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Influence of the slip composition on the properties of tape-cast alumina substrates

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Abstract

Tape-casting process was used to produce alumina (Al_2O_3) substrates in an aqueous system with poly(vinylalcohol) (PVA) and glycerine as binder and plasticizer, respectively. Various compositions of Al_2O_3 slips were prepared by dispersing the powder in water with ammonium polyacrylate (NH_4PA), with subsequently additions of different amounts of PVA and glycerine. The influence of the slip composition on the rheological properties of the slips and the properties of the resultant green tapes were studied. In addition, the properties of the sintered tapes were investigated and related to those of the green tapes. PVA and glycerine did not affect the dispersion properties of the Al_2O_3 powder which were governed by the adsorbed NH_4PA. Glycerine additions enhanced the flexibility of the green tapes but also produced a decrease in the tensile strength and in the drying shrinkage. The increase in the PVA content increased the tensile strength but resulted in a markedly decrease in the green density of the tapes. The slip composition 5 wt.% PVA–5 wt.% glycerine produced green tapes with sufficient tensile strength and flexibility which had higher green and sintered density and lower sintering shrinkage. Thus, this composition was adequate for the production of Al_2O_3 substrates by the tape-casting process.

Keywords: A. Tape-casting; D. Al_2O_3; Green and sintered properties

1. Introduction

Tape-casting or doctor-blade process has proved to be especially useful to produce thin and flat Al_2O_3 sheets mainly for the electronic industry [1–3]. As a ceramic forming method it is generally advantageous for preparing relatively large area, thin sheets with uniform and high unfired densities [2].

Tape-casting, basically, consists of preparing a suspension composed of the ceramic powder dispersed in a solvent, with addition of dispersants, binders and plasticizers [4]. This suspension is cast onto a stationary or moving surface. The solvents are evaporated leaving the dried green tape with a typical thickness in the range of 30–1000 μm which is stripped from the surface and cut to the appropriate shape. After removal all organic components, green sheets are sintered [4].

Tape-casting systems may be classified according to the type of solvent used. Organic solvents are generally used for tape-casting [5,6]; they have low boiling points and prevent the ceramic powder from hydration, but require special precautions concerning toxicity and flammability.

The slow evaporation and agglomeration due to hydrogen bonding make water-based systems less attractive. Nevertheless, water-based systems would be preferred in terms of toxicity, environmental consistency and price; the use of water-based systems represents an interesting alternative to the widespread non-aqueous tape-casting.

Compared with non-aqueous solvents, the variety of water soluble binders and plasticizers systems is restricted [7]. In this work, PVA and glycerine were used as binder and plasticizer, respectively, in an aqueous tape-casting process for Al_2O_3 substrates.

Although a number of producers of electronic ceramics located throughout the world employed the doctor-blade method, there are relatively few papers that provide many of the details about the process. The present doctor-blade technology on casting formulations is based predominantly on the state of the art with little understanding of the fundamental behavior of the constituents in a specific formulation beyond certain general objectives. In this work, the influence

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of the slip composition on the rheological properties of the slips and the properties of the resultant green tapes were studied. In addition, the properties of the sintered tapes were investigated and related to those of the green tapes.

2. Experimental procedure

2.1. Materials

A commercial Al_2O_3 powder (Alcoa A-16 SG, Pittsburgh, USA) was used in this study. The mean particle diameter and the specific surface area were 0.5 μm and 8.1 m^2/g, respectively.

The dispersant was 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. Zeta potential determinations

Zeta potential values against pH of 1 vol.% Al_2O_3 slips with 0 and 0.3 wt.% NH_4PA were determined in the pH range 4–10 with ESA measurements using an electroacoustic equipment (Model ESA-8000, Matec Applied Science, Hopkinton, MA).

2.3. Slip preparation

Al_2O_3 slips were prepared by deagglomeration of 35 g Al_2O_3 in 15 ml de-ionized water with 0.3 wt.% NH_4PA (dry weight basis of powder), by ultrasonic treatment, with subsequently additions of different PVA and glycerine contents. The pH of the suspensions was 9.5.

The solid content of the slips, expressed as wt.%, 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.

Table 1
Compositions of Al_2O_3 slips with different amounts of PVA and glycerine

PVA content[a] (wt.%)	Glycerine content[a] (wt.%)	PVA/Glycerine	Solid content (wt.%)
5	3.3	1.5	56.2
	4	1.25	56.0
	5	1	55.7
6	4	1.5	54.1
	4.8	1	53.5
	6	1	53.5
7	4.7	1.5	52.1
	5.6	1.25	51.9
	7	1	51.5

[a] The PVA and glycerine contents were expressed as the dry weight base with respect to Al_2O_3.

2.4. De-airing

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

2.5. Rheological measurements

Steady state flow curves of the fluid part of Al_2O_3 slips (the slip containing all the components without the powder) and Al_2O_3 slips were performed by measuring the steady shear stress value as a function of shear rate in the range of 0.3–100 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) is 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 100 s^{-1}.

2.6. 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 0.5 mm. The cast tapes were dried in air at room temperature during 2 days; afterwards, they were stripped from the film.

2.7. Characterization of green tapes

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

In order to determine the amount of water adsorbed, the green tapes, PVA and glycerine adsorbed on alumina, were analyzed by thermal gravimetric analysis (TGA) (Model STA 409, Netzsch Inc., Germany) at a heating rate of 10 °C/min in an air atmosphere. The amount of water adsorbed on the tapes was calculated as the difference between the weight loss of the tape and that of the PVA and glycerine in a temperature range of 20–120 °C.

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. The pore size distribution of green tapes was performed using mercury porosimetry (Porosimeter 2000 Carlo Erba, Italy). The microstructures were observed by scanning electron microscopy (SEM).

2.8. Sintering

For the sintering tests, the tapes prepared from the slip compositions with PVA/Glycerine ratios of 1 and 1.5 were used. The tapes were loaded, during the firing, inside an inverted alumina crucible to prevent warping. The elimination of the solvent and the burning out of polymer additions were obtained by slow heating (1 °C/min) up to 600 °C, with a plateau at 120, 280 and 600 °C. Then a heating rate of 5 °C/min was applied to achieve the final sintering temperature of 1550 °C and the tapes were sintered for 3 h.

2.9. Characterization of sintered tapes

The linear shrinkage during firing was geometrically measured. The bulk density of the sintered tapes was determined by water immersion (Standard Method ASTM C20). The microstructures were observed by SEM on polished sections after etching in hydrofluoric acid (10%) at room temperature for about 15 min.

3. Results and discussion

3.1. Rheological properties

Fig. 1 shows the flow curves of viscosity versus shear rate 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. Fig. 2 shows the flow curves of viscosity versus shear rate for the fluid part of the slip and the slip of two slip compositions with a constant PVA content of 7 wt.% and different glycerine contents. The fluids were nearly Newtonian and the slips exhibited a pseudoplastic behavior. Thus, the slip viscosity decreased with increasing the shear rate. A pseudoplastic behavior is desirable in the tape-casting process [6]. 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 an homogeneous distribution of the slip components in the tape by reducing their mobility [6].

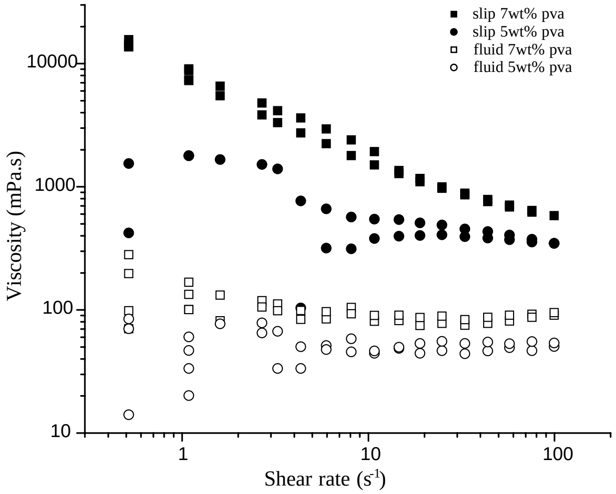


Fig. 1. Viscosity vs. shear rate curves for the fluid part of the slip and the slip of two slip compositions with a constant glycerine content of 5 wt.% and different PVA contents.

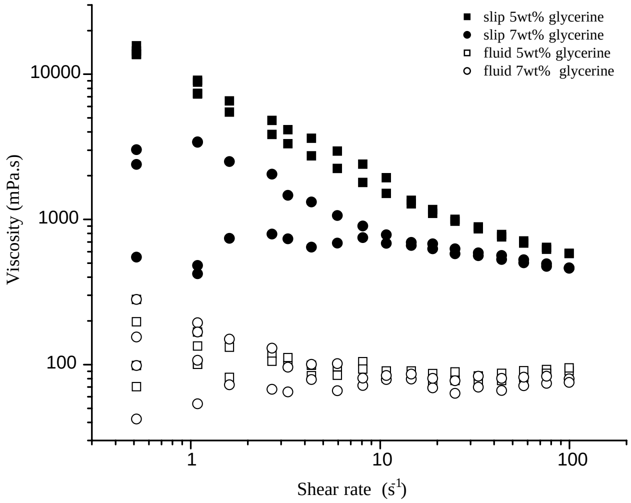


Fig. 2. Viscosity vs. shear rate curves for the fluid part of the slip and the slip of two slip compositions with a constant PVA content of 7 wt.% and different glycerine contents.

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 loading, 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) added first.

Fig. 4 shows the zeta potential as a function of pH of Al_2O_3 slips without NH_4PA and with 0.3 wt.% NH_4PA. The isoelectric point (IEP) of the Al_2O_3 powder was found to be 8.5. This pH_{IEP} was in agreement with that reported in the literature [8]. The addition of NH_4PA resulted in an increase in the negative surface charge of the powder at alkaline pH, shifting the pH_{IEP} of the Al_2O_3 powder from 8.5 to 7.

The ammonium polyacrylate dissociation according to the reaction:

$$RCOONH_4 = RCOO^- + NH_4^+$$

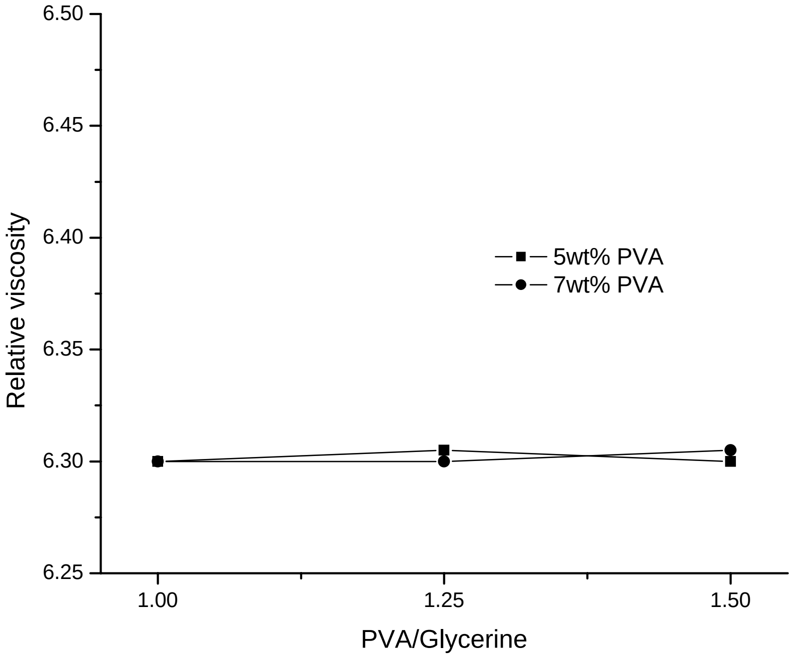


Fig. 3. Relative viscosity as a function of PVA/Glycerine for different PVA contents.

begins at pH >3.5; at pH values ≥8.5 the polymer charge is negative with the degree of ionization (α) approaching 1 [9]. The RCOO$^-$ groups of the deflocculant are adsorbed at the positive sites of the Al_2O_3 powder surface at alkaline pH [9]. Another additional effect than electrostatic consideration, e.g. an acid–base reaction between hydroxyl groups on alumina and –COOH groups on the NH_4PA chains [10], enhanced the adsorption on the Al_2O_3 powder surface. Thus, the NH_4PA adsorbed increased the negative surface charge of the powder at alkaline pH and consequently the electrostatic repulsion between particles. In addition, the steric interaction contributes to the stabilization, thus, the slip stabilization is electrosteric [9].

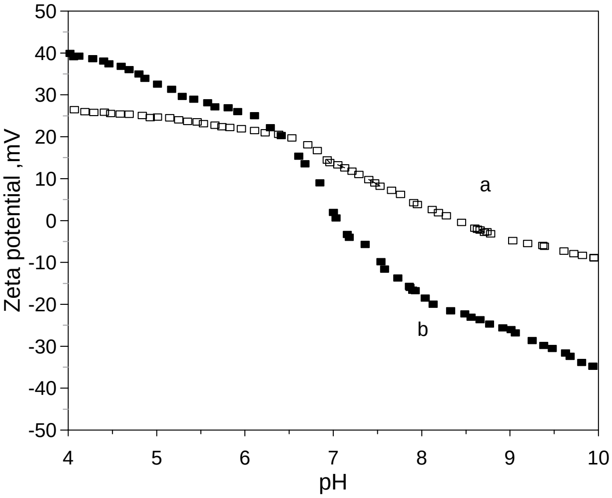


Fig. 4. Zeta potential vs. pH of Al_2O_3 slips with different amounts of NH_4PA added: (a) 0 wt.%, (b) 0.3 wt.%.

3.2. Characterization of green tapes

Figs. 5 and 6 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. The tensile strength increased with increasing the PVA content from 5 to 7 wt.%; a significant increase in the tensile strength up to 6 wt.% was found followed by a lesser increase with further increasing of the PVA content. However, 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. 5 wt.% PVA provided sufficient strength to the green tape for easy handling and storage.

The strain to failure was not dependent of 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. 6). The greater flexibility of the tapes was obtained with the 1PVA/Glycerine ratio. Therefore, glycerine additions improved the flexibility but also produced a significant decrease in the tape strength.

Fig. 7 shows the amount of water adsorbed on the dried tape as a function of the glycerine content. Fig. 8 shows the drying shrinkage in the thickness direction versus the PVA content for different PVA/Glycerine ratios. A linear correlation between the amount of water adsorbed and the glycerine content was found (Fig. 7). As the glycerine content increased higher amounts of water were present in the dried tapes. This was attributed to the hydration of the glycerine.

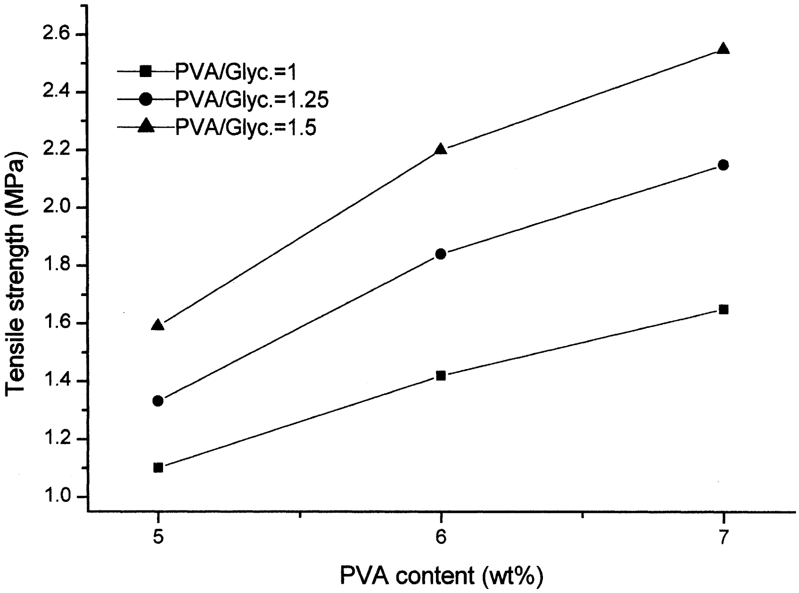


Fig. 5. Tensile strength of green tapes as a function of the PVA content for different PVA/Glycerine ratios.

The drying shrinkage increased from 50 to 57% of the blade opening when the PVA/Glycerine ratio increased from 1 to 1.5 for all the PVA contents (Fig. 8). Thus, a lower drying shrinkage was found for the compositions with higher glycerine content (PVA/Glycerine = 1) as a consequence of the hydration of glycerine. Therefore, for a given PVA content, glycerine additions enhanced the flexibility of the tapes but also produced a decrease in the drying shrinkage and in the tape strength.

Fig. 9 shows the green density of the tapes versus the solid content. A linear correlation between the green density and the solid content was found. The solid content must be as high as possible in order to achieve the higher green density. The slip compositions 5 wt.% PVA–5 wt.% glycerine and 5 wt.% PVA–3.3 wt.% glycerine which had a solid content of 55.7 and 56.2 wt.% (Table 1), respectively, resulted in the highest green density values, 60.7 and 61.7% of theoretical density, respectively. On the contrary, for the slip compositions 7 wt.% PVA–7 wt.% glycerine and 7 wt.% PVA–4.7 wt.% glycerine which had a solid content of 51.5 and 52.1 (Table 1), respectively, green density values of 52.1 and 53.2% of theoretical density, respectively, were found. Thus, the increase in the PVA content from 5 to 7 wt.% produced a markedly decrease in the solid content

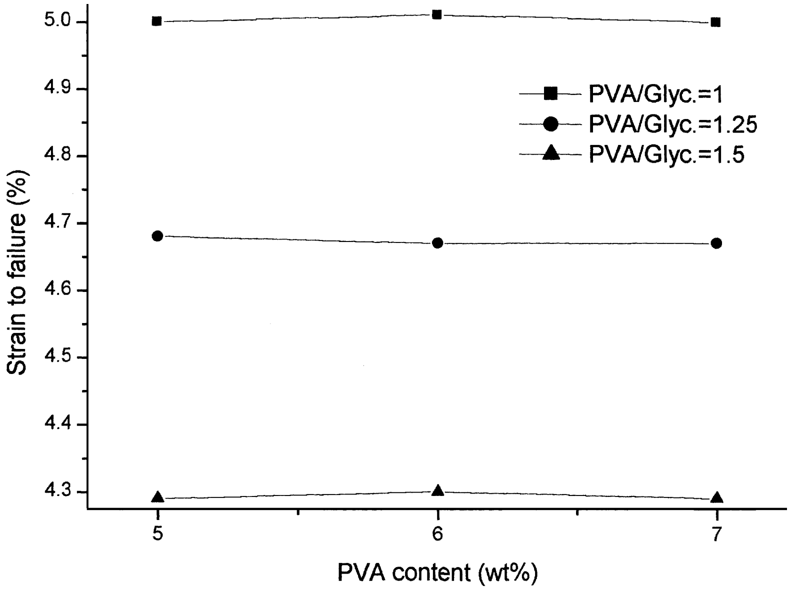


Fig. 6. Strain to failure of green tapes as a function of the PVA content for different PVA/Glycerine ratios.

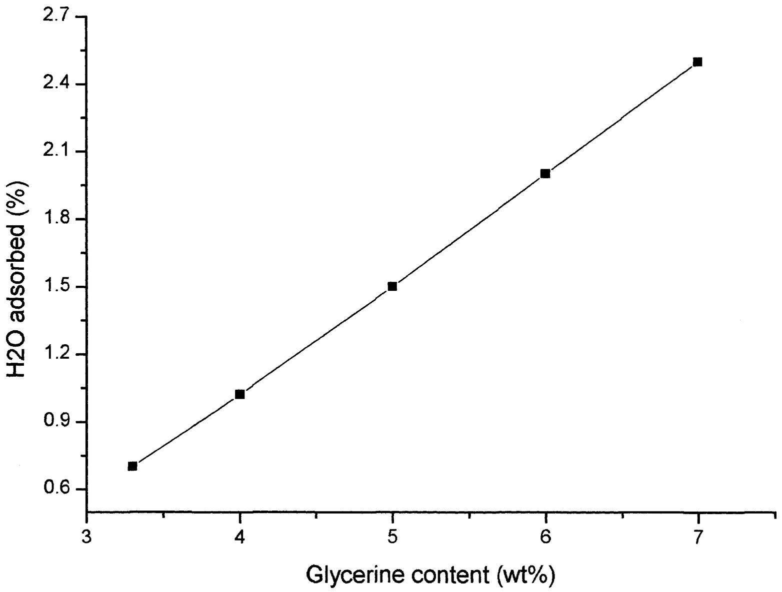


Fig. 7. Amount of water adsorbed on the dried tape as a function of the glycerine content.

and consequently in the green density of the tapes. It has also shown (Table 1, Fig. 9) that for a constant PVA content the increase in the amount of glycerine added resulted in a slightly decrease in the solid content and thereby in the tape green density. Therefore, green tapes with sufficient strength and high green density could be obtained from the slip compositions with 5 wt.% PVA.

Fig. 10a shows the cumulative micropore volume by mass unit versus pore radius curves of green tapes with two different green density values. Fig. 10b is a representation of the micropore size distribution as d*V*/dlog *r* (differential pore volume) versus pore radius. Tapes with green density values of 52.1 and 60.7% of theoretical density were obtained from slip compositions having a solid content of 51.5 and 55.7 wt.%, respectively (Fig. 9). As the green density increased from 52.1 to 60.7% of theoretical density the total micropore volume of the tapes decreased (Fig. 10a). This reduction of the total micropore volume produced the increase in the green density of cast samples. Both samples had a similar narrow micropore size distribution with pore radius between 0.037 and 3 μm and the most frequent pore radius was 0.057 μm (Fig. 10b).

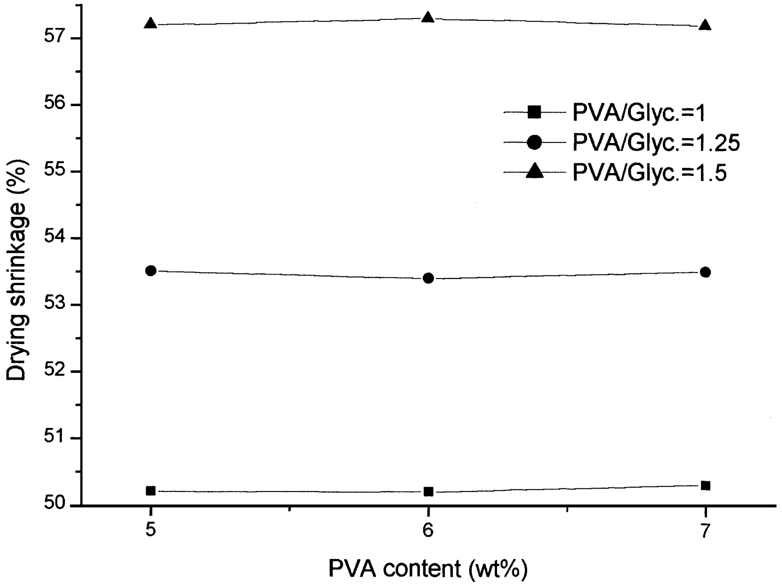


Fig. 8. Drying shrinkage vs. the PVA content for different PVA/Glycerine ratios.

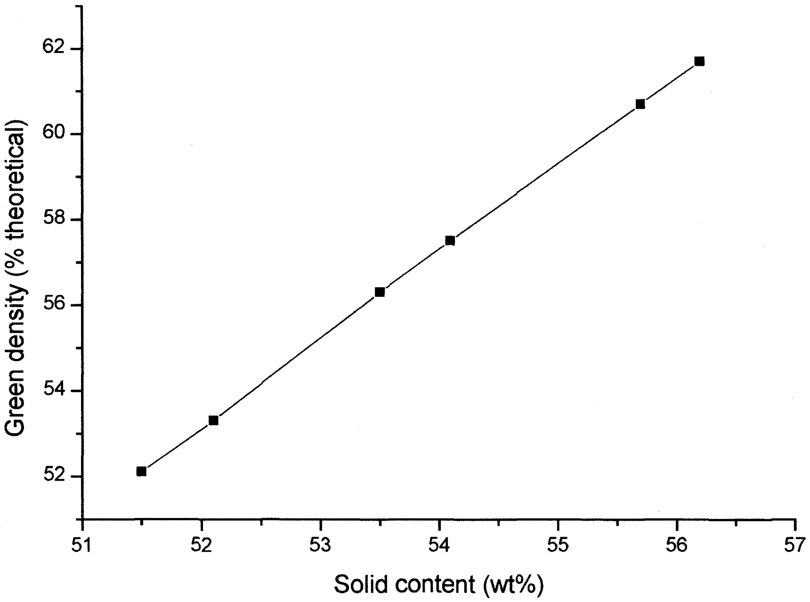


Fig. 9. Green density of the tapes vs. the solid content.

3.3. Characterization of sintered tapes

Fig. 11 shows the linear sintering shrinkage as a function of the green density of cast tapes. The increase in the green density of the tapes reduced the sintering shrinkage. The decrease in the sintering shrinkage reduces warping and enhances dimensional control [2]. The high solid content in the slip results in cast tapes with high green density for materials that are properly processed by the doctor-blade method. Consequently, the method has the distinct advantage of providing close control of dimensional tolerances during firing of large, thin sheets compared to similar parts prepared by other forming processes [2].

The tapes with green density values of 52.1 and 53.2% of theoretical density, obtained from the slip compositions with 7 wt.% PVA, showed a linear sintering shrinkage of 17.3 and 16.9%, respectively. While for the tapes with green density values of 60.7 and 61.7% of theoretical density, prepared from the slip compositions with 5 wt.% PVA, a linear sintering shrinkage of 14.5 and 14.2%, respectively, was

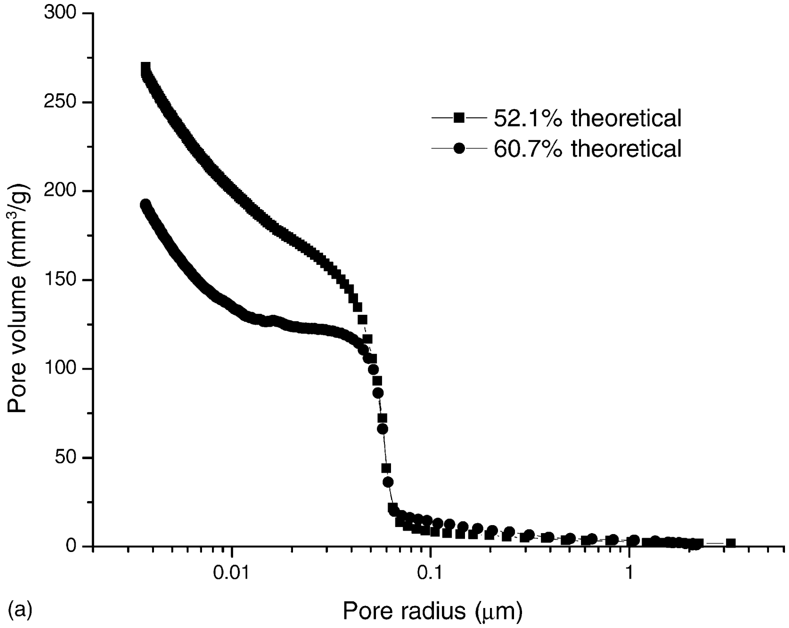


Fig. 10. (a) Cumulative micropore volume by mass unit vs. pore radius curves of green tapes with two different green density values. (b) Micropore size distribution curves of green tapes with two different green density values.

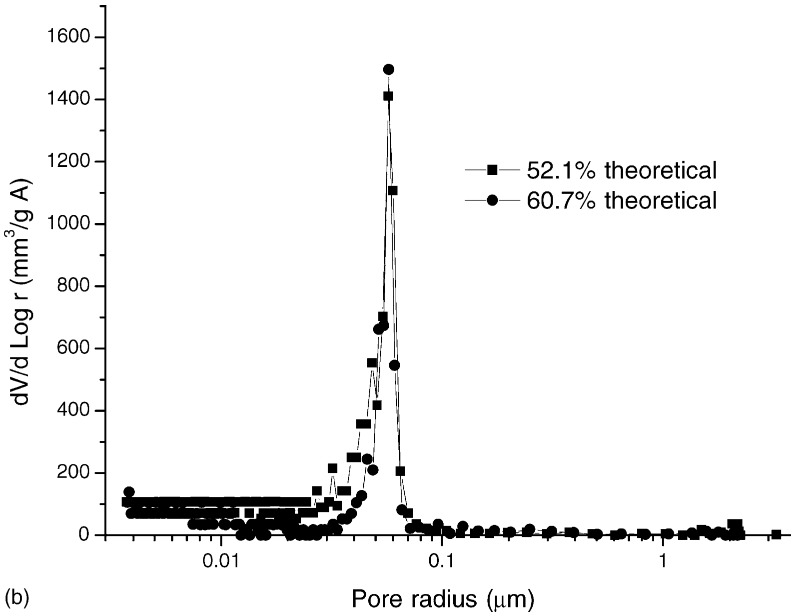


Fig. 10. (*Continued*).

found. Thus, a higher green density decreased the sintering shrinkage providing close dimensional control.

Fig. 12 shows the sintered density versus the green density of cast tapes. An important increase in the sintered density up to a green density value of 56.3% was found followed by a lesser increase with further increasing of green density. This behavior could be explained since in the tapes with higher green density values (>56.3%) less pore-solid interface reduced the excess surface area and decreased the densification rate by lowering the driving force for sintering.

The better sintering results were obtained with the cast tapes prepared from the slip compositions with 5 wt.% PVA which had higher green density values. For the tapes obtained from the slip composition with 5 wt.% PVA and PVA/Glycerine ratios of 1 and 1.5, sintered density values of 97.8 and 98.8% of theoretical density, respectively, were found. The lowest sintered density values, 87 and 88.6% of theoretical density, were obtained for the tapes prepared from the slip compositions with 7 wt.% PVA and PVA/Glycerine ratios of 1 and 1.5, respectively. Thus, tapes with higher green density values resulted in higher sintered density and lower sintering shrinkage.

The results showed that the compositions with 5 wt.% PVA produced green tapes with sufficient tensile strength

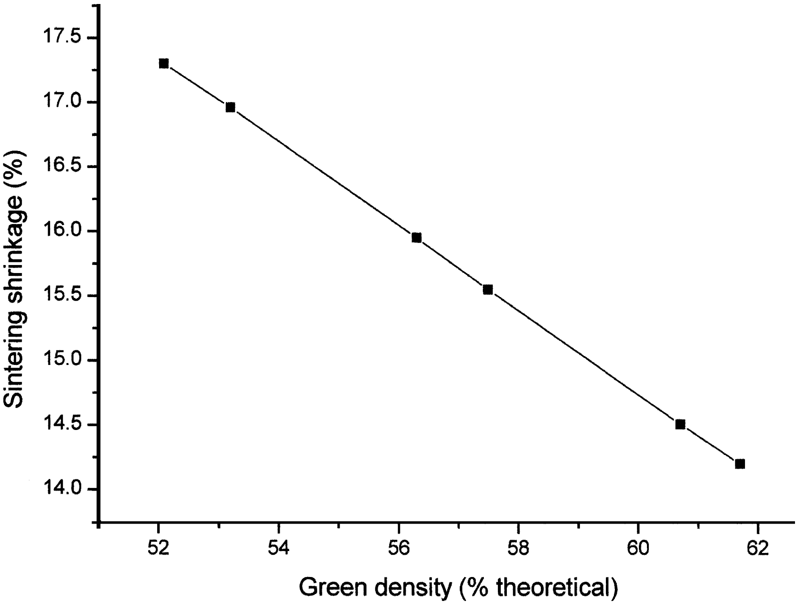


Fig. 11. Linear sintering shrinkage as a function of the green density of cast tapes.

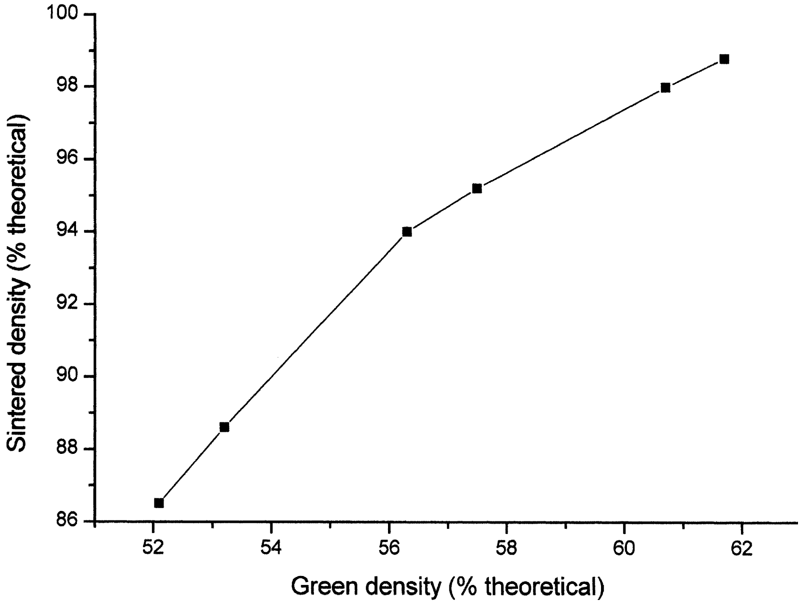


Fig. 12. Sintered density vs. the green density of cast tapes.

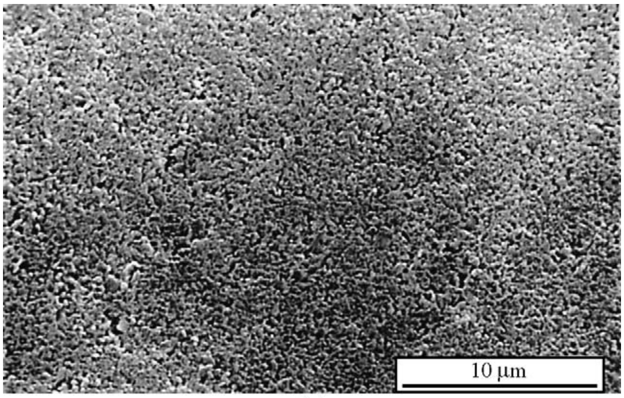
for handling and storage. They had the highest green and sintered density and the lower sintering shrinkage. This provided close control of dimensional tolerances during firing. The cast tapes prepared from the slip composition 5 wt.% PVA–5 wt.% glycerine had a greater flexibility. Therefore, this composition was adequate for the production of Al_2O_3 tapes by the doctor-blade method in the PVA–glycerine system.

Slips with higher PVA contents (>5 wt.%) increased the tape tensile strength but produced a markedly decrease in the green and sintered density; the higher sintering shrinkage did not permit a close dimensional control.

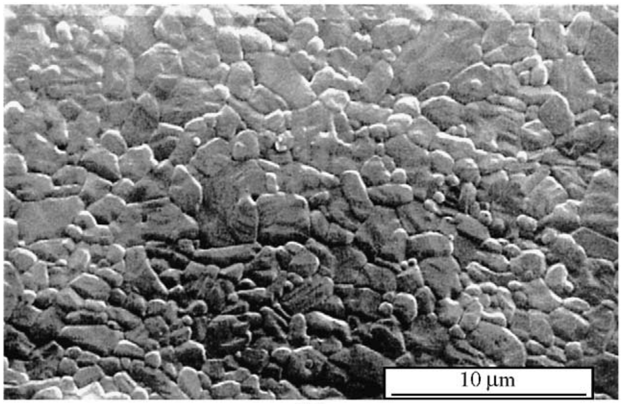
Fig. 13a shows a micrograph of the green tape obtained from the slip composition 5 wt.% PVA–5 wt.% glycerine (green density = 60.7% of theoretical density); Fig. 13b shows a micrograph of the tape after sintering at 1550 °C (sintered density = 97.8% of theoretical density). A fine microstructure with extremely small pores distributed homogeneously was found in the green body (Fig. 13a). Under this condition this body might sinter to full density. The presence of very small pores was in accordance with the porosimetry results (Fig. 10a and b). It can be seen that a high and uniformly green density was achieved by the tape-casting process.

Densification and grain growth could be observed in the sintered tape (Fig. 13b). The little porosity existed as closed pores located on the grain boundaries. It has been generally accepted that two atomic transport processes may operate simultaneously during sintering of crystalline solids [11]. These are:

(a) surface-to-surface transport which brings about growth of some crystallites at the expense of others; manifested by the coarsening of the microstructure.



(a)



(b)

Fig. 13. SEM micrographs of tapes obtained from the slip composition 5 wt.% PVA–5 wt.% glycerine: (a) green tape (green density = 60.7% of theoretical density), (b) sintered tape (sintered density = 97.8% of theoretical density).

(b) grain boundary-to-surface transport which results in densification and is manifested by simultaneous surface area and pore volume reduction.

Thus, a markedly decrease in the porosity with some grain growth accompanying the densification were found in the sintered tape.

4. Conclusions

PVA and glycerine did not affect the dispersion properties of the Al_2O_3 powder which were governed by the adsorbed NH_4PA providing an electrosteric stabilization.

The tensile strength increased with increasing the PVA content from 5 to 7 wt.%. However, 5 wt.% PVA conferred sufficient 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 and in the drying shrinkage.

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 content of the slips. For a constant PVA content, the increase in the amount of glycerine added resulted in a slightly decrease in the solid content and thereby in the tape green density.

The slip composition with 5 wt.% PVA produced green tapes with sufficient tensile strength which had the highest green and sintered density and the lower sintering shrinkage. Since a greater amount of glycerine enhanced the flexibility, the slip composition 5 wt.% PVA–5 wt.% glycerine was adequate for the production of Al_2O_3 tapes by the doctor-blade method. From this slip composition tapes with high and uniformly green density could be obtained which densified to a high density after sintering.

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