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Ceramics International 32 (2006) 567–574

CERAMICS
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Influence of the slip composition on the aqueous processing and properties of yttria stabilized zirconia green tapes

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Received 1 February 2005; received in revised form 1 March 2005; accepted 12 April 2005
Available online 8 June 2005

Abstract

The tape-casting process was used to produce yttria stabilized zirconia (YSZ) substrates in an aqueous system with poly(vinylalcohol) (PVA) and glycerine as binder and plasticizer, respectively. Various compositions of YSZ slips with different amounts of PVA and glycerine and consequently different solid/liquid ratios were prepared. The influence of the slip composition on the rheological properties of the slips and the drying kinetics of the cast tapes were studied. In addition, the effect of the slip composition on the properties of the resultant green tapes was investigated. PVA and glycerine did not affect the dispersion properties of the YSZ powder. The slip composition had influence only on the second stage of the drying kinetic; for a constant PVA content, the slips with higher amounts of glycerine resulted in tapes with higher drying rate. Glycerine additions enhanced the flexibility of the green tapes but also produced a decrease in the tensile strength. The increase in the PVA content increased the tensile strength but resulted in a marked decrease in the green density of the tapes. The slip compositions with 5 wt.% PVA produced green tapes with satisfactory tensile strength which had the highest green density. Since a greater amount of glycerine resulted in tapes with higher drying rate and enhanced the flexibility of the green tapes, the slip composition 5 wt.% PVA–7.1 wt.% glycerine was adequate for the production of YSZ substrates through the tape-casting process.

Keywords: A. Tape casting; D. ZrO_2; Slip and green tape properties

1. Introduction

Tape casting is a well-established technique for the large-scale manufacturing of thin and flat yttria stabilized zirconia ceramic products [1–3]. The typical applications for these tape cast products are solid electrolytes for sensors and solid oxide fuel cells.

Tape-casting suspensions are composed of ceramic powder dispersed in a solvent, with the addition of a dispersant, binder and plasticizer [4]. The dispersant controls the stability and rheological behavior of the slips, and the binder and plasticizer, the strength and flexibility of green tapes, respectively [5].

Organic solvents are frequently used to prepare the concentrated ceramic suspensions [1]. Due to the volatility and toxicity of these organic solvents, the development of water-based tape-casting systems is considered to be desirable. These systems have the advantages of non-flammability, non-toxicity and low cost. In addition, there is also an extensive knowledge base available for the processing of aqueous slips, which are used for other ceramic processing techniques. However, the drying rate of water-based suspensions is invariably much slower than that of the non-aqueous systems.

Compared with non-aqueous solvents, the variety of water-soluble binders and plasticizers systems is restricted [6]. PVA is a common binder for aqueous tape casting and glycerine is frequently used as plasticizer with PVA binder. Therefore, in this work, PVA and glycerine were used as binder and plasticizer, respectively, in an aqueous tape-casting process for YSZ substrates.

The organic additives affect the slurry behavior as well as the properties of the tape-cast substrates. Crack-free,

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doi:10.1016/j.ceramint.2005.04.012

uniform green tapes may only be produced using aqueous slips with optimized compositions. In this work, the influence of the slip composition on the rheological properties of the slips and the drying kinetics of the cast tapes were studied. In addition, the effect of the slip composition on the properties of the resultant green tapes was investigated.

2. Experimental procedure

2.1. Materials

A commercial yttria doped zirconia powder (Y8Z01, Saint-Gobain, France) was used in this study. The mean particle diameter and the specific surface area were 0.53 μm and 8.26 m^2/g, respectively.

The dispersant, a commercial ammonium polyacrylate solution (Dolapix CE 64, Zschimmer & Schwarz). A 16 wt.% PVA solution and glycerine (99.5%) were used as binder and plasticizer, respectively.

2.2. Slip preparation

YSZ slips were prepared by deagglomeration of 30 g YSZ in 10 ml de-ionized water with 0.3 wt.% NH_4PA (dry weight basis of powder) by ultrasonic treatment, with subsequent additions of different PVA and glycerine contents. The pH of the suspensions was 9.0.

The solid/liquid ratio of the slips changed as a consequence of the different amounts of PVA and glycerine added. In this way, adequate viscosity values for the tape-casting process could be obtained. The slip compositions prepared are shown in Table 1.

2.3. De-airing

The slips were de-aired under a mechanical vacuum for several minutes. The vacuum vessel was backfilled with air pre-saturated with the solvent to prevent the formation of a skin on the surface of the slip.

Table 1
Compositions of YSZ slips with different amounts of PVA and glycerine

PVA content[a] (wt.%)	Glycerine content[a] (wt.%)	PVA/Glycerine	Solid/liquid[b]
5	3.3	1.5	1.66
	5	1	1.62
	7.1	0.7	1.56
6	4	1.5	1.53
	6	1	1.49
	8.6	0.7	1.43
7	4.7	1.5	1.42
	7	1	1.38
	10	0.7	1.33

[a] The PVA and glycerine contents were expressed as the dry weight base with respect to YSZ.

[b] Solid/liquid = (YSZ powder + binder)/liquid.

2.4. Rheological measurements

Steady state flow curves of the fluid part of YSZ slips (the slip containing all the components without the powder) and YSZ slips were performed by measuring the steady shear stress value as a function of shear rate in the range of 0.5–600 s^{-1} using a concentric cylinder viscometer (Haake VT550, Germany) at 25 °C. As soon as stationary conditions were reached at each shear rate, the shear rate increased in steps up to the maximum value and then decreased. The relative viscosity (η_r) defined as:

$$\eta_r = \frac{\eta_s}{\eta_f}$$

where η_s is the viscosity of the suspension and η_f is the viscosity of the fluid part only, was calculated at 181 s^{-1}.

2.5. Tape-casting

Slips were cast on a fixed polyethylene carrier film using the doctor blade method. The casting speed was constant at 1 cm/s and the gap between the blade and the carrier film was adjusted at 0.4 mm. The cast tapes were dried in air at room temperature for 2 days; afterwards, they were stripped from the film.

2.6. Weight loss measurements during drying

Slips with different compositions were cast on polyethylene to produce tapes of surface area and initial tape thickness values of 32.5 cm^2 and 0.4 mm, respectively. These samples were immediately placed on a balance (Denver Instrument Model XL-3100) and their mass was recorded as a function of time. From these curves the drying rate and the water weight loss (relative to the initial total water content in the suspensions) were calculated.

2.7. Characterization of green tapes

The pore size distribution of green tapes with different solid/liquid ratios was performed using mercury porosimetry (Porosimeter 2000 Carlo Erba, Italy).

The tensile strength and the strain to failure of the green tapes were measured using an Instron 4411 universal machine.

The thickness of the green tapes was measured using a Mitutoyo absolute ID-S 1012 Digimatic Indicator then, the drying shrinkage expressed as percentage of the blade opening was calculated. The tapes were weighed and measured to determine the green density.

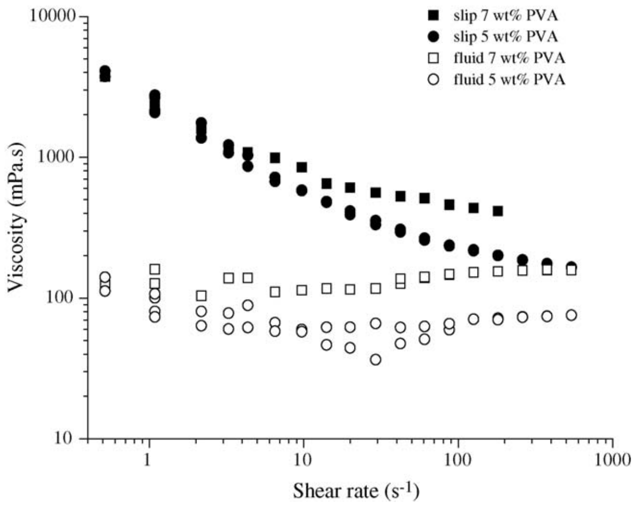

Fig. 1. Viscosity vs. shear rate curves for the fluid part of the slip and the slip of two slip compositions with a constant glycerine content of 5 wt.% and different PVA contents.

3. Results and discussion

3.1. Rheological properties

Fig. 1 shows the flow curves of viscosity versus the shear rate for the fluid part of the slip and the slip of the two slip compositions with a constant glycerine content of 5 wt.% and different PVA contents. Fig. 2 shows the flow curves of viscosity versus the shear rate for the fluid part of the slip and the slip of the two slip compositions with a constant PVA content of 5 wt.% and different glycerine contents. The fluids were nearly newtonian and the slips exhibited a pseudoplastic behavior. Thus, the slip viscosity decreased with the increase in the shear rate. A pseudoplastic behavior is desirable in the tape-casting process [2]. The slip viscosity decreases under the shear rate generated by the blade; immediately after the shear rate is released and during storage, the slip viscosity returns to a high level. This avoids any settling of the particles and preserves a homogeneous distribution of the slip components in the tape by reducing their mobility [2].

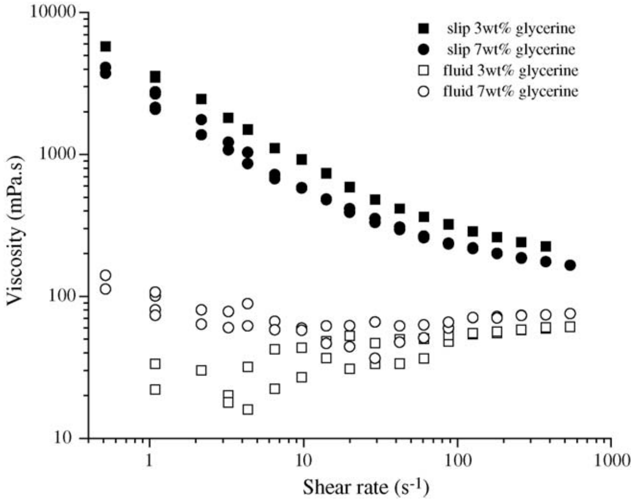

Fig. 2. Viscosity vs. shear rate curves for the fluid part of the slip and the slip of two slip compositions with a constant PVA content of 5 wt.% and different glycerine contents.

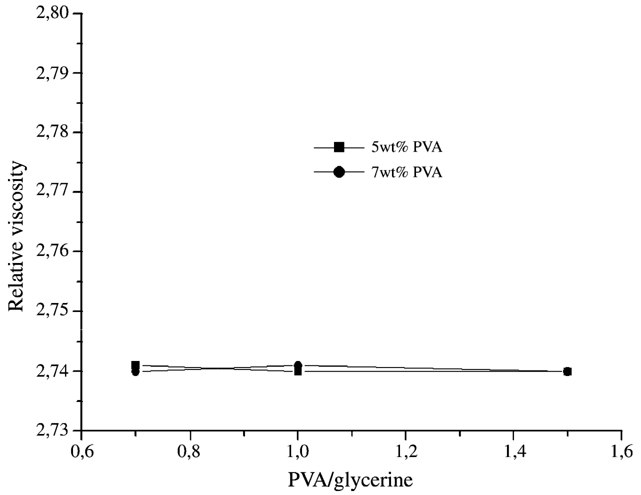

Fig. 3. Relative viscosity as a function of PVA/Glycerine for different PVA contents.

An increase in the PVA content resulted in a more viscous fluid phase, which increased the slip viscosity (Fig. 1). On the contrary, a greater amount of glycerine produced a slightly decrease in the viscosity of the fluid part and consequently in the slip viscosity (Fig. 2). Thus, the curves indicated that the differences in the slip viscosity were merely due to the differences in the viscosity of the fluid part. Thereby, nearly the same relative viscosities of the slips, which have a narrow range of solid/liquid ratios, were expected.

Fig. 3 shows the slip relative viscosity as a function of the PVA/Glycerine ratio for different PVA contents. Almost the same relative viscosities were found for different PVA contents and PVA/Glycerine ratios. This indicated that the slip dispersion was nearly the same irrespective of the PVA and glycerine contents. The PVA and glycerine did not affect the dispersion properties of the powder, which were basically controlled by the dispersant (NH_4PA) that was added first.

The ammonium polyacrylate dissociation according to the reaction

$$\mathrm{RCOONH_4 = RCOO^- + NH_4{}^+}$$

begins at pH > 3.5; at pH values ≥ 8.5 the polymer charge is negative with the degree of ionization (α) approaching 1[7]. The $RCOO^-$ groups of the deflocculant are adsorbed at the positive sites of the YSZ powder surface at alkaline pH increasing the negative surface charge of the powder and consequently the electrostatic repulsion between particles [8]. In addition, the steric interaction contributes to the stabilization, thus, the slip stabilization is electrosteric [7].

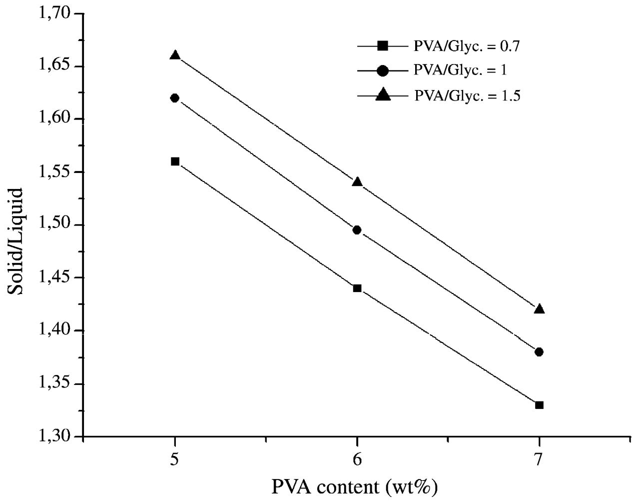

Fig. 4. Solid/liquid ratio of the slips as a function of the PVA content for different PVA/Glycerine ratios.

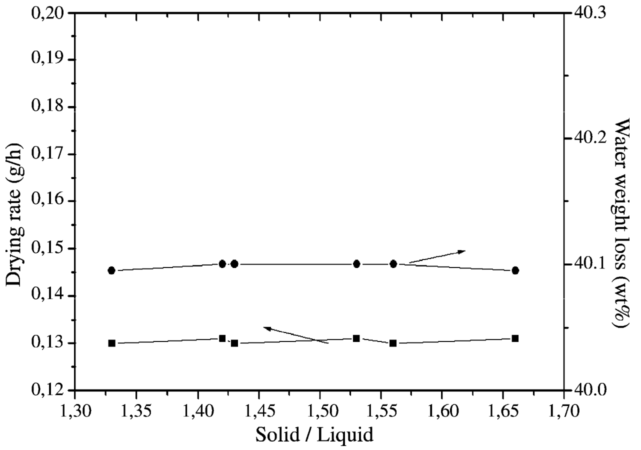

Fig. 6. Drying rate and water weight loss during the initial stage as a function of the solid/liquid ratio.

3.2. Drying kinetics

Fig. 4 shows the solid/liquid ratio of the slips as a function of the PVA content for different PVA/Glycerine ratios. For a constant PVA/Glycerine ratio, the solid/liquid ratio decreased with the increase in the PVA content. For each PVA content, the solid/liquid ratio increased with the increase in the PVA/Glycerine ratio and consequently with the decrease in the glycerine content.

Fig. 5 shows the sample weight as a function of drying time for tapes with different solid/liquid ratios. For all the compositions, the curves showed a linear initial stage followed by a falling rate stage. Therefore, the drying process of the tapes was divided into the constant rate and the falling rate periods.

During the initial stage the rate of drying remained remarkably constant; this process was similar to the evaporation of a liquid from a liquid surface in which the overall rate of the drying process is controlled by the interfacial evaporation at the surface [9]. Therefore, it might be concluded that the drying process of the tapes was controlled by the evaporation process from the interface phase until the drying curve deviated from the straight line. During the initial stage, the resistance for the transport of water to the surface of the sample was negligible compared with the resistance at the liquid/vapor interface.

Fig. 6 shows the drying rate and the water weight loss during the initial stage as a function of the solid/liquid ratio. The drying rate and the water weight loss were not dependent of the solid/liquid ratio since constant values of 0.13 g/h and 40.1 wt.% were found, respectively. Since the linear region was an interfacial evaporation-controlled process the system behaved as it was composed only on water and the solid/liquid ratio had no influence upon the drying process.

As the liquid content of the tapes decreased the rate of drying decreased (falling rate). In the falling rate period (second stage of drying), the dying kinetics is controlled by

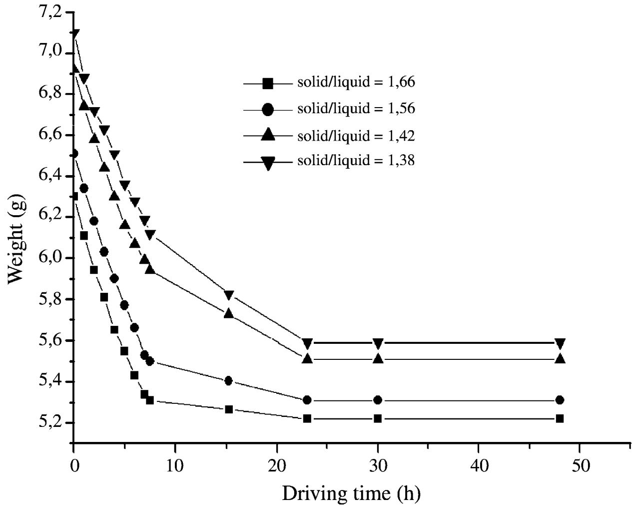

Fig. 5. Sample weight as a function of drying time for tapes with different solid/liquid ratios.

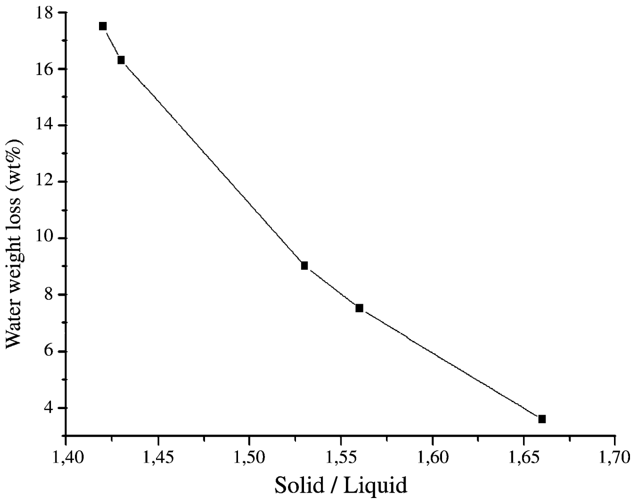

Fig. 7. Water weight loss during the second stage as a function of the solid/liquid ratio.

the transportation of water to the solid surface, thus it is a diffusion-controlled process [9]. Fig. 7 shows the water weight loss during the second stage as a function of the solid/liquid ratio. This curve is markedly different from that observed in the initial stage (Fig. 6). The water weight loss during the diffusion controlled process increased with the decrease in the solid/liquid ratio (Figs. 5 and 7). The water weight loss increased from 3.6 wt.% for 1.66 solid/liquid ratio to 17.5 wt.% for 1.42 solid/liquid ratio. Therefore, the larger portion of water in the suspension (40.1 wt.%) was lost during the first stage (Fig. 6). This indicated that the majority of the drying process of YSZ tapes was controlled by the interfacial evaporation.

The water flow process through a porous matrix (second stage of drying) can be described by the Darcy' s law equation. This law states that the flow is proportional to the pressure gradient in the liquid and to the permeability of the porous matrix and inversely proportional to the viscosity. The permeability is proportional to $\varepsilon^3/(1-\varepsilon)^2$, where ε is the porosity. Thus, the water flow would be strongly affected by the porosity of the tape.

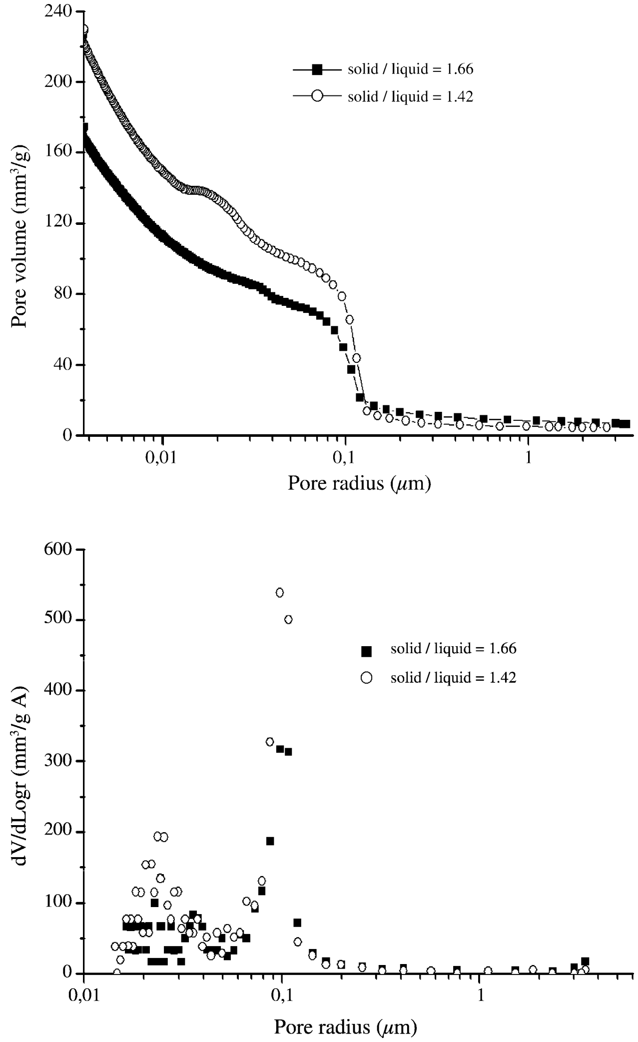

Fig. 8. (a) Cumulative micropore volume by mass unit vs. pore radius curves of tapes with two different solid/liquid ratios. (b) Micropore size distribution curves of tapes with two different solid/liquid ratios.

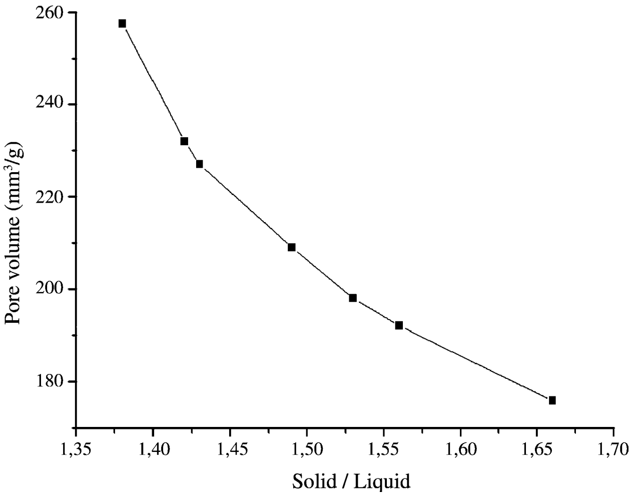

Fig. 9. Total pore volume of the tapes vs. the slip solid/liquid ratio.

Fig. 8a shows the cumulative micropore volume by mass unit versus pore radius curves of tapes with two different solid/liquid ratios. Fig. 8b is a representation of the micropore size distribution as d*V*/d log *r* (differential pore volume) versus pore radius. Both samples had a similar micropore size distribution with pore radius between 0.004 and 0.8 μm (Fig. 8a). The most frequent pore radius of both samples was about 0.09 μm; a less frequent pore radius of 0.025 and 0.035 μm was found for the samples with 1.42 and 1.66 solid/liquid ratios, respectively. However, the total micropore volume of the tapes was different. Fig. 9 shows the total pore volume of the tapes versus the slip solid/liquid ratio. The reduction in the solid/liquid ratio produced an increase in the total micropore volume (Figs. 8a and 9).

Fig. 10 is a representation of the water weight loss during the second stage versus the total micropore volume. A linear correlation between the water weight loss and the pore

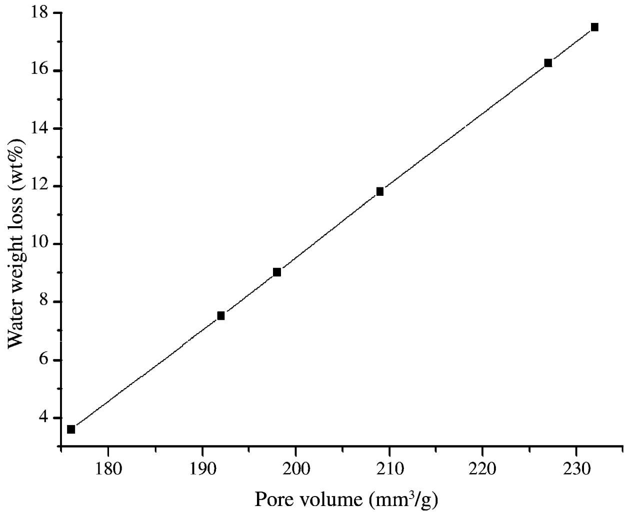

Fig. 10. Water weight loss during the second stage vs. the total pore volume.

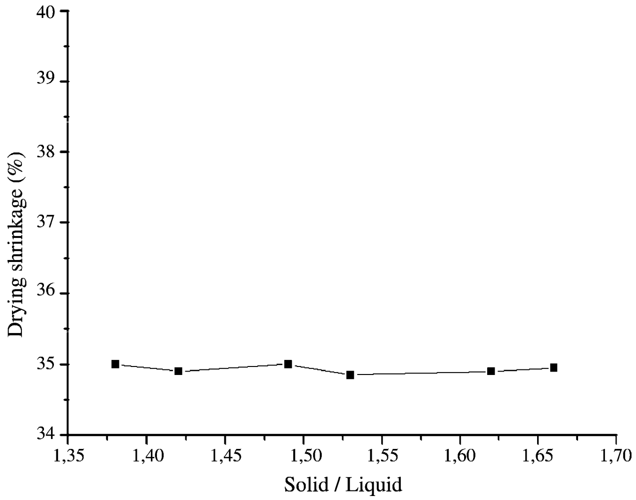

Fig. 11. Drying shrinkage of the tapes in the thickness direction vs. the slip solid/liquid ratio.

volume was found; the water diffusion was enhanced by increasing the porosity of the matrix. Thus, as the solid/liquid ratio decreased the pore volume of the tapes increased thereby increasing the water flow during the second stage of the drying process (Figs. 9 and 10). Consequently, the slips with lower solid/liquid ratio lost greater amount of water and resulted in tapes with higher drying rate. For a constant PVA content, the increase in the amount of glycerine added reduced the solid/liquid ratio (Fig. 4) and consequently increased the drying rate; while for all the PVA/glycerine ratios the increase in the PVA content (Fig. 4) increased the drying rate.

3.3. Characterization of green tapes

Fig. 11 shows the drying shrinkage of the tapes in the thickness direction versus the slip solid/liquid ratio. Almost the same drying shrinkage was found for all the solid/liquid ratios. During the first stage, the solvent starts to evaporate from the tape surface, allowing particles to approach each others [10]. As a consequence, the curvature of the liquid/vapor interface in the pore channels between particles progressively increases. For a liquid that completely wets the solid surface, the difference in pressure across these curved surfaces, ΔP, is given by [11]:

$$\Delta P = \frac{-2\gamma_{\mathrm{LV}}}{r} \tag{4}$$

where γ_{LV} is the liquid/vapor interfacial energy (or surface tension) and r is the radius of curvature of the menisci. When the center of curvature is in the vapor phase, the radius of curvature is negative and the liquid is in tension ($\Delta P > 0$). This tension of the liquid corresponds to a compressive force between ceramic particles, which is responsible for the shrinkage of the green tape [10].

At the beginning of the drying (first stage), the viscosity of the fluid phase is low enough to allow ceramic particle rearrangement. As the evaporation proceeds, the liquid in the tape becomes enriched in organic additives (binder and plasticizer); this involves an increase of the viscosity [10]. The high viscosity reached by the fluid phase in the second drying step hinders particle rearrangement; therefore during the second stage the drying shrinkage in the thickness direction stops. Thus, the thickness shrinkage of the tapes was expected to be proportional to the water weight loss during the initial stage. The constant value of the drying shrinkage found for the different solid/liquid ratios was in accordance with the constant water weight loss during the first stage of the drying process (Figs. 6 and 11).

Figs. 12 and 13 show the tensile strength and the strain to failure of green tapes, respectively, as a function of the PVA content for different PVA/Glycerine ratios. A linear correlation between the tensile strength and the PVA content was found (Fig. 12). The tensile strength increased with the increase in the PVA content from 5 to 7 wt.% for all the PVA/

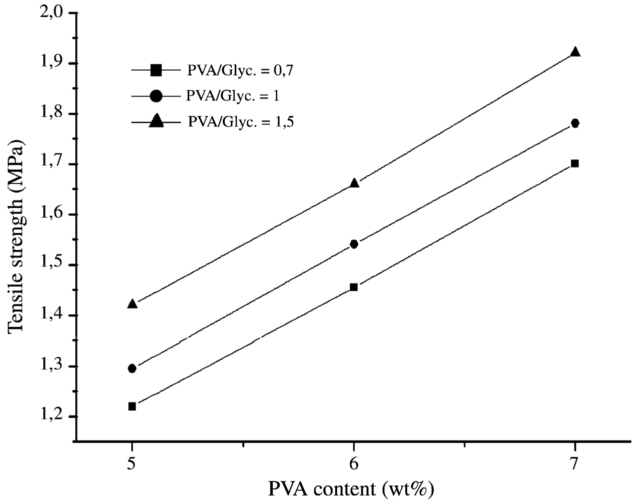

Fig. 12. Tensile strength of green tapes as a function of the PVA content for different PVA/Glycerine ratios.

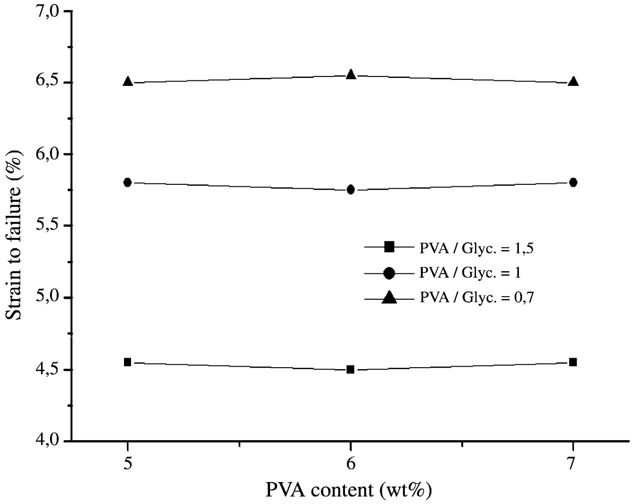

Fig. 13. Strain to failure of green tapes as a function of the PVA content for different PVA/Glycerine ratios.

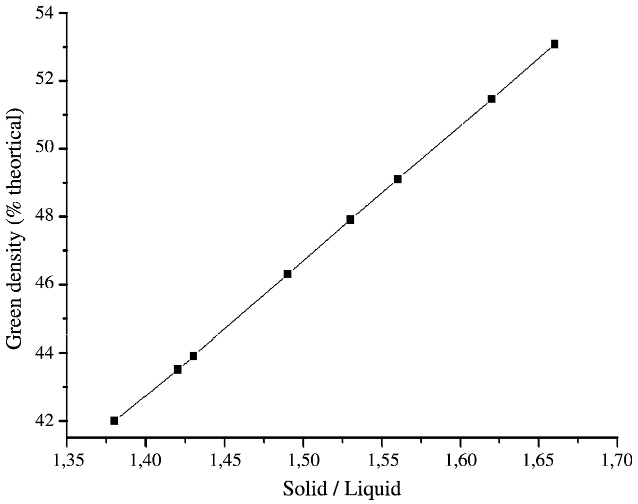

Fig. 14. Green density of the tapes vs. the solid/liquid ratio of the slips.

Glycerine ratios. The strength of ceramic green bodies is correlated to cohesive strength and consequently to quantities of binder [5]. However, the tapes with 7 wt.% PVA tended to curl after drying, whereas the tapes with 5 and 6 wt.% PVA remained flat. This suggested that in tapes with 7 wt.% PVA a larger amount of hydrogen bonds between PVA chains might generate higher stress in green tapes and lead to their deformation after drying. 5 wt.% PVA provided sufficient strength to the green tape for easy handling and storage.

For each PVA content, the tensile strength decreased with the decrease in the PVA/Glycerine ratio and consequently with the increase in the glycerine content. This was attributed to the reduced amount of active binder in the green tapes since the binder was effectively plasticized. The more effectively the PVA is plasticized, the lower is the strength of green tapes [5].

The strain to failure was not dependent on the PVA content; the increase in the strain to failure with the decrease in the PVA/Glycerine ratio for all the PVA contents indicated that the flexibility of green tapes was enhanced by the glycerine additions (Fig. 13). The greater flexibility of the tapes was obtained with the 0.7 PVA/Glycerine ratio. Therefore, glycerine additions improved the flexibility but also produced a decrease in the tape strength.

Fig. 14 shows the green density of the tapes versus the solid/liquid ratio of the slips. A linear correlation between the green density and the solid/liquid ratio was found. The solid/liquid ratio must be as high as possible in order to achieve the higher green density values. The slip compositions with 5 wt.% PVA which had a high solid/liquid ratio (Fig. 4) resulted in the highest green density values. On the contrary, for the slip compositions with 7 wt.% PVA which had lower solid/liquid ratio, the lowest green density values were found (Figs. 4 and 14).

The slip composition 5 wt.% PVA–3.3 wt.% glycerine (PVA/Glycerine = 1.5) and 7 wt.% PVA–4.7 wt.% glycerine (PVA/Glycerine = 1.5) which had a solid/liquid ratio of 1.66 and 1.42, respectively (Table 1), resulted in green density values of 53.1 and 43.5% of theoretical density, respectively (Fig. 14). Therefore, the increase in the PVA content from 5 to 7 wt.% produced a marked decrease in the solid/liquid ratio and consequently in the green density of the tapes (Figs. 4 and 14). It has also been shown that for a constant PVA content the increase in the amount of glycerine added resulted in a slight decrease in the solid/liquid ratio and thereby in the tape green density.

Although the tape strength was improved with 7 wt.% PVA, the low density and the deformation of green tapes after drying might limit application of this content of binder on tape casting. The results showed that the slip compositions with 5 wt.% PVA produced green tapes with satisfactory tensile strength for handling and storage which had the highest green density. Since a greater amount of glycerine resulted in tapes with higher drying rate and enhanced the flexibility of green tapes, the slip composition 5 wt.% PVA-7.1 wt.% glycerine was adequate for the production of YSZ tapes by the doctor blade method.

4. Conclusions

Various compositions of YSZ slips with different amounts of PVA and glycerine and consequently different solid/liquid ratios were prepared. For a constant PVA/Glycerine ratio, the solid/liquid ratio decreased with the increase in the PVA content; and for each PVA content, the solid/liquid ratio decreased with the increase in the amount of glycerine.

PVA and glycerine did not affect the dispersion properties of the YSZ powder, which were governed by the adsorbed NH_4PA providing an electrosteric stabilization.

The drying of YSZ tapes involved a two-stage process: the initial stage was a constant rate period and the second one was a falling rate period.

Constant values of the drying rate and water weight loss were found during the first stage for the different slip solid/liquid ratios. Thus, the solid/liquid ratio of the slips had no influence on the first stage of the drying process since it was controlled by the interfacial evaporation at the surface. However, the second stage of drying (diffusion-controlled process) was linked mainly to the pore volume of the matrix, which depended on the slip solid/liquid ratio. As the solid/liquid ratio decreased the pore volume of the tapes increased thereby increasing the water flow during the second stage. For a constant PVA content, the slips with higher glycerine content and lower solid/liquid ratio, lost greater amount of water in the drying process and resulted in tapes with higher drying rate.

Since the drying shrinkage of the tapes in the thickness direction was proportional to the water weight loss during the initial stage, nearly the same thickness shrinkage was observed irrespective of the slip solid/liquid ratio.

The tensile strength the increase in the PVA content from 5 to 7 wt.%. However, 5 wt.% PVA conferred satisfactory strength to the green tape for easy handling and storage.

For a given PVA content, glycerine additions enhanced the flexibility of the green tapes but also produced a decrease in the tape strength.

The increase in the PVA content from 5 to 7 wt.% produced a decrease in the green density of the tapes as a consequence of the decrease in the solid/liquid ratio of the slips. For a constant PVA content, the increase in the amount of glycerine added resulted in a lesser decrease in the solid/liquid ratio and thereby in the tape green density.

The slip compositions with 5 wt.% PVA produced green tapes with satisfactory tensile strength which had the highest green density. Since a greater amount of glycerine resulted in tapes with higher drying rate and enhanced the flexibility of the green tapes, the slip composition 5 wt.% PVA–7.1 wt.% glycerine was adequate for the production of YSZ tapes by the doctor blade method.

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