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Tape-casting: Relationship Between Organic Constituents and the Physical and Mechanical Properties of Tapes

M. Descamps,[a] G. Ringuet,[a] D. Leger[b] & B. Thierry[a]

[a]CRITT Céramiques Fines, Laboratoire des Matériaux Avancés Céramiques, Université de Valenciennes et du Hainaut-Cambrésis, France
[b]Laboratoire des Matériaux Minéraux, Conservatoire National des Arts et Métiers Paris, France

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Abstract

Alumina tapes, obtained by tape-casting, were produced from different slurry compositions. The effects of organic phase concentration on the mechanical and physical properties of green and fired tapes was measured.

The amount of organic phase used did not influence the apparent density of green tapes as long as the volume of organics introduced in the slurry was lower than the pore volume of the tape. Beyond this limit, grain separation occurred, which induced a decrease in material density.

Mechanical properties of tapes, in particular the maximum strength and the rupture elongation, were strongly influenced by the organic phase concentration. Variations in these properties were dependent on the level of filling of the tape porosity by the organic phase.

1 Introduction

Tape-casting is becoming a routine process for the formation of thin ceramic sheets.[1,2] The production of ceramic tapes by this process requires the use of significant amounts of organic compounds (solvents, binders, plasticizers, and dispersing agents).

Studies carried out on tape-casting show that a large diversity of slurry compositions are used.[3] For this process of shaping ceramics, the mechanical and physical characteristics of the green tapes are very important for further processing and the final properties of the material. Indeed, after the drying stage, the tape can be either stored (roller) or made in to the desired shape and dimension (cutting, punching, etc). The ceramic tape must then have the flexibility and strength required for tape handling. On the other hand, the powder compactness inside the green tape will have an effect upon the physical properties of the fired material and in particular upon the tape density. The physical and mechanical properties for a given powder will depend upon the type and quantity of the organic phase introduced inside the suspension.

Generally, work carried out on this theme showed an increase in the mechanical strength of tapes with the rise of the binder content[4] and a tape elongation which increased with the increase of the plasticizer content to the detriment of the mechanical resistance of the material.[5,6]

However, little of the work showed the evolution of mechanical and physical properties as a function of filling level of the porous volume of tape by the organic phase. The purpose of this study was to determine the significant relationship between the physical and mechanical properties of green and sintered tapes, the concentration of organic phases used and the porous volume of tapes.

2 Experimental Study

2.1 Starting material

The raw material used for tape production was an alumina powder (Al_2O_3, CT530SG, Alcoa, USA). Its physical characteristics are shown in Table 1. This powder was a low soda grade (Na_2O = 0·08 wt%) with a nominal purity higher than 99·7% in weight of alumina.

2.2 Slurry composition

Al_2O_3 slurry dispersion was carried out in an azeotropic solvent mixture of trichloroethylene–ethanol (72/28 wt%) using a phosphate ester type (Beycostat C213 CECA, France) dispersing

Table 1. Physical characteristics of Al_2O_3 powders

Specific surface area (m^2/g)	*Mean particle diameter (μm)*	*Density (g/cm^3)*
4·2	1·3	3·98

agent.[7–9] Cohesion between powder grains was ensured with a polyvinylbutyral resin (PVB, Butvar B98 Monsanto) which was plasticized by dibutylphthalate (DBP, Aldrich Chemical). So, the production of a tape-casting suspension requires the use of numerous organic compounds. Competition can occur between the adsorption of the different compounds onto the particle surface to reduce the effectiveness of these products.[10–12] For this reason, the introduction sequence of different organic compounds inside the slurry was important. Thus, the dispersing agent was introduced in order to optimize the slurry defloculation. A first milling, within 4 h, was carried out with the powder, the solvent and the dispersing agent.

The binder and the plasticizer were then added and the suspension was mixed again after 20 h in order to obtain a good homogenization between mineral and organic compounds. These milling operations were carried out with a planetary grinding. Alumina containers and balls were used in order to minimize the pollution.

Slurries were produced with a binder content varying between 2 and 7 wt% (of Al_2O_3 concentration) and a plasticizer content varying between 0 and 300 wt% (of binder concentration). Dry matter content was fixed at 68 wt% and dispersing agent content was equal to 0·8 wt% (of Al_2O_3 concentration) for all experiments. The slurry viscosities were maintained at 1500 ± 100 mPa s using suitable solvent content.

2.3 Casting

Al_2O_3 slurries were cast on a bench by means of the doctor–blade method. The mobile carrier consisted of a polyester film, with the blade height adjusted in order to obtain tapes with a thickness of about 300 μm. Tape drying was carried out at room temperature and in the open air.

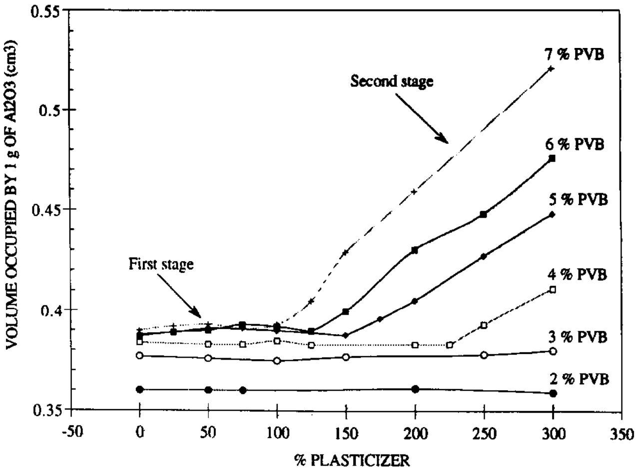


Fig. 1. Evolution of tape volume apparent as a function of plasticizer content at different binder (PVB) concentrations.

Table 2. Volume of the tape containing 1 g of Al_2O_3 and organic limit volume of the tapes (cm^3)

	Tape composition (% binder)					
	2%	*3%*	*4%*	*5%*	*6%*	*7%*
V_{mea} Volume of tape occupied by 1 g of Al_2O_3	0·360	0·376	0·384	0·389	0·391	0·392
V_{lim} Maximum volume to be filled	0·109	0·125	0·133	0·138	0·140	0·141

2.4 Tape characterization

The influence of organic composition on the density of the material was studied by mercury porosimetry (Poresizer 9310 Coultronics). This instrument determines the apparent volume of 1 g of sample (powder + organic). Therefore, the powder weight inside 1 g of tape varies with the amount of organic phase used. For this reason, the accurate volume occupied by 1 g of Al_2O_3 was calculated using the porosimetry results and tape formulations.

Mechanical properties, in particular the maximum strength and the rupture elongation were

Table 3. Organic volume contained in tapes of different formulations (cm^3)

	% Plasticizer						
% Binder	*0*	*100*	*125*	*150*	*200*	*250*	*300*
2	0·0257	0·0449	—	—	0·0641	—	0·0832
3	0·0348	0·0636	—	—	0·0923	—	0·1211
4	0·0439	0·0822	0·0918	0·1014	0·1206	0·1398	0·1589
5	0·0530	0·1009	—	0·1249	0·1488	0·1728	0·1968
6	0·0621	0·1196	0·134	0·1483	0·1771	0·2059	0·2346
7	0·0712	0·1383	0·1550	0·1718	0·2054	—	0·2725

measured for different tape formulations. Measurements, performed 1 week after the slurry casting, were carried out on tapes of 300 μm thickness and dimensions corresponding with NFT51034 standard. Stress and elongation values obtained on the tape, were dependent on the loading rate.[13] For studied compositions, preliminary trials showed a stabilization of these characteristics from rates equal to or higher than 20 mm/min. Thus, the loading rate of the testing machine (Adamel Lhomargy DY30) was then fixed at 20 mm/min, for all experiments.

The rupture elongation of the tapes was measured by the cross-slide movement. Force cells used for these trials were of 10 and 100 N. Twenty specimens of each formulation were tested.

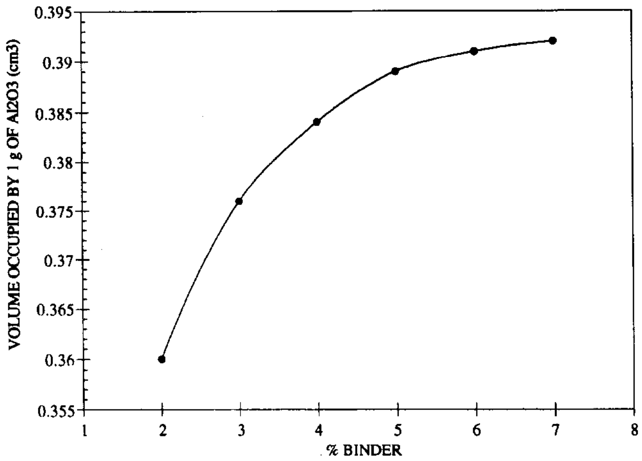


Fig. 2. Evolution of tape volume apparent for different binder contents and plasticizer contents giving an organic volume lower than porous volume of the tape (first stage).

3 Results and Discussion

3.1 Physical properties

The effect on the apparent volume of the tape (volume occupied by 1 g of Al_2O_3) as a function of increasing plasticizer content was studied on tapes fabricated with different binder contents (Fig. 1). When the binder content was equal to or higher than 4 wt% of powder content, two regions were observed as the plasticizer content was increased:

In the first stage, the volume occupied by 1 g of alumina remained constant. Organic compounds (binder, plasticizer, dispersing agent) filled the porous structure of the material without changing the distance between powder grains. In the second stage, a rearrangement of the structure occurred. The distance between the grains increased and there was a significant increase in tape volume. In this stage, the organic volume was higher than the porous volume of the tape.

For binder contents equal to 2 and 3 wt%, only the first stage is observed. The difference between the experimental volume occupied by 1 g of powder inside the tape (volume measured in the first stage, which remained constant up to a certain plasticizer concentration for the different binder contents, V_{mea}) and the theoretical volume of 1 g of Al_2O_3 (V_{th} = 0·251 cm^3) gave the limit value of organic volume (V_{lim}) beyond which structural modification of the tape occurred (Table 2)

$$V_{\text{lim}} = V_{\text{mea}} - V_{\text{th}} \qquad (1)$$

Comparison between V_{lim} and V_{org} values for the different compositions (Table 3) shows that total filling of the porous structure of the tape by the organic phase would not be reached for tapes with 2 and 3 wt% of binder content, whatever plasticizer content used. However, for tapes containing 4, 5, 6 and 7 wt% of binder content, V_{org} would exceed V_{lim} for plasticizer amounts of about 250, 200, 150 and 125% respectively. These calculated values, are in agreement with the observed increases of tape volume (Fig. 1).

Whereas increasing plasticizer content did not change the volume filled by 1 g of Al_2O_3 for a given binder amount (when $V_{\text{org}} < V_{\text{lim}}$), increasing binder content induced an increase in this volume, measured in the first stage. However, for binder concentrations greater than 5% a structure stabilization occurred (Fig. 2). Two hypotheses are proposed in order to explain this behaviour:

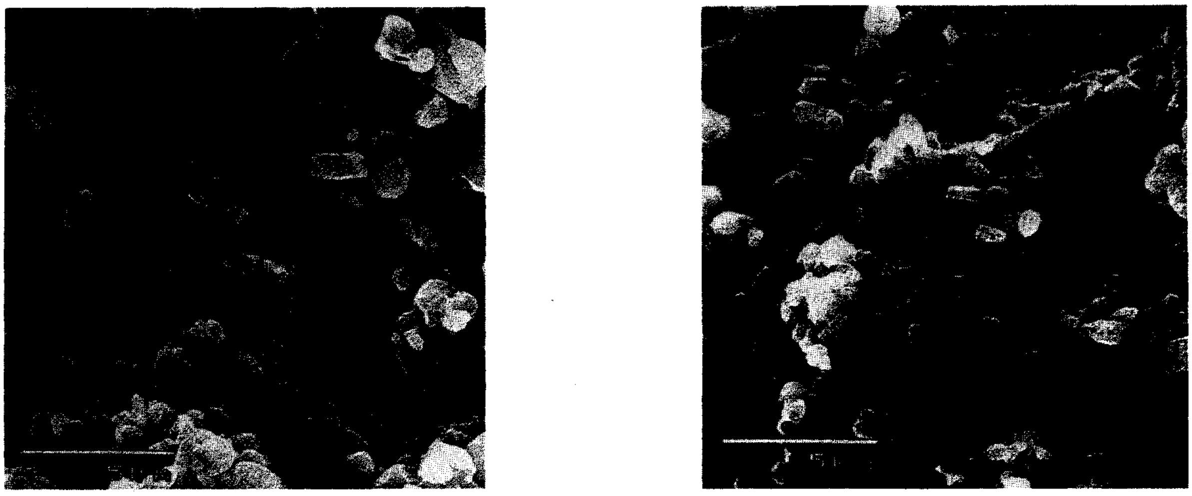
(1) Low amounts of binder did not allow a total coating of the Al_2O_3 grain surface. Thus, powder specific surface area had a strong influence.
(2) The binder film adsorbed to the grain surfaces tended to a thickness limit.

Study of the fracture surface of green tapes, with different plasticizer concentrations corroborated the proposed model. For organic compositions lower than the filling volume limit (V_{lim}), the grain surface was 'clean'. When this limit was exceeded, a coating of the powder grain could be observed as well as the formation of granules induced by the organic phase. Micrographs shown in Fig. 3 correspond to a binder concentration of 5 wt%.

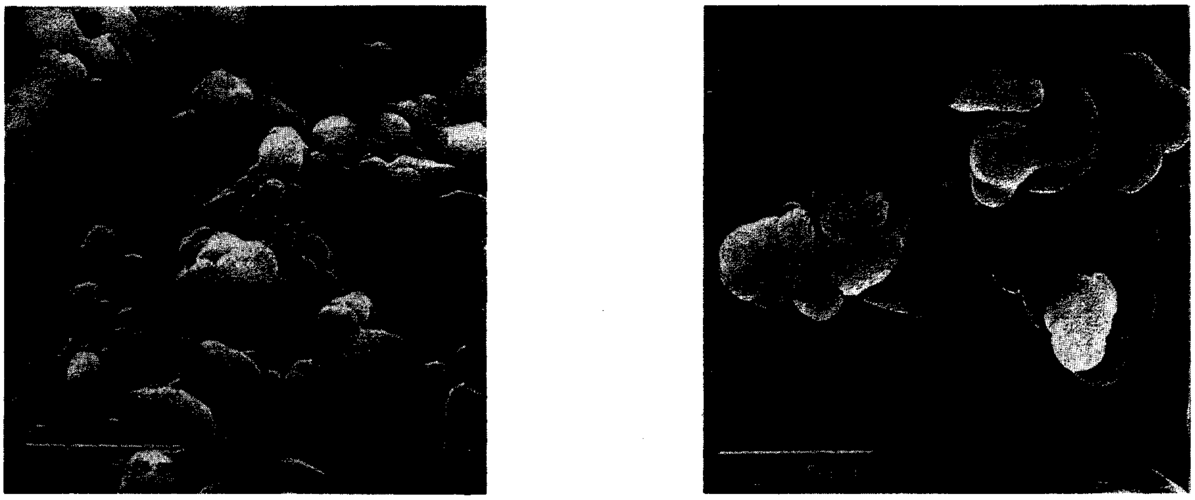
Measurements carried out on debinded tapes (1 h at 600°C) and fired tapes (1 h at 1650°C) also showed significant decrease of the tape density when the organic volume was higher than the pore volume of the tape (Fig. 4).

3.2 Mechanical properties of tapes

The maximum strength and the rupture elongation of green tapes were measured on materials introduced from different formulations (Figs 5 and 6).



a) 50% DBP b) 150% DBP



c) 200% DBP d) 250% DBP

Fig. 3. Fracture surfaces of green tapes produced with 5% of binder and different plasticizer concentrations.

The effect on these properties of the plasticizer amount can be divided into several stages:

(1) In the first stage, results showed a strong decrease of the mechanical strength and a limited increase of tape elongation values. Plasticizer molecules inserted themselves inside the macromolecular network formed by the binder. This insertion destroyed locally intermolecular strength responsible for the mechanical cohesion of the compound. Chain movement is thus facilitated to the detriment of the material resistance.

(2) In the second stage, strength increased (the amplitude of which increased with binder amount). The development of this characteristic is induced by the action of two antagonistic phenomena: On the one hand, the strength decrease of the binder phase was induced by the increasing amount of plasticizer and on the other hand, the reinforcement of the mechanical strength was caused by the filling of the pores in the tape by organic compounds. This reduction in the defect number (pores) increased the mechanical strength of the tape, which occurred all the more for higher binder contents. In this stage, an increase of tape elongation values occurred.

(3) When the organic volume in the slurry was higher than the pore volume of the tape, a third stage was observed. In this stage, the mechanical strength of the tape depended only on the mechanical properties of the binding phase. The characteristics of this phase, saturated by the plasticizer agent, explained the significant decrease in the rupture strength. However, as the plasticizer content was increased, lubrication was improved and this promoted sliding between powder grains, which was manifested by a large increase of tape elongation.

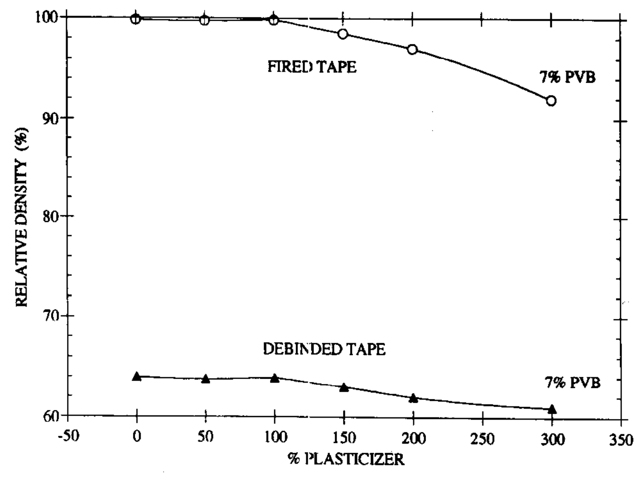


Fig. 4. Evolution of debinded and sintered tape density as a function of plasticizer content for a binder (PVB) concentration equal to 7 wt%.

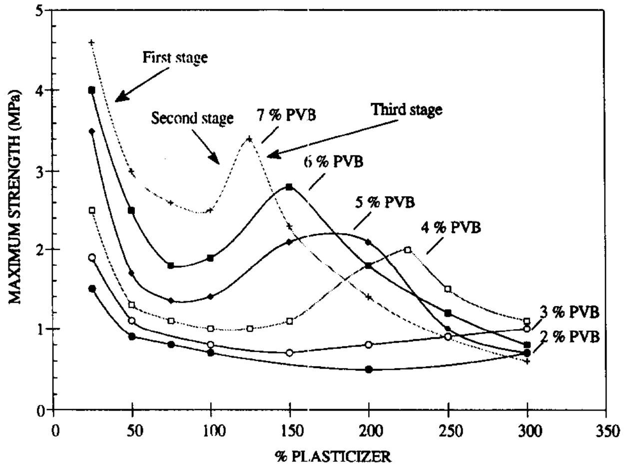


Fig. 5. Evolution of maximum strength as a function of plasticizer content at different binder (PVB) concentrations.

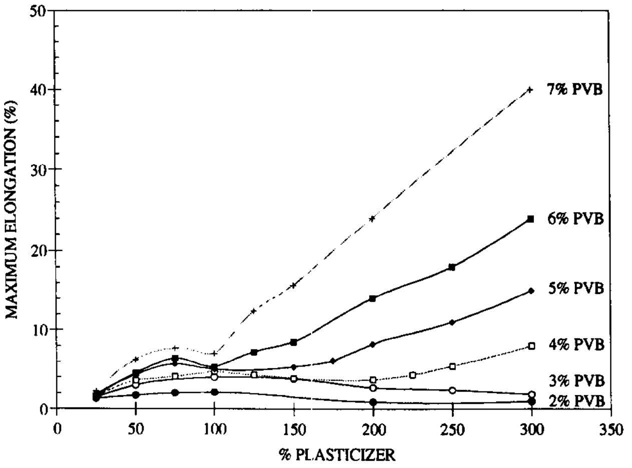


Fig. 6. Evolution of maximum elongation as a function of plasticizer content at different binder (PVB) concentrations.

The variations in rupture strength as a function of percentage binder present showed the importance of the powder particle size on the choice of slurry composition. Figure 7 shows the variation in this property for two DBP concentrations (100%, 200%).

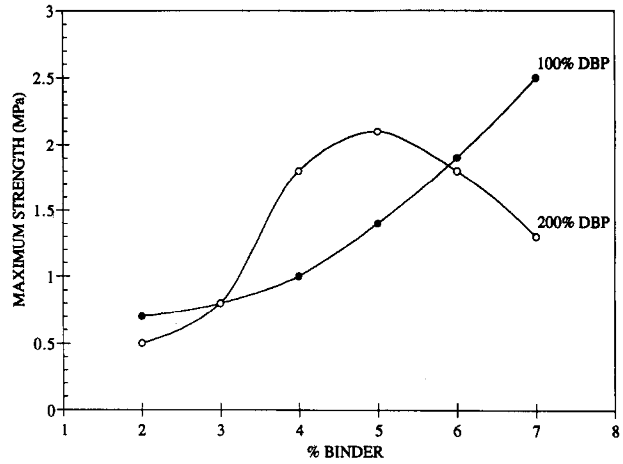


Fig. 7. Evolution of maximum strength as a function of binder content at two different plasticizer (DBP) percentages.

Indeed, for slurry compositions in which the organic volume was lower than the pore volume of the tape, i.e. for the formulation at 100% of plasticizer whatever the content binder and the composition at 200 wt% of plasticizer up to 5% of binder (Tables 2 and 3), increasing the binder content resulted in an increase in the tape mechanical strength. However, when the organic volume was higher than the pore volume (from 5% PVB and 200% DBP) a large decrease of strength was observed, in spite of the increase in binder content.

4 Conclusions

The results of this study showed the important effect of the porous structure of the tapes on their mechanical and physical properties.

When the volume of organics used was lower than the porous volume of the tape, the material volume remained constant whatever the amount of plasticizer used (binder content fixed). On the other hand the volume increased slowly (volume measured in the first stage) when the binder concentration was increased and then tended to stabilise when a critical amount was reached. During this stage, the organic phase filled the tape porosity. When the organic volume was higher than the tape porous volume, powder grains were forced apart which induced an increase of apparent tape volume and a large decrease of fired tape density.

The tape mechanical characteristics were affected by the action of two antagonistic phenomena.

(1) The plasticization and lubrication effects caused by the plasticizer agent produced

an increase in material elongation and a decrease in network resistance.

(2) The reduction in the number of defects caused by the filling of the tape porosity by the organic phases led to an increase of the maximum strength.

The predominance of either effect determines the mechanical behaviour as a function of the amount of organic phases used.

So, for a fixed binder content, increasing of the plasticizer amount induced an increase in the mechanical resistance of the tape. However, from a certain filling level of the tape porosity by the organic phase, this behaviour was inversed and the mechanical resistance reached a maximum corresponding at an organic volume which allowed the complete filling of tape porosity. In this stage, the tape elongation increased appreciably. Beyond this maximum point a drastic reduction of the mechanical resistance appeared, induced by the weak strength of the binder phase (satured in plasticizer agent). These results showed that a judicious choice of the plasticizer concentration allow us to obtain green tapes with optimized mechanical properties, according to the desired application. Plasticizer contents corresponding to an organic volume near to the maximum filling of the tape porosity seems to give a correct compromise between mechanical strength and elongation of the tape. For applications where elongation and flexibility will predominate, significant contents of binder and plasticizer will be required. However these properties will be obtained to the detriment of mechanical resistance of the green tape and the density of sintered material.

On the other hand, increase in binder content for a fixed plasticizer amount, induced the increase of the rupture strength of the tape up to a certain amount of binder. Indeed, for binder concentrations corresponding to organic volumes higher than the porous volume, an important diminution of this characteristic appeared. When particle size distribution of the powder was optimized, the compactness of the powder can be very significant and can produce a very weak, porous volume of tape.[14-15] Thus, low binder content will be sufficient to obtain organic volumes higher than the porous volume of the tape and to induce an important decrease of the network mechanical resistance: behaviour opposed to the desired effect.

This study, carried out on interactions between porous volume and organic content for the production of ceramic tape by tape-casting must allow a better understanding of the evolution of tape properties and an optimization of slurry formulation for a given application.

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