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Aqueous Tape Casting of Alumina Substrates

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Abstract

Alumina substrates were processed by aqueous tape casting. An aqueous slurry was prepared with a cellulosic binder. This binder was used to achieve slurries with a low viscosity and a shear thinning rheological behaviour. The influence of the organic phase on the properties of the green tapes was studied. The tensile strength increases, whereas the apparent density decreases, when the binder content increases. The tensile strength decreases, whereas the apparent density increases, when the powder content in the suspension increases.

Die Herstellung von Aluminiumoxidsubstraten erfolgte durch wässriges Bandgießen. Ein wässriger Schlicker wurde mit Hilfe eines zellulosehaltigen Binders eingestellt. Der Binder diente zur Erzeugung eines Schlickers mit kleiner Viskosität und scherdünnendem rheologischen Verhalten. Der Einfluß der organischen Phase auf die Eigenschaften der Grünbänder wurde untersucht. Mit zunehmendem Binderanteil nahm die Zugfestigkeit zu, während die durchschnittliche Dichte abnahm. Bei Erhöhung des Pulveranteils der Suspension nahm die Zugfestigkeit ab, während die durchschnittliche Dichte zunahm.

Des substrats en alumine ont été réalisés par coulage en bande en milieu aqueux, en utilisant un liant cellulosique. Ce liant a été choisi afin d'obtenir des suspensions de faible viscosité avec un comportement rhéologique rhéofluidifiant. L'influence de la phase organique sur les propriétés des bandes crues a été étudiée. Bien que la densité apparente décroisse, la charge à la rupture en tension croît, lorsque le taux de liant augmente. Bien que la densité apparente croisse, la charge à la rupture en tension décroît, lorsque la concentration en poudre dans la suspension augmente.

1 Introduction

Tape casting is one of the most prominent techniques for producing thin flat ceramic sheets. Tape casting is used to produce electronic substrates and multilayer capacitors, which represent two principal markets in electronic ceramics.[1–6]

Tape casting slurries are prepared by dispersion of a powder in a solvent with addition of dispersant, binders and plasticizers. Solvents allow powders to be deagglomerated and dispersed with the help of the dispersant; they make it possible for organic compounds to be dissolved. After casting, the evaporation of the solvent yields a manipulable tape. Common solvents are organic systems, such as azeotropic mixtures of 2-butanone–ethanol[7–9] or trichloroethylene–ethanol.[4,6,10]

The volatility, the toxicity and the cost of organic solvents lead to increasing interest in research and development relating to aqueous-based tape casting slurries. Aqueous systems offer the advantage of being cheap and non-toxic. Nevertheless, Nahass *et al.*[11] reported some drawbacks of aqueous-based systems, namely (i) a low evaporation speed, (ii) a good cohesion of the green sheets requires a high binder concentration, (iii) they can lead to flocculation due to strong agglomeration effects related to hydrogen bonding, and (iv) they react with hygroscopic ceramic powders such as the Y–Ba–Cu–O superconductors.

This paper is devoted to the preparation of cellulosic-based slurries for tape casting of alumina substrates with a thickness of about 0·8 mm in the green state. In order to understand the role of each component and to optimize the system, the influence of organic components on the rheological behaviour of the slurries and on some properties of the green sheets such as density and mechanical properties has been examined.

2 Experimental Procedure

2.1 Starting materials

The powder used was alumina (P172 SB, Pechiney, France) with an average particle size of 0·5 μm and a surface area of 10 m^2 g^{-1}. The dispersant was an ammonium polyacrylate (Darvan C, Vanderbilt Co.,

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Norwalk, CT). An hydroxypropylmethylcellulose (Methocel 20-214, Dow Chemical, Midland, MI) was used as binder. This binder provides a good cohesion to the green sheet with a minimum addition and a relatively low viscosity with a shear thinning rheological behaviour of the slurry. This behaviour allows a low viscosity during casting due to shear forces which occur when the slurry is passing under the blades and a high viscosity at rest. It also preserves the homogeneity of the slurry by preventing particles from settling during storage and during drying. In order to obtain an homogeneous suspension, the Methocel solution was prepared in two steps. First, the Methocel was dispersed by energetic stirring in hot water (95°C) in which it was not soluble, then an homogeneous hydration of the cellulose ether was achieved by progressively decreasing the temperature. Glycerol (Prolabo, France) and polypropylene glycol (PPG 1000, Aldrich Chimie, France) were used as plasticizers. It is also interesting to note that glycerol acts as a release agent, promoting easy tape stripping from the glass support, and that PPG acts as an antifoamer by allowing the elimination of air bubbles during homogenization.

2.2 Green sheet preparation

The tape casting slurry is prepared in two stages (Fig. 1). Firstly, alumina powder was deagglomerated and dispersed in water with the dispersant by ball milling for 3 h. Secondly, the binder and plasticizers were added and the slurry was mixed for 12 h, to achieve a good homogeneity.

Tape casting was performed on a laboratory bench (Cerlim, Limoges, France). The casting slab was a glass plate. A moving two-blade configuration was used to minimize hydrodynamic effects and to achieve a uniform thickness of the sheet. Casting was performed at a speed of 1·2 m min^{-1}, at ambient temperature of 22°C and with an ambient humidity of 60%.

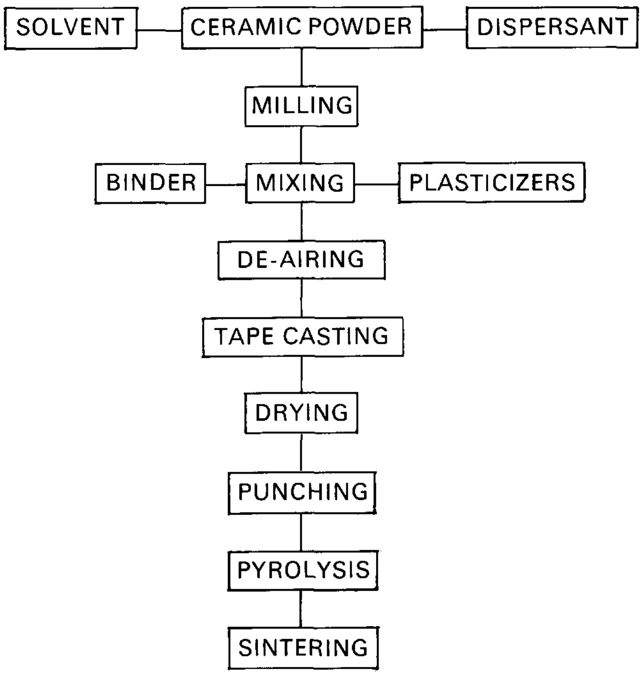

Fig. 1. Aqueous tape casting process.

The green sheets were punched to produce 30 mm diameter disks for density measurement and to produce dog-bone samples for mechanical properties. Pyrolysis of the organic components was performed at a slow heating rate (1°C min^{-1}) up to 600°C with a plateau of 6 h. Sintering was performed at 1550°C for 3 h.

2.3 Characterization

The volume fraction of each component (powder, organic phase and residual water, porosity) and the apparent density of green sheets, excluding the organic phase, were calculated by measuring the volume (V) and weight of sheets before (M) and after calcination (Mcal). Apparent density was expressed by the ratio $M\mathrm{cal}/V$.

The tensile strength and strain were measured on dog-bone samples using a tensile machine (M30K, J.J. Lloyd Inst. Ltd, Warsash, UK). The loading cell sensitivity was 0·1 N and the loading rate was 2 mm min^{-1}.

Rheological measurements (at 20°C) were performed using a rotating cylinder viscometer (Rotovisco RV12, Haake, Germany). The shear rate was continuously increased from 0 to 145 s^{-1} over a 1 min interval.

3 Results and Discussion

3.1 Effects of binder/plasticizer ratio (X)

The amounts of binder and plasticizers were adjusted to yield binder/plasticizer ratios (X = vol. Methocel/(vol. glycerol + vol. polypropylene glycol)) ranging from 0·34 to 0·55 (Table 1). The total amount of the binder + plasticizer and the powder/organic ratio (Y = vol. powder/(vol. Methocel + vol. glycerol + vol. polypropylene glycol)) were maintained constant at 9·39 vol.% and 1·66 vol.% respectively.

Based on the gap between the casting slab and the blade, and on the casting speed, the shear rate during casting was evaluated at 20 s^{-1}. In the range of the shear rate tested (0 to 145 s^{-1}), all suspensions show a shear thinning behaviour. This behaviour was analysed using the Ostwald power law:

$$\tau = K \cdot D^n$$

where τ is the shear stress, D the shear rate, n the shear rate exponent ($n = 1$ refers to a Newtonian fluid) and K a constant.

Table 1. Slurry compositions (vol.%), $Y = 1{\cdot}66$

Components	*Density* ($g\,cm^{-3}$)	*X1*	*X2*	*X3*	*X4*
Al_2O_3	3·98	15·60	15·60	15·60	15·60
Water	1·00	74·51	74·51	74·51	74·51
Darvan C	1·00	0·50	0·50	0·50	0·50
Methocel	1·40	2·39	2·67	3·10	3·33
Glycerol	1·25	4·20	4·03	3·77	3·64
PPG	1·01	2·80	2·69	2·52	2·42
X	—	0·34	0·40	0·49	0·55
Relative green density (%)	—	52·91	51·80	51·43	50·15

Figure 2 shows that, in the range of X tested, the viscosity ($\eta = K \cdot D^{n-1}$) calculated at a shear rate of $20\,s^{-1}$ increases with increasing binder content. As shown in Fig. 3, the rheological behaviour did not vary significantly with X ratio. The shear rate exponent varies from 0·6 to 0·56. The adjustment of the viscosity without changing the shear thinning behaviour of the slurry is an advantage for tape casting.

Tensile strength is a sensitive indication of the homogeneity of the green tape because failure generally occurs at the critical flaw. Green tensile strength increases and tensile strain decreases with increasing X ratio (Fig. 4). This behaviour indicates that the Methocel binder exhibits higher strength when unplasticized and has a brittle behaviour. Plasticizers reduce the glass transition temperature of the polymer and the viscosity of the suspension. The low molecular weight species of the plasticizer increases the flexibility of the green tape, but at the expense of the tensile strength.[12] The increase in tensile strain with increasing plasticizer content means that the plasticizers act, in this system, by an internal mechanism as true plasticizers and not as lubricants. Forte *et al.*[13] reported that the presence of residual solvent may lower the strength of green tapes. The residual water content was approximated with the assumption that the powder/organic ratio was the same in the green tape and in the corresponding slurry composition. The calculated values were 7·9, 7·08, 3·69 and 3·72 vol.% for X1, X2, X3 and X4 compositions, respectively. The high amounts of residual water in the plasticizer-rich compositions (X1, X2) may also explain their low strength.

A low X ratio leads to green tapes with higher density and lower porosity than high X ones (Fig. 5). The low viscosity of the plasticizer-rich organic phase may flow between the ceramic particles and fill the porosity, leading to lowest porosity samples.[14]

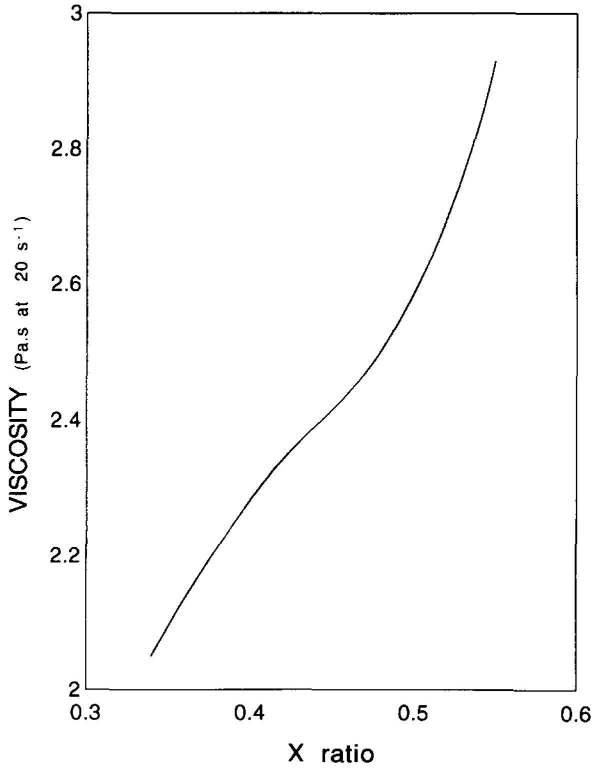

Fig. 2. Apparent viscosity of aqueous alumina suspensions for various values of X.

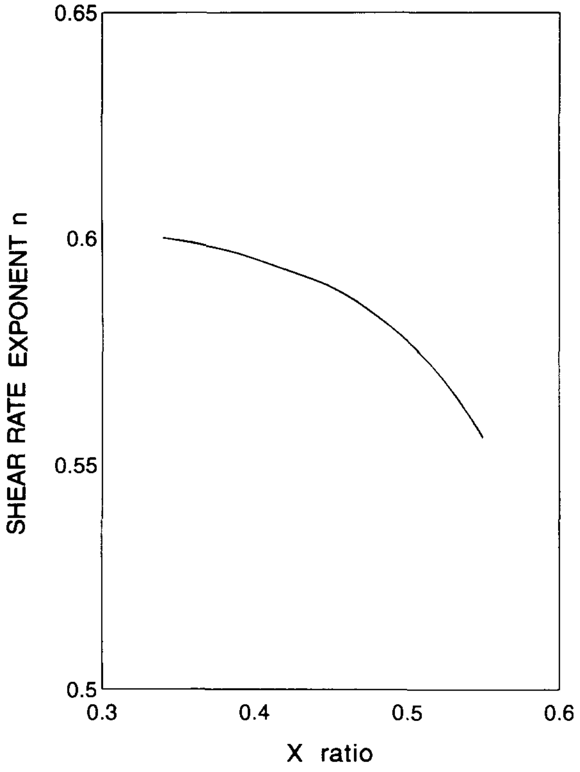

Fig. 3. Shear rate exponent n ($\tau = K \cdot D^n$) for various values of X.

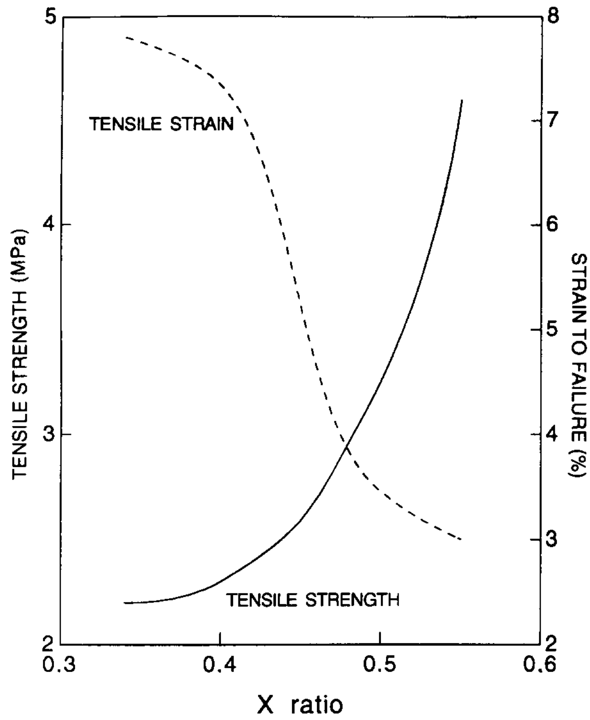

Fig. 4. Tensile strength and strain to failure of green tapes for various values of *X*.

Particles may also rearrange easily in a low viscosity organic phase during and immediately after casting.

3.2 Effects of powder/organic ratio (*Y*)

The composition X2 was modified by changing the powder/organic ratio (*Y*). The powder amount was increased at the expense of the organic content. The organic composition was maintained constant (Table 2). When *Y* decreases, the organic phase prevents particles from packing together and the density decreases.

Figure 6 shows decreasing strength and strain to failure of green tapes with increasing powder content. There are two possible explanations for this behaviour. The first one is that the amount of binder, for Y2 and Y3 compositions, could be too low to ensure a good cohesion of the green tape. The second explanation is that the strength of the green tapes strongly depends on the rheology of the slurry (8). At high powder concentration (high *Y* value), the viscosity of the slurry is high and the resultant tape is non homogeneous and subsequently strength and strain to failure are low. To support this point, a further study could be to keep the viscosity of the compositions with various *Y* ratios constant by adding water.

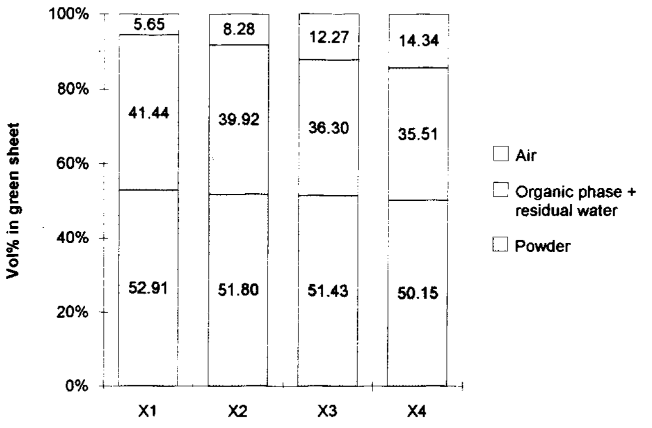

Fig. 5. Composition of the green sheets cast with various values of *X*.

Table 2. Slurry compositions (vol.%), *X* = 0·40

Components	*Y1*	*Y2*	*Y3*
Al_2O_3	13·55	15·60	18·55
Water	76·33	74·51	71·89
Darvan C	0·50	0·50	0·50
Methocel	2·75	2·67	2·59
Glycerol	4·12	4·03	3·88
PPG	2·75	2·69	2·59
Y	1·41	1·66	2·05
Relative green density (%)	50·81	51·80	53·20

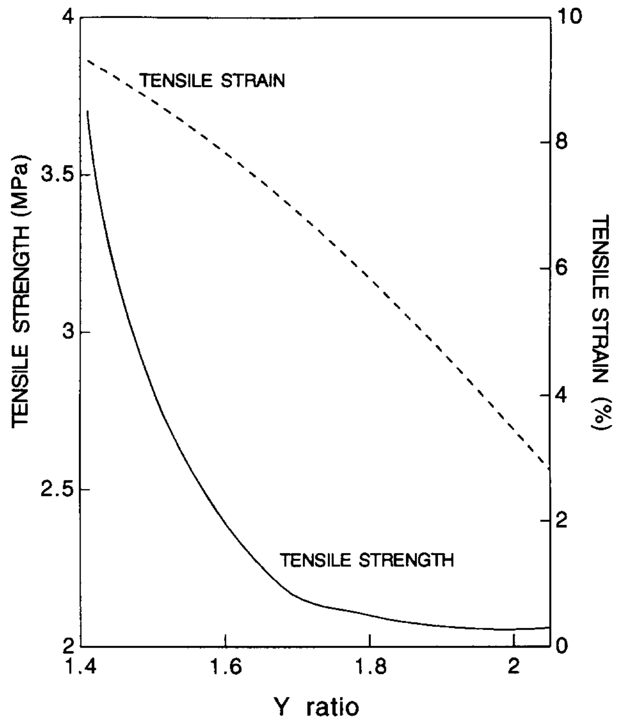

Fig. 6. Tensile strength and strain to failure of green tapes for various values of *Y*.

4 Conclusions

Alumina substrates have been fabricated by tape casting of aqueous suspensions using one cellulose ether as binder. This study confirms that the organic phase of the slurry greatly influences the green properties of tape cast substrates. The influences of two parameters were studied here, namely the binder to plasticizer ratio (*X*) and the inorganic to organic ratio (*Y*). A high apparent density requires a low value of *X* and a high value of *Y*. A high green strength requires a high value of X and low value of Y. These results show that a compromise must always be found in the formulation of a tape casting slurry. The amount of residual water contained in the green sheets seems also to depend on the composition of the slurry and may influence the green strength.

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