / 12.8
3	S ₃	73.5	40.2	4.12	92.5 / 7.5	89.1 / 10.9

Table II. Density values of the green and sintered samples

Suspension	Lactone / wt%	Green density / %TD ±1	Sintered density / %TD
1	0.5	-	-
	2.0	58	95.8 ± 0.1
	4.0	58	95.2 ± 0.1
	6.7	59	95.1 ± 0.3
2	0.5	59	97.0 ± 1.0
	2.0	59	95.8 ± 0.2
	4.0	59	95.4 ± 0.1
	6.7	59	94.5 ± 0.2
3	0.5	56	96.5 ± 0.2
	2.0	59	95.5 ± 0.4
	4.0	60	94.9 ± 0.1
	6.7	59	94.3 ± 0.6