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Tape casting of Y-TZP with low binder content

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Abstract

The rheology of Y-TZP slurries with a low content of an acrylic/styrene binder is studied. The optimum amount of dispersant was found to be 0.3 wt.% for the starting slurry. After a 5 wt.% of binder addition the dispersant amount needed to achieve a minimum viscosity increases to 0.5 wt.%. Tapes obtained from slurries with a solid content of 45 vol.% shows the higher green density of 51 th.%. Higher solid contents do not yield to better green densities due to the high viscosity.

Keywords: A. Suspensions; A. Tape casting; Rheology

1. Introduction

Tape casting has been extensively used to produce substrates and pieces in a wide range of materials and microstructures [1–4]. For most of the applications, the tape casting method has been selected due to its precise control of the thickness, allowing the miniaturization and packaging of the devices. Organic solvents have been traditionally used as vehicle for dispersion of ceramic particles, due to their compatibility with the most common binders and plasticizers [5,6]. As an alternative to the established processes, the use of water as the dispersion medium for tape casting slurries has both advantages and disadvantages. Advantageous is the know-how derived from other water-based processing techniques that require highly stable slurries [7–11]. On the other hand, the slow drying rate of the cast tape, the higher crack sensitivity and the reactivity of the powders with water are causes of concern [12–14]. To overcome these problems, a high solid loading is required to increase the drying rate and simultaneously minimize drying stresses in the tape.

The binders based on latexes in water emulsions combine the presence of polymers that assure adhesion, cohesion and flexibility while slightly affecting viscosity. These emulsions are usually obtained by free radical polymerization of monomers in water. During this process, the composition of the monomers can be designed for specific properties [15,16] according to the requirements of the final product. Latex binders are grouped into acrylic and acrylic/styrene. Both are extensively documented and numerous processing studies are devoted to the relationships between the particle/binder characteristics and concentration with the rheological behaviour of the slurries as well as the characteristics of the green tapes [3,4,9,17–24]. These better mechanical properties are related to the binder–binder and binder–ceramic interactions as well as to the particle size of the binder. All these parameters play an important role in the dispersion of both ceramic and latex particles as well as in the state of stresses within the drying tape [14,18].

Moreover, acrylic/styrene binders has been more commonly used as an adhesive to pile up tapes in order to fabricate more complex metal and ceramic structures like thick monolithics [3,20,25,26], multilayers [27–30] or porous coatings [31,32]. The formulation of the tapes employed to create those complex structures requires a relative elevated amount of acrylic/styrene binders (25–30 vol.%) if compared with other casting processes. This high amount of organic leads to low sintered densities and consequently, to a higher flaw population as a consequence of the high porosity. To fabricate dense materials that can be used for structural applications, it is required to increase the solids content of the slurries and minimize the organics content. Suspensions with high solid loading can be obtained by ensuring the proper stability between ceramic–ceramic, latex–latex and ceramic–latex particles [22]. This is only possible through a precise control of the rheology of the slurries used for tape casting.

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In this paper the rheology of Y-TZP slurries with small amounts (13 vol.% referred to solids corresponding to 5–6 vol.% of the total slurry) of a commercial acrylic/styrene binder is studied in order to develop optimum tape casting conditions. The final goal is to fabricate tapes to be employed in the piling up of multilayer systems with structural reinforcement.

2. Experimental

The starting powder was a 3 mol% yttria stabilized tetragonal circonia (TZ-3YS, Tosho, Japan) with a mean particle size of 0.4 μm and a specific surface area of 6.7 $m^2 g^{-1}$. As dispersant an ammonium polycarboxilate-based polyelectrolyte (DolapixCE64, Zschimmer & Schwarz, Germany) was used and a water-based polymeric emulsion, Mowilith DM 765 E (Celanese, Spain), with a T_g of −6 °C, solid content of 50 vol.% and particle size of 0.05–0.15 μm was used as binder.

Slurries were fabricated by adding the powder to the water with the required amount of dispersant under mechanical stirring. The slurry was ball milled for 4 h using alumina vessel and milling media. 5 wt.% of binder, referred to solids content, was added to the milled suspensions followed by mixing with a blade mixer for 30 min. Rheological measurements were performed using a viscosimeter (Haake RS 50, Germany) operating in control rate (CR) mode at 25 °C. The measurement conditions were from 0 to 1000 s^{-1} in 2 min, maintaining at this rate for 1 min and going back to 0 s^{-1} in 2 min. Data were adjusted in different models using a regression software (Rheowin 3 Data manager, Haake, Germany).

The tape casting was performed on a stationary polypropylene film coated with a hydrophobic paste using a moving tape casting device with two doctor blades. The casting parameters were 10 mm s^{-1} of casting velocity and 500 μm of gap height between the blades and the carrier film. After drying in air at room temperature conditions for 24 h, the green ceramic tapes were further dried at 60 °C for 48 h. The green density of the tapes was measured using the geometrical method. Reported values are the average of three measurements of discs of 26 mm diameter processed under nominally identical conditions, error bars are the standard deviations.

3. Results and discussion

The flow curves for 43 vol.% (83 wt.%) slurries with different dispersant contents from 0.3 to 1% of solid content are shown in Fig. 1. Slurries of such solid content without any dispersant addition yield very high viscosity values that could not be recorded. Suspensions with 0.3% of dispersant show the lowest viscosity and yield stress. In all cases, the flow curves show higher values of viscosity and yield stress with increasing dispersant content. The rheological behaviour of the slurries was adjusted to the common models (Bingham, Herschel-Bulkeley, Casson, Cross and Ostwall de Waelle) being the generalized Casson model [17] which gives a better correlation factor (higher than 0.998) in all the cases. The Casson model

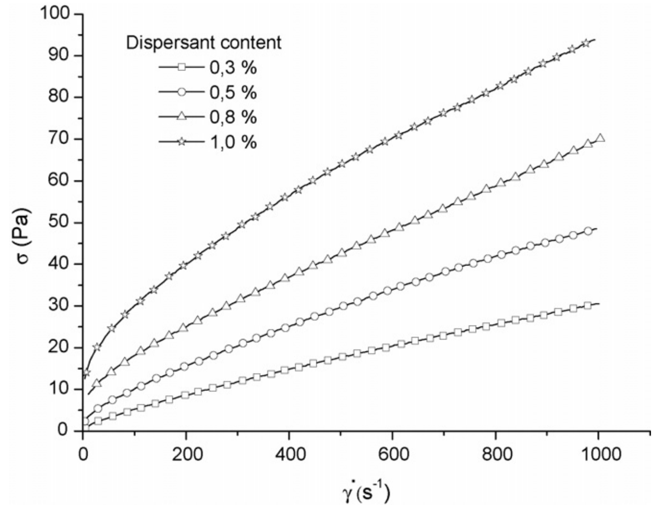

Fig. 1. Flow curves of the 43 vol.% Y-TZP slurry with different dispersant contents.

$[\sigma^n = \sigma_0^n + (\eta_c\dot{\gamma})^n]$ defines a shear thinning behaviour, where τ_0 is the yield stress, η_p the plastic viscosity or the viscosity at a high shear rate and n is an adjusting factor being 1 when the slurry flows following a Bingham pattern. Deviations of n from 1 indicate that the slurry shows a shear thinning behaviour been the value of 0.5 to the original form of Casson model. The lower the n factor the more shear thinning is observed. Table 1 summarizes the parameters obtained using the generalized Casson equation.

It can be seen that with the dispersant increment a higher yield stress as well as higher plastic viscosity and lower shear thinning capability is observed. This indicates that 0.3 wt.% is the optimum amount of dispersant for the formulation of highly dispersed slurries. Higher amounts of dispersant lower the rheological behaviour due to polymer–polymer interactions.

In order to study the effect of the binder addition, a 5 wt.% of binder emulsion, referred to solids, was added to the slurries with 43 vol.% of solids loading. After this the slurries had a final solid content of 38.2 and 5.6 vol.% of dry binder (13% if referred to dry powders). Fig. 2 shows the flow curves for the slurries after the addition of the binder emulsion. It is clear that the addition of the binder destabilizes the 0.3 wt.% slurry and increases its viscosity while the 0.5 wt.% containing slurry reaches the lower viscosity. This fact has been reported previously by other authors in alumina slurries with similar binder and dispersant contents [19]. This increment in the viscosity for low dispersant content indicates that the binder addition generate a defect of dispersant in the slurry.

Table 1
Parameters corresponding to the flow curves shown in Fig. 1 fixed to the generalized Casson model

Dispersant content (wt.%)	σ_0 (Pa)	η_c (Pa s)	n	r
0.3	0.02145	0.01471	0.2499	1.0000
0.5	1.062	0.0271	0.4127	0.9999
0.8	7.1	0.04213	0.5958	0.9999
1.0	12.33	0.0446	0.55	0.9987

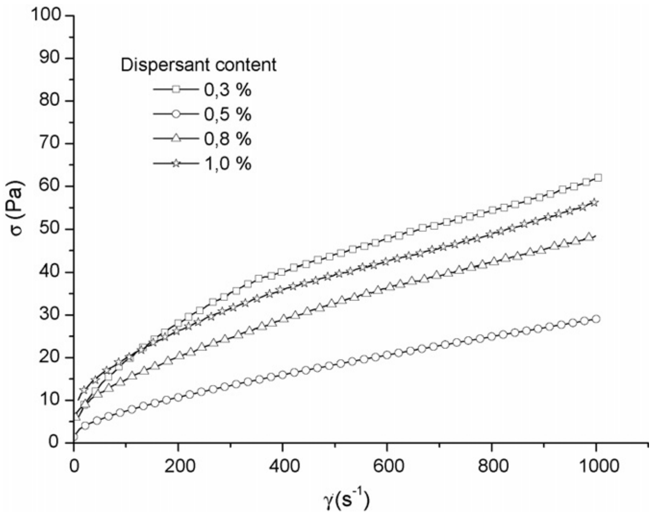

Fig. 2. Flow curves of the 43 vol.% Y-TZP slurry with different dispersant contents after the addition of a 5 wt.% of binder.

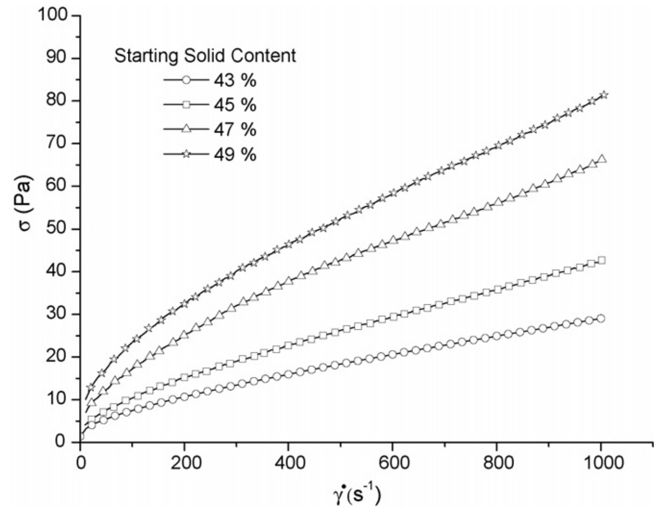

Fig. 3. Flow curves of the Y-TZP slurries with 0.5 wt.% of dispersant and 5 wt.% of binder prepared from starting slurries with different solid contents.

Data extracted from the adjustment of these curves to the Casson model can be seen in Table 2.

With the exception of the 0.3 wt.% slurry (that has been destabilized), the other slurries show a lower yield point and plastic viscosity as a consequence of the lowering in the solids content after the binder addition (binder is a 50 vol.% emulsion). The slurry having 0.5 wt.% of dispersant maintains a yield point similar to the one observed in the slurry prior to the binder addition. But the plastics viscosity decreases and higher shear thinning behaviour is observed (*n* value is decreases, Table 2). These characteristics of the Casson parameters indicate that this dispersant addition satisfies the requirement for both the binder content and the binder free slurries. In other words, it shows a viscosity low enough for milling and further mixing with binder additions in order to obtain stabilized ceramic suspensions.

Once the 0.5 wt.% was selected as the proper amount of dispersant for binder contents of 5 wt.%, the influence in the solid content was studied with two main goals. Firstly to provide the slurry with the plasticity required for the tape casting process. Secondly, to improve the final green density of the tapes fabricated. Four different slurries where studied with solid contents of 43, 45, 47 and 49 vol.% and binder and dispersant contents (referred to solids) of 5 and 0.5 wt.%, respectively. Slurries with higher solid contents were possible to fabricate, but the tape casting process did not yield any usable tape due to the high viscosity.

Fig. 3 shows the flow curves recorded for these materials. It can be seen that increments in the solid content provide a higher viscosity to the slurry. This increment is not only due to higher concentration in ceramic particles. As it can be seen in Table 3, the increment in the solids content is associated to an increment in the binder content. So both effects are responsible for the increment in viscosity.

The rheological parameters obtained after fixing the flow curves to the generalized Casson model are indicated in Table 4.

It can be seen that both the yield point and the plastic viscosity slightly increase with the solids content of the slurry. On the other hand the *n* factor (Table 4) decreases with solids content, indicating that the shear thinning effect is more profound at higher yield point.

All these slurries were cast on a polypropylene film coated with an hydrophobic tape. Slurries having starting solids content of 43 vol.% shrink as fluids on a not wetting surface due to their low viscosity. In the other samples, with a higher viscosity and yield point, no shape changes were observed in the tape after casting. Table 5 summarizes the green density for dry tapes cast using those slurries and blades gaps of 500 μm.

Samples obtained from slurries with 47 and 49 vol.% showed the presence of large pores after visual inspection in the top surface as well as extensive cracking. On the other hand samples with 43 and 45 vol.% had a smooth surface. In these

Table 2
Parameters for the flow curves shown in Fig. 2 fixed to the generalized Casson model

Dispersant content (wt.%)	σ_0 (Pa)	$\ni_c$ (Pa s)	*n*	*r*
0.3	2.287	0.04474	0.484	0.9999
0.5	1.392	0.01117	0.387	0.9996
0.8	4.609	0.01874	0.440	0.9999
1.0	6.304	0.01398	0.380	0.9993

Table 3
Solids and binder final contents for the slurries calculated before and after the binder addition

Y-TZP (vol.%)		Binder (vol.%)	Final vol.% of solids
Starting	After binder		
43	38.1	5.6	42.7
45	39.7	5.9	45.6
47	41.3	6.1	47.4
49	42.8	6.3	49.1

Table 4
Parameters for the flow curves shown in Fig. 3 fixed to the generalized Casson model

Solid content (vol.%)	σ_0 (Pa)	$\ni_c$ (Pa s)	n	r
43	1.392	0.01117	0.387	0.9996
45	1.504	0.01492	0.357	0.9999
47	1.834	0.01899	0.310	0.9998
49	2.641	0.01751	0.269	0.9999

Table 5
Green density of dry tapes cast from slurries with different starting solids loading

Y-TZP (vol.%)		Density (th.%)
Starting	After binder	
43	38.1	49.4
45	39.7	51.0
47	41.3	50.1
49	42.8	48.1

samples cracking also was present but to a much lesser extent. The cracks are due to the adhesive capability of the binder that joins the tape to the substrate therefore resulting in the development of high residual drying stresses. These stresses are relieved by the cracks observed. In Table 5 it can be seen that the higher density is achieved for the 45 vol.% slurry. At this solid content the viscosity is low enough to allow rearrangements of the cast particles in order to achieve a better density while maintaining the tape shape after casting. Fig. 4 shows a SEM micrograph for the top surface of the tape cast tape using slurry with 45 vol.% solids content. High packaging of particles with small pores (≈1 μm), dispersed throughout the surface, can be observed. Those pores act as stresses concentrators where from cracks initiate. Bigger the pores lower the stress necessary to initiate a crack. For this reason samples cast from 47 and 49 vol.% showed more extensive cracking.

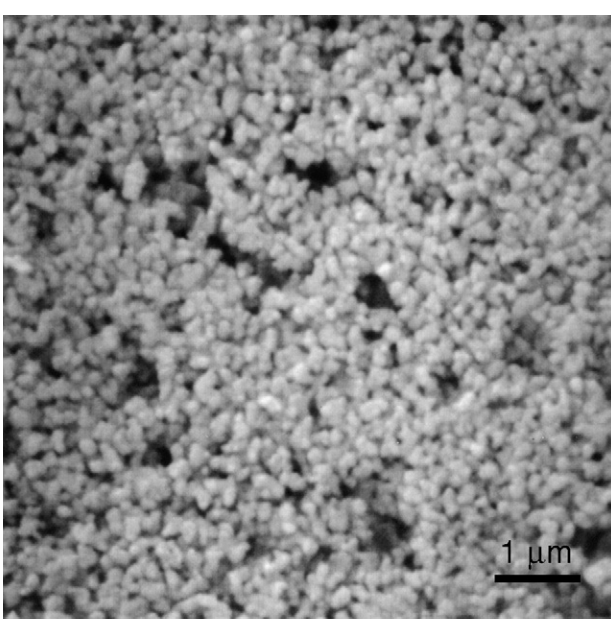

Fig. 4. SEM micrograph of the top surface of a sample cast using a 45 vol.% slurry.

4. Conclusions

Ceramic samples of Y-TZP have been obtained by tape casting using low additions of an acrylic/styrene binder. The addition of the binder component increases the required amounts of dispersant to retain stable the slurry. Solids content is critical to tape casting of these slurries. If the solids content is too low, the viscosity is also low and cast tapes do not retain their shape. If the solids content is too high, the tapes shows defects in the form of bubbles that acts as crack initiators. By optimizing the processing conditions tapes with low solid contents and a green density of 51 th.% were fabricated.

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