Journal of the European Ceramic Society 17 (1997) 1393–1401
© 1997 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(97)00034-4
0955-2219/97/$17.00

Preparation of Concentrated Aqueous Alumina Suspensions for Tape Casting

R. Greenwood, E. Roncari* & C. Galassi

Research Institute for Ceramics Technology, IRTEC-CNR, Via Granarolo 64, 48018 Faenza (Ravenna), Italy

(Received 4 October 1996; accepted 10 February 1997)

Abstract

Aqueous suspensions suitable for the tape casting of alumina were produced, such that ceramic bodies with very high final sintered densities were obtained (100% of theoretical). This enables high purity, smooth, substrates to be produced without using environmentally damaging solvents.

To prevent competitive adsorption of the binder with the dispersant, which leads to an increase in the viscosity and in the elastic modulus of the suspension, the binder was mixed very slowly for a short time in a ball mill. In the presence of the binder the optimum amount of dispersant was 0·3 mg m^{-2} (dry weight basis). These suspensions were not thixotropic.

The minimum amount of binder required to produce a flexible, robust tape was established from tape casting experiments, as was the minimum amount of binder required to produce a tape that did not crack on drying. All suspensions were cast with both blades set at a gap of 0·4 mm and a Mylar tape speed of 20 cm min^{-1}; the removal of air bubbles was achieved by exposing the slip to a vacuum for a few minutes.

The final sintered density could be correlated directly with the volume fraction of powder (at a fixed binder content) and directly with the binder content (at fixed volume fraction). Sintering the discs revealed a greater shrinkage in the thickness direction than laterally owing to the non-spherical nature of the particles. However no correlation could be found between the thickness of the green body after casting/drying and the suspension viscosity. © 1997 Elsevier Science Limited.

1 Introduction

Tape casting is a low cost process for making high quality thin ceramic sheets for which an adequate thickness control and good surface finish are required. Basically, it involves the preparation of a stable suspension of a ceramic powder in an aqueous or non-aqueous liquid. Usually a dispersant is added in order to assure the stability of the suspension. As large tapes are produced it is necessary to confer adequate strength and flexibility by the addition of binders and plasticizers. Once the suspension has been prepared, it is cast onto a surface by the action of a blade that levels the slurry. The cast tape is then dried until the solvent has evaporated. Finally, the tape is treated until the required geometry is obtained and sintered.

Tape casting is used for large-scale manufacture of ceramic substrates, multilayer structures and special components comprised of several materials for quite different applications. Substrates of Al_2O_3 and AlN are used for thick and thin film circuitry; $BaTiO_3$ for capacitors; solid electrolytes for sensors and solid oxide fuel cells; piezoelectric ceramics for actuators and transducers, SiC for heat exchangers, and MgO based materials for photovoltaic solar energy cells. From a structural point of view the tape casting process yields laminated and multilayered composites with reinforced mechanical properties.

As in other ceramic forming methods, e.g slip casting, the arrangement and packing of the particles in the green body influences the sintering behaviour and the final properties. Assuming a well-dispersed slurry the microstructure will be determined by two key factors. First, particle arrangement during the casting process and drying, and second the flowing conditions generated when the slurry passes under the blade.

The organic dispersant and binder components remain in the piece after casting, but they are generally eliminated by burning out, thus generating an open porosity in the green body. Obviously a homogeneous uniform product can only be

---

*To whom correspondence should be addressed.

obtained if the starting suspension itself has a high homogeneity and stability. This homogeneity must be preserved during all the processing steps of casting, drying, burning out and sintering, and requires a careful selection and accurate control of the processing additives in the slurry. Reviews of the roles of different types of additives, their function and properties in relation to tape casting are given by Moreno,[1,2] Mistler[3] and Hotza and Greil.[4]

To achieve a good surface finish the powder must have a small particle size, however this increases the specific surface area, which unfortunately leads to higher shrinkage rates and requires higher concentrations of additives, which can lead to drying and burn-out problems. But, on the other hand, small sized particles require lower sintering temperatures. Hard agglomerates must be avoided since they lead to a low packing density, soft agglomerates are usually destroyed during milling. A well-characterised powder is necessary for reliability, a fine monodisperse powder that undergoes little grain growth can allow fabrication of technological devices. Much work has already been carried on aqueous suspensions of alumina[5–7] by itself and in composites with zirconia.[8,9]

The main role of the solvent is to allow the powder to be de-agglomerated and dispersed. It must also dissolve the organic additives whilst being inert with respect to the powder, so in many cases organic media have been used. Another important solvent property is the surface tension, which effects the wettability of the slip on the substrate tape. Organic solvents have a low viscosity, low boiling point and high vapour pressure, so evaporation is much easier, however they are also flammable and toxic, and cause great environmental concerns, so there are advantages in moving to aqueous systems.

At high volume fractions the interparticle electrostatic repulsive forces are insufficient to keep the particles apart, due to double layer overlap leading to flocculation. Thus, the addition of a polyelectrolyte introduces some electrosteric repulsion over short distances. As polyelectrolytes are of low molecular weight it is unusual for steric effects to play a major role in the stabilisation of the powder. The electrostatic repulsive force is generated by dissociation of the ionisable groups of the adsorbed polyelectrolyte.

Binders are added to slips in order to enhance the strength of the green tape for easy handling and storage. The binder remains in the tape forming organic interparticle bridges resulting in a strong adhesion after solvent evaporation. It also improves wetting and delays sedimentation through an increased viscosity. The ideal binder should be compatible with the dispersant, function as a stabiliser, act as a lubricant between the particles, have no interference with the solvent or trap air, have an effective burn out without residue, be effective at low concentrations, have a high molecular weight which is advantageous to good strength and toughness and have a low glass transition temperature. The binder must not adher to the casting surface.

These organic components of the slip should be treated in a transient way such that they can be eliminated after casting and before sintering, but they must be carefully controlled in order to achieve high reliability and avoid the introduction of impurities. Optimum levels of dispersant are normally found from settling experiments, rheology, adsorption isotherms and zeta potential measurements.[5–7,10,11,14]

With all these different additives, processing is crucial. Milling and mixing break down agglomerates to produce stable homogeneous slips. The order of addition is also crucial to prevent competitive adsorption.[12]

High viscosity slips produce thick tapes, whilst low viscosity slips produce thinner tapes. A good rule of thumb is that the blade gap setting should be twice the required final green tape thickness, although this is only true for Newtonian slips[13] and concentrated ceramic suspensions are usually non-Newtonian.

The solids loading must also be as high as possible in order to obtain the highest green density and the lowest liquid content to be evaporated after casting, thus reducing final shrinkage. On the other hand the viscosity must be low enough to facilitate the flow of the slip past the blade. Shear thinning curves are convenient as at low shear rates the viscosity is high enough to delay sedimentation, whilst at the higher shear rates the viscosity is low enough to produce a castable tape.

This study reports the identification of the optimum conditions for the preparation of aqueous alumina slips using a specific dispersant and binder system. The overall aim was to produce a stable slip with the highest volume fraction possible, whilst maintaining a viscosity suitable for tape casting, but at the same time producing a flexible and robust tape on casting.

2 Experimental Procedure

2.1 Materials

The starting powder was a high purity (>99·8%) submicrometer particle size ($d_{50} = 0{\cdot}5\,\mu m$) and relatively monodispersed (0·2–1·0 μm) commercial alumina (Alcoa A-16SG). The specific surface area was 9·58 m^2 g^{-1} (BET single point method). The dispersant used was Duramax D3021 (Rohm and Haas) a low molecular weight (MW = 2500) ammonium polyacrylate salt with a density at 23°C of 1·16 g cm^{-3}; Duramax D3021 ceramic dispersant was supplied as a 40 wt% solution in water. All dispersant concentrations are expressed in terms of the active component per unit surface area of powder.

The binder Duramax B1035 was described as an 55 wt% aqueous emulsion which has low foaming properties. It has a low glass transition temperature (−40°C) and its density at 23°C was 1·05 g cm^{-3}.

Double-distilled water was used in all formulations. NaOH was not used to alter the pH to avoid the deleterious effects of sodium on the mechanical properties of alumina[15] so NH_4OH was used instead. All the products are chemical grade reagent.

The binder content of the suspension was expressed as a percentage dry weight based on the mass of alumina powder. Once the optimum conditions were identified the suspensions were cast and sintered. The thickness of the green body after casting and the properties of the final sintered product were then related to the suspension characteristics. Tape casting was performed with a laboratory tape-casting bench with a stationary double blade system. Slurries were tape cast onto a Mylar sheet moving at constant speed of 20 cm min^{-1}.

2.2 Procedure for mixing binder

Two suspensions were prepared at volume fractions 0·374 and 0·387 using the previously developed procedure, i.e. ball mill the powder with an equal mass of alumina grinding media for 6 h with a dispersant concentration of 0·2 mg m^{-2} at which the powder-dispersant-water system shows the minimum value of the viscosity.[14] The binder was then added to these samples at a concentration of 8·25% by weight. To mix the binder, the suspensions were then gently ball milled at the lowest possible mill speed on the mill (5 rpm), and the viscosity and moduli noted every 30 min for 3·5 h for the first sample, then every 15 min for 75 min for the second sample.

The viscosity measurements were carried out in the steady shear rate mode of the Bohlin CS (Metric Group, Cirencester U.K.) which has been described.[14] Another mode of the Bohlin CS was also used to characterise the samples; oscillatory shear. In this mode, instead of applying a continuous stress, a sinusoidal stress (amplitude σ_0) is applied. The suspension responds to this with a sinusoidal strain (amplitude γ_0) which can be detected. From the magnitude of these two variables the complex modulus G^* can be defined:

$$G^* = \frac{\sigma_0}{\gamma_0} \tag{1}$$

The complex modulus can then be split into real and imaginary parts;

$$G^* = G' + iG'' \tag{2}$$

where i is the square root of −1.

Due to the viscoelasticity of the sample, the strain is out of phase with the stress by a phase angle θ. This allows two further moduli to be defined, the elastic (or storage) modulus G' and the loss modulus G'':

$$G' = G^* \cos\theta. \tag{3}$$

$$G'' = G^* \sin\theta. \tag{4}$$

A perfectly Newtonian viscous fluid has $\theta = \pi/2$, whilst a perfectly Hookean elastic solid has $\theta = 0$, whereas a viscoelastic material will have a phase angle between these two extremes. It is important to note that all these moduli are frequency dependent, i.e.

$$G^*(\omega) = G'(\omega) + iG''(\omega). \tag{5}$$

These moduli must be measured in the linear viscoelastic region, where the rheological parameters are independent of the stress amplitude. In order to locate this region a stress sweep was carried out in which the magnitude of the stress is increased at a fixed frequency (typically 1 Hz). The Bohlin CS can supply stresses in the range 0·025–245 Pa, however, the range 0·1–20 Pa was typically studied. From this stress sweep the maximum stress that gives a linear response in all the rheological parameters measured was noted. Once this has been established measurements are carried out at this fixed stress as a function of frequency, covering the range 0·04–4 Hz. All this essentially ensures that we are probing the sample without destroying the structure therein.The measurements were conducted at the same intervals as for the viscosity measurements. All rheological experiments were carried out at 25°C.

2.3 Optimum dispersant concentration in the presence of the binder

Once the optimum dispersion concentration has been identified, the binder content was held constant at 8·25% (by dry weight on alumina) and the amount of dispersant varied whilst maintaining the same volume fraction of 0·387. Six different samples (1–6) were prepared by the procedure previously identified (Table 1). The rheological properties (steady shear and oscillation) were then measured immediately after preparation.

2.4 Tape casting experiments

Initial tape casting experiments were then performed using the samples. Sample 1 was cast on to a Mylar tape moving at a tape speed of 20 cm min^{-1} and a gap setting of 0·30 mm for the first blade and 0·28 mm for the second blade. Sample 6 was also cast, but with the first blade set at a gap of 0·40 mm and the second at 0·38 mm, whilst the speed was held constant. The gap was increased to realise a final tape more than 0·30 mm in thickness. Prior to casting the suspensions had all the air bubbles removed by exposing the sample to a vacuum for a few minutes. The samples were cast at room temperature and humidity. The tapes were left to dry by evaporation overnight.

To reduce the shrinkage and drying time for the tapes and to increase the final green body density, higher volume fraction samples were prepared at 0·42 with the optimum dispersant concentration, but with different binder concentrations (samples 7–15 in Table 1), so that the minimum amount of binder required to impart a suitable flexibility to the tape could be determined. As usual the rheological properties in steady shear mode and oscillatory shear mode were recorded. These suspensions were then cast under the same conditions as before, but with both blades set at a gap of 0·4 mm. Once dry a small sample (10 cm × 6 cm) was carefully removed from the backing tape and its thickness measured with a micrometer, using an average of 10 points across the tape. The tape was then stored between sheets of tissue paper and between two large flat ceramic tiles, the flexibility was then noted after several days storage.

Table 1. Characteristics of the suspensions, (dispersant concentration is expressed in terms of active component per unit surface area of powder)

Sample no.	*Volume fraction*	*Dispersant (mg m^{-2})*	*Binder (wt%)*
1	0·387	0·2	8·25
2	0·387	0·3	8·25
3	0·387	0·4	8·25
4	0·387	0·5	8·25
5	0·387	0·8	8·25
6	0·387	1·0	8·25
7	0·420	0·3	4·40
8	0·420	0·3	4·95
9	0·420	0·3	6·05
10	0·420	0·3	6·60
11	0·420	0·3	7·15
12	0·420	0·3	8·25
13	0·420	0·3	8·80
14	0·420	0·3	9·35
15	0·420	0·3	9·90
16	0·450	0·3	7·149
17	0·458	0·3	7·151
18	0·460	0·3	4·945
19	0·477	0·3	4·950
20	0·485	0·3	4·950
21	0·489	0·3	4·950

The flexibility of the dried tape or green body was judged by placing the sample on a flat surface and bending one side around a glass rod (radius 3 mm). If the tape could be bent through an angle greater than 135°, about 10 times, it was judged to be flexible enough.

Previously, thixotropic alumina dispersions have been encountered;[6] so to check for this phenomenon, further studies were carried out using the Haake RV20 constant shear rate rheometer, again at 25°C. A previously developed shear rate step profile[6] was used which consisted of subjecting the suspension to a given shear rate until equilibrium conditions were reached and then applying a lower shear rate. The shear stress response gives information as to whether the sample is thixotropic or just undergoing shear degradation. The 'cup and bob' geometry (MV1) were used and a thin layer of vaseline oil poured over the sample to prevent evaporation losses. Ten minutes were then allowed for the sample to reach thermal equilibrium before the experiment was started. Only samples 11–15 were investigated.

2.5 Increasing the volume fraction at two fixed binder concentrations

Once the optimum binder content for a flexible green tape was identified, further suspensions were made at increased volume fractions and tape cast under the same conditions, samples 16 and 17 (Table 1). Similarly increased volume fraction samples were prepared under the conditions of the minimum amount of binder required to produce a robust enough green tape, samples 18–21 (Table 1). These suspensions were also tape cast under the same conditions as before.

2.6 Sintering

The ultimate test of whether the system is a good one or not lies in the sintering process. The 15 green bodies (samples 7–21) produced from the suspensions were sintered at 1600°C according to a previously developed temperature profile for green bodies produced from aqueous alumina suspensions.

Two circular discs of diameter 40 mm were punched from the middle section of each green tape. The thickness of the disc and its mass were noted prior to sintering. After sintering the mass of the disc and its thickness and diameter were noted, and the mass loss and the average shrinkage in two directions calculated. The final sintered density was then calculated by using the Archimedes principle of recording the mass of the disc in air and then in water. From the dry mass and the volume, the density is easily calculated.

3 Results and Discussion

3.1 Nature of the binder

The binder is a stable emulsion (latex) of a synthetic acrylic polymer which generalized structure is illustrated in Fig. 1 where R = H and R′ = alkylic group.

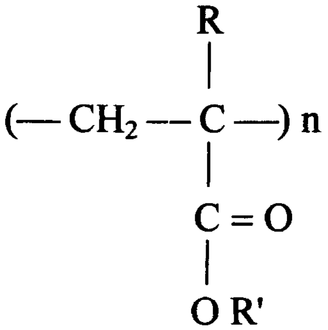
A typical formulation for a synthetic latex includes water, monomer, water soluble initiator and a surfactant. After the polymerisation reaction, micelles are formed which contain the polymer stabilised by surfactants with the hydropilic part extending out into the aqueous medium. The latex used has a negative surface charge (anionic binder). When the water evaporates the latex particles are forced closer and closer together until the coalescence between the particles takes place; the coalescence leads to phase inversion and subsequently to the formation of the polymer film.

Solubilization tests performed in methanol, acetone, chloroform and ether support the fact that the binder is a reticulated polymer.

3.2 Procedure for mixing the binder

From Fig. 2 it can be seen that the viscosity of the suspension increased with increased time of mixing. A visual confirmation of this was that the suspension had gone from being fairly fluid to almost paste-like. Investigating this phenomenon further by measuring the rheological properties every 15 min, it was noted that the minimum viscosity and the minimum complex modulus and elastic modulus were achieved with 15 min mixing, whilst further milling again just led to increased viscosities (Fig. 3) and increased moduli especially after 75 mins (Fig. 4).

Prolonged milling induces destabilization of the suspension and milling at faster rotation rates would have the same effect, only more quickly. So for optimum preparation conditions the binder was added to the suspension and gently mixed at the lowest possible angular velocity for 15 min. This was sufficient to produce a homogeneous suspension.



$$\begin{array}{c} \mathrm{R} \\ | \\ (-\mathrm{CH_2}-\mathrm{C}-)\,n \\ | \\ \mathrm{C=O} \\ | \\ \mathrm{O\,R'} \end{array}$$

Fig. 1. General structure of the binder.

3.3 Optimum dispersant concentration in the presence of the binder

The viscosity and the complex moduli G^* at 1 Hz of the suspension at fixed volume fraction (0·387) and binder concentration (8·25 wt%) are plotted as a function of the dispersant concentration in Figs 5 and 6 respectively.

It can be seen that the minimum viscosity and minimum G^* were obtained with a dispersant concentration of 0·3 mg m^{-2} and not the 0·2 mg m^{-2} previously identified as being the optimum concentration for stability. This could be due to some reaction between the binder and the dispersant, but exactly what is difficult to say. This effect has been noted before in this laboratory in other aqueous suspensions of alumina.[5] So 0·3 mg m^{-2} is now taken as the optimum dispersant concentration.

3.4 Initial tape casting/rheology

Both initial test samples cast very good tapes with no cracks, which could easily be removed from the Mylar backing substrate. Smooth tapes were obtained so it was decided to fix both the blades at a gap of 0·40 mm in order to produce a reasonably thick tape. The tape speed of 20 cm min^{-1}, seemed reasonable. The bubbles were removed by exposure to a vacuum which proved to be very effective and was established as the most efficient method of removing these sources of defects.

Tapes were cast from nine different slips all of the same volume fraction (0·42) and a dispersant concentration of 0·3 mg m^{-2}, but with binder contents ranging from 4·4–9·9% by weight. Figure 7 shows that increasing the binder content of the suspension increases the viscosity. All the slips produced good smooth tapes, except sample 7 (binder concentration 4·4%) which produced a cracked tape, indicating that there was obviously insufficient binder present. So a concentration of 4·95% binder can be identified as the minimum amount of binder required to produce a robust tape. From the flexibility tests, conducted a few days after casting, it was concluded that the minimum amount of binder for a flexible tape was 7·15 wt% (see Table 2).

The final thickness of the green body was also noted with a micrometer and is reported in Table 2. To re-emphasise, all the samples are at the same volume fraction and the same dispersant level and were cast under the same conditions of a tape speed of 20 cm min^{-1} and a blade gap of 0·40 mm. The only difference is the binder content. Under these casting conditions the shear rate that the slip experiences when passing under the blade is 8·3 s^{-1}. The nearest shear rate to this as measured on the Bohlin CS is 7·4 s^{-1}, so the viscosity at this shear rate is also reported in Table 2.

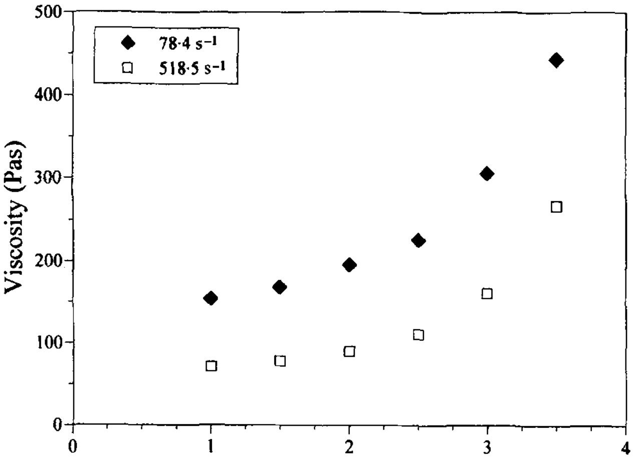


Fig. 2. Effect of binder mixing time on the viscosity at two different shear rates.

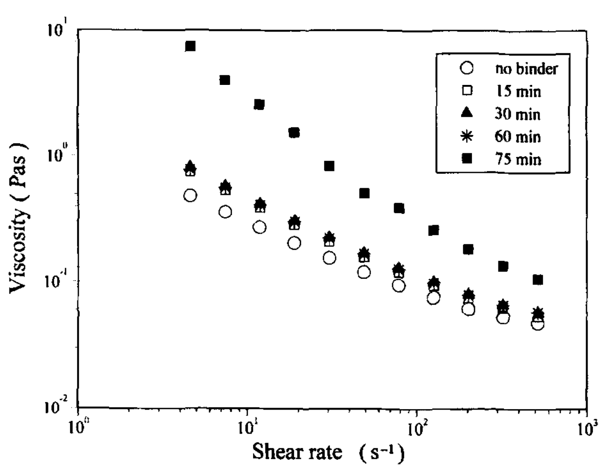


Fig. 3. Effect of binder mixing time on the viscosity.

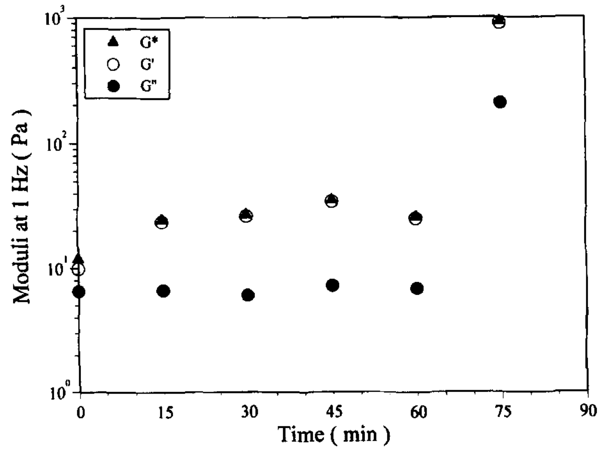


Fig. 4. Effect of binder mixing time on G^*, G' and G''.

It can be seen that on drying the green bodies have shrunk from their original size (0·4 mm) but unfortunately no correlation with the viscosity can be noticed. It would be expected that slips of higher viscosity and a higher G' would produce thicker green bodies. Also these more viscous samples contain less water so again there would be less shrinkage on drying. The linear shrinkage of green tapes after casting has been studied by Hyatt[16] who noted that the linear shrinkage correlated inversely to the amount of the organic phase present, whether the system was aqueous or not, i.e. the more binder present the less the shrinkage. This effect may be hidden here due to slight inaccuracies in setting the blade gap. Plus there is only a small change in the viscosity, a factor of about six.

Previous experiments in this laboratory have shown aqueous alumina suspensions to be thixotropic also at lower volume fraction, however these slips were not thixotropic. The Bohlin flow curves of viscosity against shear rate superimposed on one another for the up and down cycle of the shear rate, plus the specifically designed Haake experiment also failed to detect any thixotropic behaviour. Table 3 shows the final green body thickness for the higher volume fractions and the suspension viscosity at 7·4 s^{-1}. Again no correlation could be obtained between the green thickness and the suspension viscosity.

3.5 Sintering

All the sintered tapes produced good, smooth, robust and uniform discs with no cracks. Taking the effect of the binder first, at constant volume fraction. In Fig. 8 there is good correlation between the mass loss on sintering the green body and the % binder present in the original suspension,

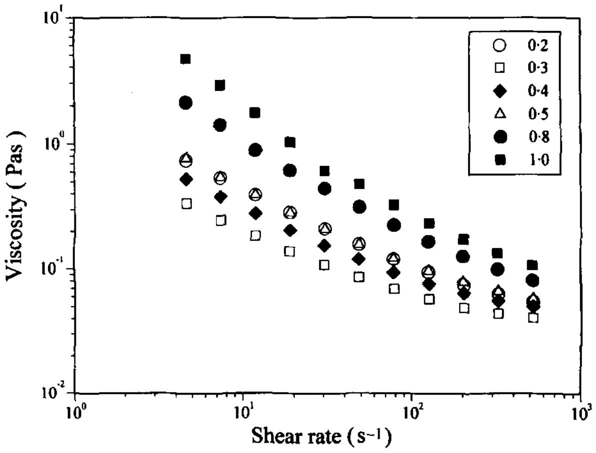


Fig. 5. Effect of dispersant concentration (mg m^{-2}) at fixed binder concentration of 7·85 wt%.

as the greater the binder content in the green body then the more there is to be burnt out on sintering, leading to a greater mass loss. The higher experimental weight loss is due to the water adsorbed on the ceramic powder surface and still present after the evaporation at room temperature.

The average shrinkage of the two discs increased with increasing binder content; the shrinkage was greater in the thickness measurement than in the diameter measurement, specifically at low binder concentration (4·4 wt%) the shrinkage of diameter and thickness was 14·6 and 16·7% respectively; at high binder concentration (9·9 wt%) the shrinkage was 16·9 and 21·3% respectively. Finally, and most importantly, in Fig. 9 the final sintered density is plotted against the % binder content in the suspension. The sintered densities increase with increasing binder content, until almost 100% theoretical density is reached. The lowest sintered density is 96% of theoretical, indicating that all these samples sinter extremely well with effective burn-out of the binder and dispersant.

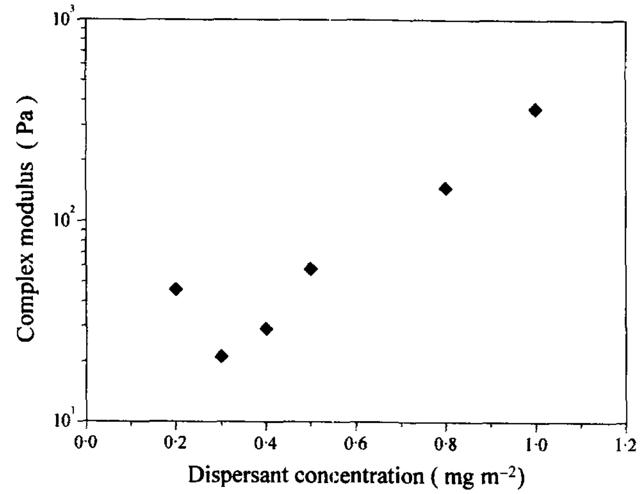


Fig. 6. Complex Modulus (at 1 Hz) against dispersant concentration.

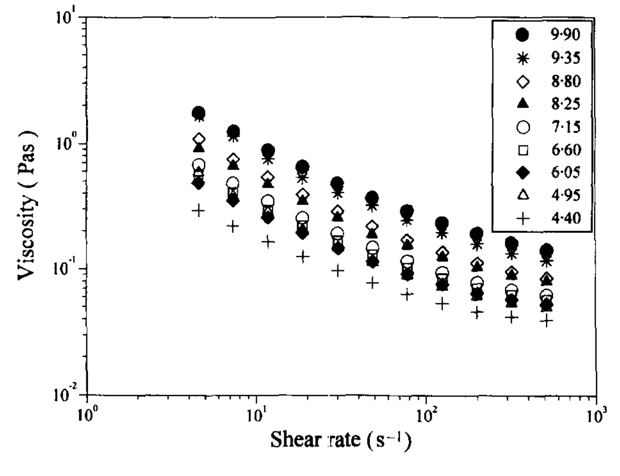


Fig. 7. Effect of binder content (wt%) on the viscosity of the optimised suspension.

Turning now to investigating the effect of volume fraction at a fixed binder content of 4·95%. It was noticed that the % mass loss was constant which is as expected as the organic content is the same in all the casting suspensions. The shrinkage in the average thickness on sintering was once again greater than the % shrinkage in average diameter on sintering. This could be ascribed to some orientation of the particles under shearing, due to their irregular shape. The packing structure within the green body is such that the particles have a higher density of contact points at which sintering can occur in the thickness direction than laterally, hence the shrinkage is greater. In Fig. 10 it is possible to see that the degree of shrinkage becomes less with increasing volume fraction, as the particles are increasingly closer together.

But the most important result is that the greatest final sintered density can be obtained with the highest volume fractions, see (Fig. 10). The discs produced from these high volume fraction suspensions sintered to 100% theoretical density, so all the binder and dispersant were cleanly burnt out to leave a non-porous disc of pure alumina.

4 Conclusions

When the binder is added to the optimised suspension the optimum dispersant concentration becomes 0·3 mg m^{-2} (or 0·29 wt% not the 0·2 mg m^{-2} as identified previously. The binder should be mixed very slowly (5 rpm) on the mill for a short

Table 2. Thickness and flexibility of the green body related to the suspension viscosity at fixed volume fraction (0·42) and dispersant concentration (0·30 mg m^{-2})

Sample no.	*Binder (wt%)*	*Viscosity at 7·4 s^{-1} (Pas)*	*Thickness (mm)*	*Flexibility*
7	4·40	0·218	0·384 ± 0·013	bad
8	4·95	0·380	0·346 ± 0·020	bad
9	6·05	0·351	0·325 ± 0·008	bad
10	6·60	0·407	0·338 ± 0·007	bad
11	7·15	0·482	0·291 ± 0·006	good
12	8·25	0·658	0·333 ± 0·005	good
13	8·80	0·750	0·315 ± 0·007	good
14	9·35	1·143	0·312 ± 0·004	good
15	9·90	1·246	0·310 ± 0·007	good

Table 3. Green body thickness related to the viscosity (shear rate 7·4 s^{-1}) at two different binder concentrations, whilst increasing the volume fraction

Sample no.	*Volume fraction*	*Viscosity at 7·4 s^{-1} (Pas)*	*Binder (wt%)*	*Thickness (mm)*
8	0·421	0·380	4·95	0·346 ± 0·020
18	0·460	0·593	4·95	0·376 ± 0·007
19	0·477	1·009	4·95	0·354 ± 0·007
20	0·485	1·237	4·95	0·377 ± 0·009
21	0·489	1·735	4·95	0·366 ± 0·005
16	0·450	1·409	7·15	0·324 ± 0·007
17	0·458	1·586	7·15	0·303 ± 0·008

time (15 minutes in this case). This is sufficient to produce good homogeneity without shearing off the dispersant and allowing the binder to absorb, reducing the stability of the suspension and resulting in its increased viscosity and elastic modulus.

Good, smooth, flexible green body tapes could be obtained with both blade gaps set at 0·4 mm and with a Mylar tape speed of 20 cm min^{-1}, on the casting apparatus. The vacuum technique proved to be efficient in removing air bubbles from the suspension.

For suspension with 0·42 volume fraction the optimum amount of binder to produce a flexible tape is 7·15% by dry weight (based on alumina), whilst the minimum amount of binder to produce a green body that could be handled and did not crack after casting was 4·95% by dry weight. These slips were not thixotropic, as previously noted. All the final green bodies had shrunk in size after casting, but it was difficult to see any correlation with the viscosity as would be expected.

On sintering the tapes, all the discs had high densities, however, the highest density of 100% theoretical (3·99 g cm^{-3}) was obtained from the suspension with the highest volume fraction (0·49). High sintered densities (99% of theoretical) could also be obtained at a fixed volume fraction by increasing the binder content. In all the sintered discs the average shrinkage in the thickness measurement was greater than that in the diameter measurement due to the non-spherical nature of the particles. The shrinkage in both measurements decreased with increasing volume fraction, whereas the shrinkage increased with increasing binder content. There was also excellent correlation between the mass loss on sintering the green body and the amount of binder present within the suspension.

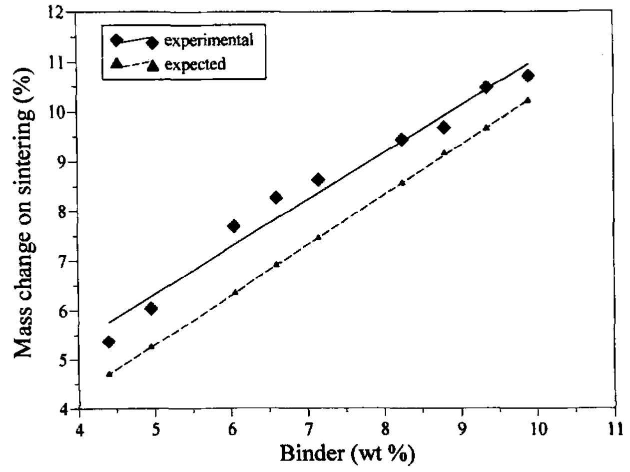


Fig. 8. Mass loss on sintering against binder concentration in the suspension.

Conditions, therefore, have been identified that lead to thin (about 0·3 mm), robust, smooth alumina tapes being produced from aqueous suspensions

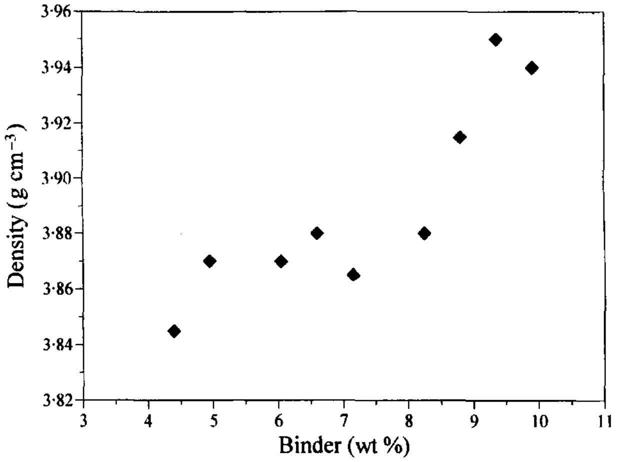


Fig. 9. Final sintered density against binder content of the suspension.

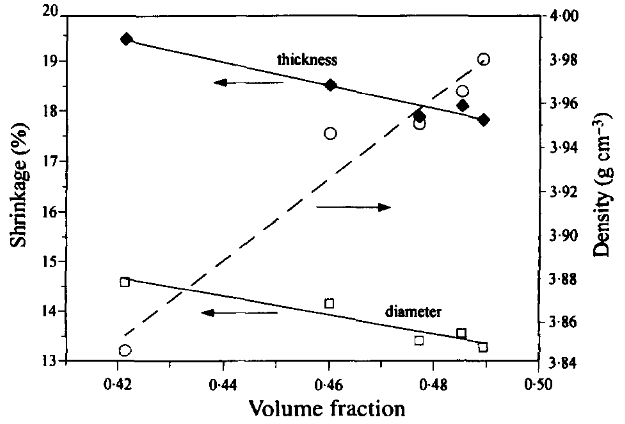


Fig. 10. Shrinkage of the green body on sintering and final density against volume fraction of the suspension.

which have extremely high final densities of 100% of theoretical.

Acknowledgements

This work was financed by the European Commission CEC Human Capital and Mobility Programme, Contract CHRX-CT94-0574, 'Application of fundamental principles of colloid and interface science and rheology to ceramic forming processes.' The contribution of Myriam Gourmand of the Laboratoire de Physico-Chemie Macromoleculare, Paris, concerning the dispersant characterisation, is gratefully acknowledged. Paola Pinasco and Andreana Piancastelli at IRTEC are also thanked for their technical assistance.

References

1. Moreno, R., *Am. Ceram. Soc. Bull.*, 1992, **71**(10), 1521.
2. Moreno, R., *Am. Ceram. Soc. Bull.*, 1992, **71**(11), 1647.
3. Mistler, R. E., *Am. Ceram. Soc. Bull.*, 1990, **69**(6), 1022.
4. Hotza, D. and Greil, P., *Mat. Sci and Engineering*, 1995, **A22**(1–2), 206.
5. Galassi, C., Esposito, L., Rastelli, E. and Roncari, E., *Third Euro-Ceramics*, Vol 1, eds P. Duran and J. F. Fernandez, Faenza Editrice Iberica, 1993, p. 609.
6. Galassi, C., Rastelli, E., Roncari, E. and Basile, Advances in science and technology, **3C**. In *Ceramics: charting the future*, ed. P. Vicenzini, Techna, Italy, 1995, 1633.
7. Nagata, K., *Journal of Ceram. Soc. Jpn, International Edition*, 1992, **100**, 1251.
8. Galassi, C., Biasini, V. and Guiccirdi, S., *Journal of Eur. Ceram. Soc.*, 1993, **12**, 441.
9. Bellosi, A., Galassi, C. and Guiccirdi, S., *Journal of Mater. Sci.*, 1990, **25**, 4331.
10. Galassi, C. and Roncari, E., *Handbook on Characterisation Techniques for the Solid-Solution Interface*. The American Ceramic Society, USA, 1993, p. 239.
11. Roncari, E., Galassi, C., Piancastelli, A. and Pinasco, P., *Advances in Science and Technology 3C*. In Ceramics: charting the future, ed. P. Vicenzini, Techna, Italy, 1995, p. 1517.
12. Braun, L., Morris Jr, J. R. and Cannon, W. R., *Am. Ceram. Soc. Bull.*, 1985, **64**(5), 727.
13. Ring, T. A., Ceramic Substrates and Packages for Electronic Applications, *Advances in Ceramics* Vol. 26, eds M. F. Yan, K. Niwaa, H. M. O'Bryan Jr and W. S. Young. The American Ceramic Society, USA, 1989, p. 569.
14. Roncari, E., Galassi, C. and Greenwood, R., Research Institute for Ceramic Technology, Faenza, Italy, Report n. 17/96, 1996.
15. Bleir, A. and Westmoreland, C. G., *Journal of Am. Ceram. Soc.*, 1991, **74**(12), 3100.
16. Hyatt, E. P., *Am. Ceram. Soc. Bull.*, 1986, **65**(4), 637.