Journal of the European Ceramic Society **18** (1998) 311–321
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PII: S0955-2219(97)00144-1
0955-2219/98/$19.00 + 0.00

Processing of Aqueous Tape-casting of Alumina with Acrylic Emulsion Binders

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(Received 18 April 1997; accepted 2 July 1997)

Abstract

Two commercial acrylic emulsion binders (Tg = −40°C and Tg = 10°C) have been investigated as potential binders for aqueous alumina suspensions for the tape casting process. Coupled with an aqueous low-molecular weight ammonium polyacrylate salt solution as dispersant, they lead to homogeneous systems which seem very compatible. The aqueous suspensions do not show apparent foaming. The suspensions exhibit a typical shear-thinning character with a very few time dependent rheological behaviour, whatever the binder compositions tested. Fabrication of homogeneous green tapes with very smooth surfaces and relative densities above 50% has proven to be relatively easy from these suspensions. © 1998 Published by Elsevier Science Limited.

1 Introduction

The tape casting process has proved its efficiency for the fabrication of thin ceramic substrates for electronic applications for several years.[1–4] Tape casting is also an interesting colloidal process to prepare ceramics with improved mechanical properties and it is widely used to produce thin ceramic sheets and multilayer structures for different applications such as solid oxide fuel cells (SOFC), piezoelectric ceramics for actuator and transducers or laminated composites.[5,6]

Until these last past years, the most common way to perform tape-casting was to use a slurry based on organic solvents. Today, a lot of efforts are concentrated on the preparation of water-based slurries which are less expensive and less toxic. Water-based systems are used for many years,[7] but only for the preparation of very thin layers because of the problems linked to the drying. The velocity of the water elimination could be a critical factor for use the aqueous tape casting process at the industrial scale, but satisfactory conditions could be expected using heating to accelerate the drying step. Beyond this crucial point, Nahass *et al.*[7] have shown that alumina aqueous slurries enable the production of green tapes which exhibit similar physical properties as those prepared from organic slurries.

This work will not come back on the nature or on the role played by the different additives on the slurry behaviour. Some interesting papers have been written on this subject, for example by Moreno[8,9] or more recently by Hotza and Greil[10] in the case of aqueous tape casting. The aim of this study is to investigate the rheological behaviour and the tape casting of aqueous slurries of alumina powder, using two commercial acrylic emulsions as binders. The main advantage of emulsion binders is their low viscosity. On the other hand, they include some surfactants in order to stabilize the emulsion which can promote foam formation. However, in the selected binders, the surfactants are strongly adsorbed onto the alumina powder surface and consequently inactivated.[11] So, emulsions seem to be very promising binders for tape-casting slurry formulations owing to their features expected to reduce some drawbacks linked to aqueous preparation.

The aim of this work was to search into the ability of acrylic aqueous emulsion binders to prepare water-based alumina suspensions with properties compatible with the tape casting process and to produce homogeneous high density green sheets.

2 Experimental Procedure

2.1 Starting materials

The powder used was the alumina A16 SG (Alcoa, TN). The mean particle size is 0·4 μm and the specific surface area is 11 m^2 g^{-1}.

The binders were two stable acrylic emulsions dispersed in water: Duramax B-1035 and Duramax B-1050 (Rohm and Haas, Philadelphia, PA). These binders are expected to give slips with low foam and viscosity and to lead to green tapes with good mechanical and lamination behaviours, avoiding the use of additional organic additives such as plasticizers or defoamers. Characteristics given by the manufacturer are reported in Table 1.

The dispersant used for stabilize the alumina suspensions was a low molecular weight ammonium polyacrylate salt solution (Duramax D-3005, Rohm and Haas, Philadelphia, PA) (Table 1), a surface active agent expected to act by an electrosteric mechanism. Some previous tests were also conducted using 4,5-dihydroxy 1,3-benzenedisulfonic acid (Tiron, Aldrich-Chemie, Germany) which has proven to be very efficient dispersant for alumina powder.[12] Unfortunately, this dispersant associated with the acrylic emulsion binders leads to slurries which exhibit an important ageing behaviour, in comparison with Duramax D-3005.

A high solid loading in the slurry is beneficial to avoid particle segregation effects, to minimize the shrinkage during drying and to achieve a high green density. For a given powder (particle size and shape distributions), the maximum solid loading depends on the efficiency of the dispersant and on the deagglomeration step. The starting suspensions used in this work contain 83 wt% of alumina, 17 wt% of deionized water and more 0·3 wt% (based on dry weight alumina powder) of dispersant. This composition corresponds to a solid loading of 55·2 vol%, which is close to the maximum obtained with A16 SG alumina powder (Alcoa, TN) in the presence of very effective dispersants.[13]

The amount of Duramax D-3005 dispersant was investigated in the 0·1 to 0·7 wt% range with respect to alumina. The concentration adopted (0·3 wt%) corresponds to the minimum viscosity, namely to the best state of dispersion of the aqueous alumina suspension. Taking into account the specific area of the alumina powder (i.e. 11 $m^2 g^{-1}$), the best dispersion is obtained for an amount of dispersant corresponding to 0·27 $mg\ m^{-2}$.

Three different concentrations (corresponding to 5, 10 and 15 wt% of latex particles, based on the alumina powder) of a mixture of B-1035 and B-1050 binders was added, in different proportions, to the as prepared suspension. The two binders used have not the same latex, or active binder concentration (55 wt% and 49 wt% for the B-1035 and B-1050, respectively). Hence, the solid loading of the suspensions (i.e. alumina powder + latex) is depending on the total amount and on the composition of the binder system and strictly maintaining the solid loading at a constant level implies adjustment by water addition. Nevertheless, this procedure was not followed. Table 2 reports the total solid loading (alumina + latex) and the alumina concentration of each prepared suspension.

2.2 Preparation and characterization of the slurries

The different steps of the slurry preparation are presented in Fig. 1. Initially, deionized water was mixed with the dispersant by mechanical stirring for 2 min. Then the alumina powder was added and blended for 30 min. Deagglomeration and dispersion of alumina particles were performed by ball-milling for 12 h in a plastic container with silicon nitride balls as grinding media. Then, binders were added to the resulting slurry (starting suspension) and keep under stirring for at least 4 h. When a mix of the two binders were used, they were introduced simultaneously. The duration of each step has been determined to achieve a well homogeneous suspension, and at the same time to avoid ageing phenomenon.

The slurries were characterized by means of rheological measurements. They were performed at 20°C with a stress controlled rheometer (CSL 500, Carri-med, UK), using concentric-coaxial cylinder configuration. Before starting a measurement, a pre-shearing was applied at at high shear rate ($550\ s^{-1}$), followed by a 2 min rest in order to transmit the same rheological history to all the slurry being tested. The rheological behaviours of the suspensions were characterized by stress sweep and steady shear measurements in the shear rate range of 0·1 to $100\ s^{-1}$. The stress sweep measurements were conducted by increasing and decreasing the shear rates between the above extremes. Plastic viscosity and Bingham (apparent) yield stress were determined by linearising the data of the ascending flow curves ($\tau = f(\dot{\gamma})$). The plastic viscosity (η_p)

Table 1. Main characteristics of the organic additives (solid: concentration of active species in the additive, Ø: mean size of latex particles in acrylic emulsion, Tg: glass transition temperature, η: viscosity, Mw : molecular weight) (data from Rhom and Haas company)

	Solid (wt%)	*Ø(µm)*	*Tg (°C)*	*Density*	*η (mPa.s)*	*pH*	*Mw*
D-3005 dispersant	35	—	—	1·16	< 100	6·0–7·0	2400
B-1035 binder	55	0·37	−40	1·05	< 200	7·5–8·7	—
B-1050 binder	49	0·1–0·14	10	1·06	100–1000	8·5–9·5	—

Table 2. Total solid loading (Al_2O_3 powder + latex particles) and alumina concentration of the different suspensions

Binder composition	*Active binder content*					
	5 wt%		*10 wt%*		*15 wt%*	
	Alumina + latex	*Alumina*	*Alumina + latex*	*Alumina*	*Alumina + latex*	*Alumina*
B-1035						
wt%	81·00	76·85	79·32	71·91	77·82	67·49
vol%	54·86	46·07	54·60	39·75	54·40	34·96
70 wt% B-1035 + 30 wt% B-1050						
wt%	80·83	76·76	78·95	71·58	77·30	67·06
vol%	54·50	45·86	53·97	39·43	53·58	34·59
50 wt% B-1035 + 50 wt% B-1050						
wt%	80·68	76·62	78·70	71·35	76·96	67·49
vol%	54·25	45·71	53·55	39·21	53·02	34·33
30 wt% B-1035 + 70 wt% B-1050						
wt%	80·55	76·49	78·46	71·12	76·63	66·46
vol%	54·00	45·56	53·14	39·00	52·12	34·10
B-1050						
wt%	80·34	76·30	78·08	70·79	76·13	66·02
vol%	53·64	45·35	52·52	38·69	51·69	33·74

corresponds to the slope of the straight line so obtained, whereas the Bingham (apparent) yield stress (τ_0) corresponds to its intercept on the y-axis. The equilibrium viscosity was determined by steady shear measurement conducted at 10 different shear stresses, until equilibrium was reached (the maximum equilibrium time was set up to 5 min).

2.3 Tape casting

Tape casting experiments were carried out on a laboratory tape caster (Elmetherm, Oradour sur Vayres, France). This device enables the production of tapes of 12 cm width and until 120 cm long by moving a container with 2 blades along a fixed support. Micrometric screws allow to set the gap of blades from 0·025 up to 1 mm.

In the tape casting process, the support is of prime importance. The slurry has to sufficiently wet the support in order to promote a regular coating, but the adherence of the dried tape onto the support should not be too strong in order to allow an easy stripping and to give a proper continuous green tape. Glass plate and two plastic films were

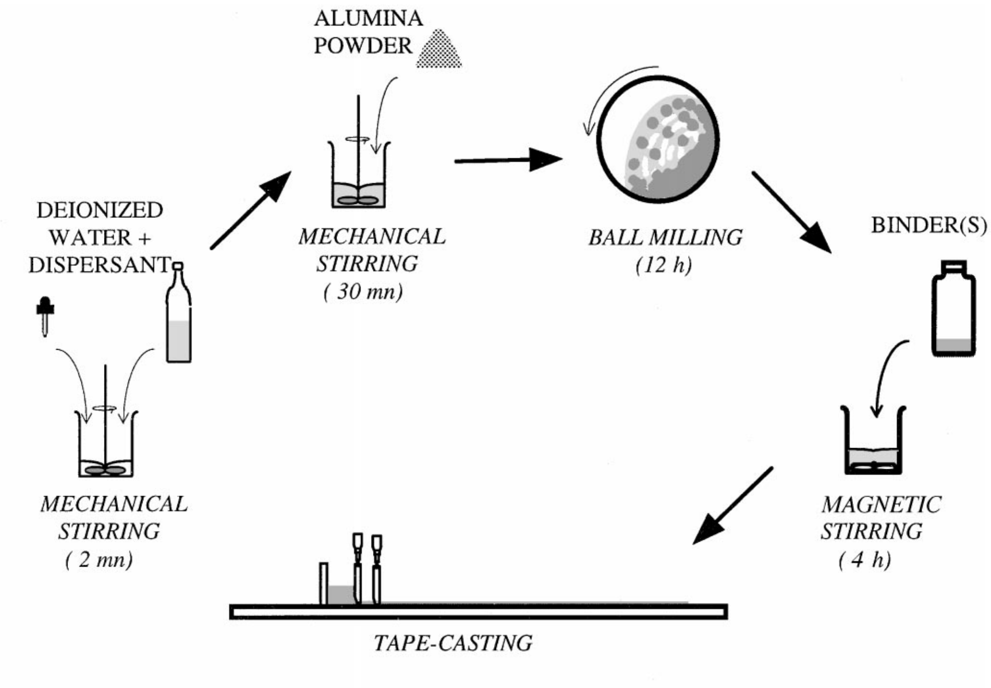


Fig. 1. Schematic representation of the alumina layer fabrication by tape casting of aqueous suspensions.

tested, namely a polyethylene terephtalate (PET) film (Melinex type S, ICI, UK) and a polypropylene (PP) film (Western Wallis, USA).

After some previous tests, a gap of 350 μm under the blade and a casting speed of 1·7 cm s^{-1} have been selected for all the casting tests. Under these conditions, the shear rate generated under the blade is estimated to be 50 s^{-1}.

2.4 Characterization of the green tapes

Apparent densities were determined by measuring the weight and the apparent volume of discs punched from the green tapes. Reported values correspond to the average value of five measurements performed along the green tapes.

Some microstructural investigations were carried out using an emission field scanning electron microscope, SEM (Hitachi S-4100, Japan).

3 Results and Discussion

3.1 Properties of the suspensions

The rheological behaviours of the slurries prepared with pure binders exhibit similar flow properties, characterized by a typical shear-thinning behaviour with a decrease in viscosity when the shear rate increases (Fig. 2(a) and (b)). Such a behaviour is in good agreement with the requirements for the tape casting process. The relatively high shear rate of about 50 s^{-1} enables the slurry to have a low viscosity under the blade during casting, facilitating the tape coating. After deposition, the slurry recovers a high viscosity level, avoiding settling of the particles along the tape thickness.

At a shear rate of 50 s^{-1}, equilibrium viscosity appears to remain approximately constant for the B-1035 binder and to slightly decrease for the B-1050 binder when their contents increase (Fig. 2(c)). Two antagonistic mechanisms could be expected from binder addition. The first one tending to increase the viscosity due to active polymer (latex particles) presence and the second one tending to decrease the viscosity due to dilution effect by water addition coming from the emulsions. However, from Fig. 2 it is not possible to separate the effect of binder content and of solid loading on the equilibrium viscosity. Indeed, increasing the binder content decrease the solid loading (Table 2). Hence, in order to evaluate the contribution of the above factors, some additional rheological measurements were performed at strictly constant solid (alumina + latex) loading adjusted at 54·4 vol% and at 51·69 vol% for the B-1035 and B-1050 binders, respectively (Fig. 3(a) and (b)). These values correspond to the 15 wt% latex content, i.e. slurries with the highest water content. The solid loading of the other three suspensions prepared with 0, 5 and 10 wt% active binder were adjusted to the same value by adding water. At constant solid concentration, the first trend is a decrease in viscosity for an addition of 5 wt% of binder (Fig. 3(c)). For a further addition of binder, two different behaviours occurred with respect to the binder nature. The viscosity increases with the content of B-1035 binder contrarily to the trend observed in Fig. 2(a). On the other hand, adding B-1050 binder at constant solid loading maintains the

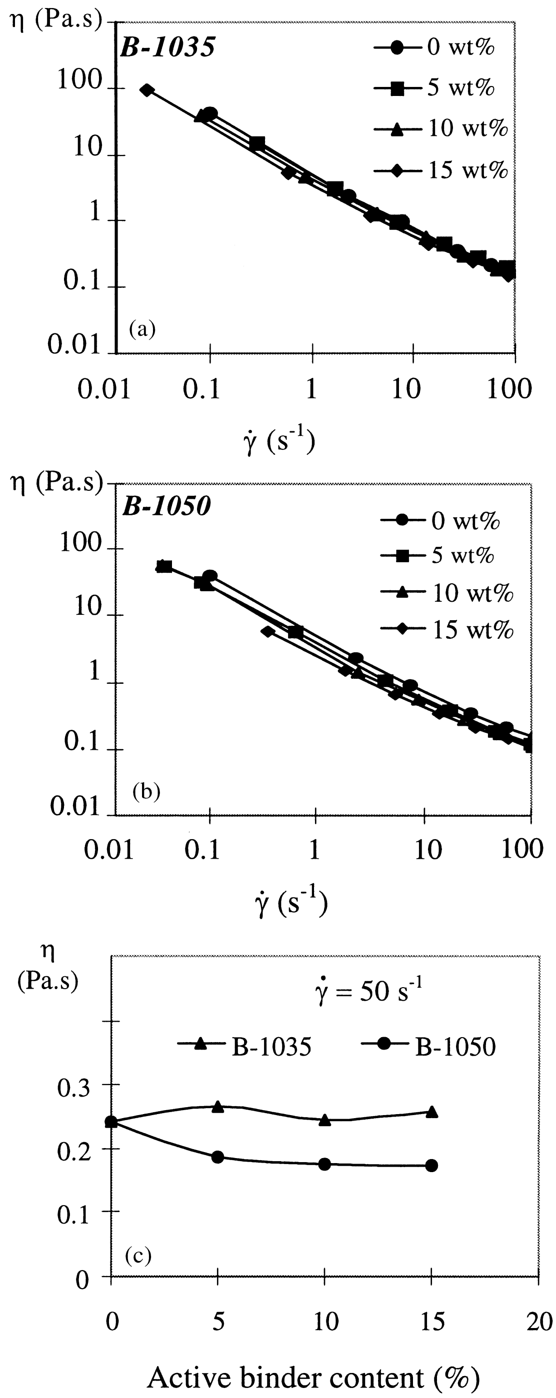


Fig. 2. Viscosity curves of the slurries prepared with the pure binders for different binder contents without solid loading adjustment (Table 2).

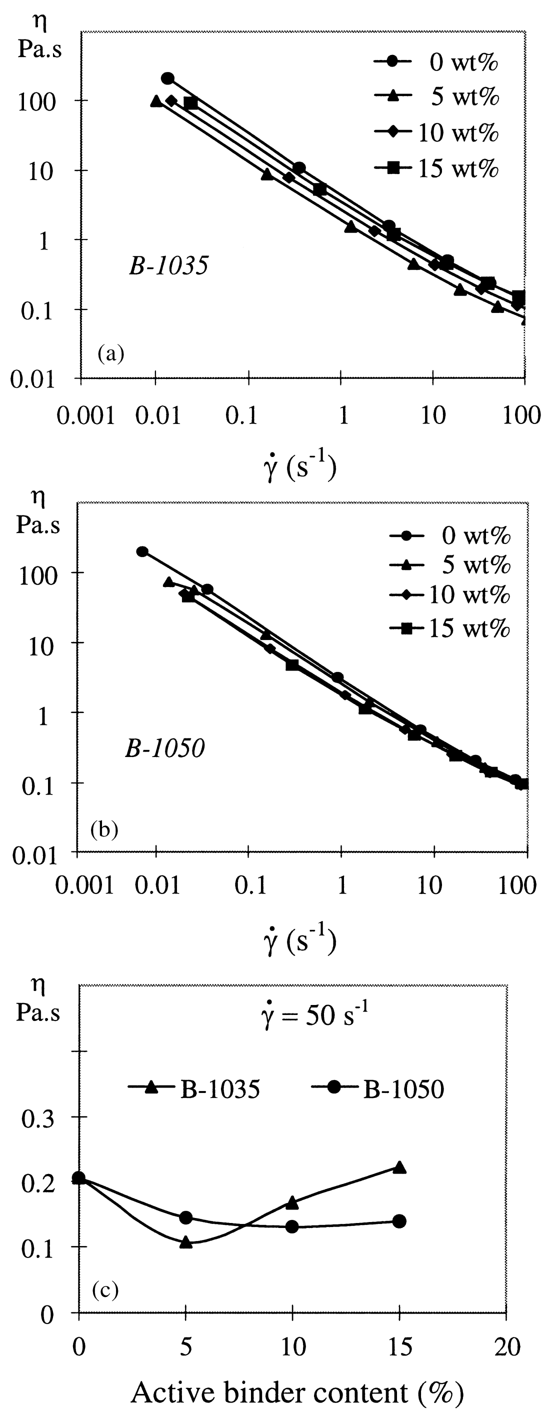


Fig. 3. Viscosity curves of the slurries prepared with the pure binders for different binder contents at strictly constant solid loading (B-1035: 54·4 vol%, B-1050 51·69 vol%).

viscosity slightly constant according to the trend observed in Fig. 2(b).

At constant solid loading, the volumic part of alumina powder + latex binder remains unchanged and so an increasing binder content corresponds to a decreasing proportion of alumina particles and vice versa.

3.1.1. Pure B-1035 binder

In the case of the B-1035 binder, the increase in binder content corresponds to a substitution of alumina particles, which have an average size of 0·4 μm, by latex particles which have a diameter of 0·37 μm (Table 1). From a particle size point of view, the suspension are similar whatever the binder content. One great difference resides in the particle shapes. The decrease in viscosity, with an addition of 5 wt% active binder (B-1035 or B-1050), could be explained by the substitution of alumina particles with complex shapes by latex particles of similar size, but with a spherical shape. On the other hand, interactions could occur between the stabilizants of the latex particles into the emulsion binders and the dispersant of the alumina powder (i.e. ammonium polyacrylate). Two phenomena are able to explain the stability of the viscosity when increasing the B-1035 binder content, despite the substitution of ceramic particles with complex shapes by spherical latex ones. Firstly, the temperature of the test (20°C) is 60°C above the glass transition of this binder. Latex particles are consequently 'soft' and could be easily deformed by low stresses. Therefore, as their amount increases, they could impede the relative motion of alumina particles, giving rise to an increase in viscosity. The second assumption concerns the surface of the latex particles which could have some free chains which could react with the medium.

3.1.2. Pure B-1050 binder

In the case of the B-1050 binder, the increase in binder content corresponds to a substitution of alumina particles which have an average size of 0·4 μm by latex particles with a smaller diameter in the range of 0·1 to 0·14 μm. The temperature of the test is only 10°C above the glass transition temperature of the B-1050 binder. Consequently B-1050 latex particles behave as small 'hard' spheres. Then, the expected decrease in the viscosity of the mixture, which can be attributed to an increase of the number of these smaller 'hard' spheres and, at the same time, to a decrease of the number of alumina particles, could probably be limited by interactions between the surface of the latex particles and the medium. Two antagonistic mechanisms might interact, namely a lubrication mechanism, with small 'hard' latex spheres and a thickening mechanism due to interactions between the polymer and its medium.

Finally, it appears that it is difficult to conclude without knowing the exact chemical composition of the binder, mainly the nature of the stabilizants used in these emulsion binders, which can react with the dispersant of the slurry. Nevertheless, changes in viscosity remain weak and from the tape casting process point of view, the binder nature (B-1035 or B-1050) and its concentration

(0 to 15 wt%) have small influence on the dispersion of the ceramic particles in the tape casting suspensions.

3.1.3. Mixtures of B-1035 and B-1050 binders

Figure 4 shows the viscosity curves of the slurries prepared with a mixture of the two binders for different binder contents. Whatever the considered system, the rheological behaviour is similar and the viscosity values are very close. However the small differences observed appear more pronounced with increasing binder content. The highest viscosity is obtained for the slurry without binder, and for the slurries prepared with pure B-1035 binder. Finally, the lowest viscosities were exhibited by the slurries containing a mixture of the two binders.

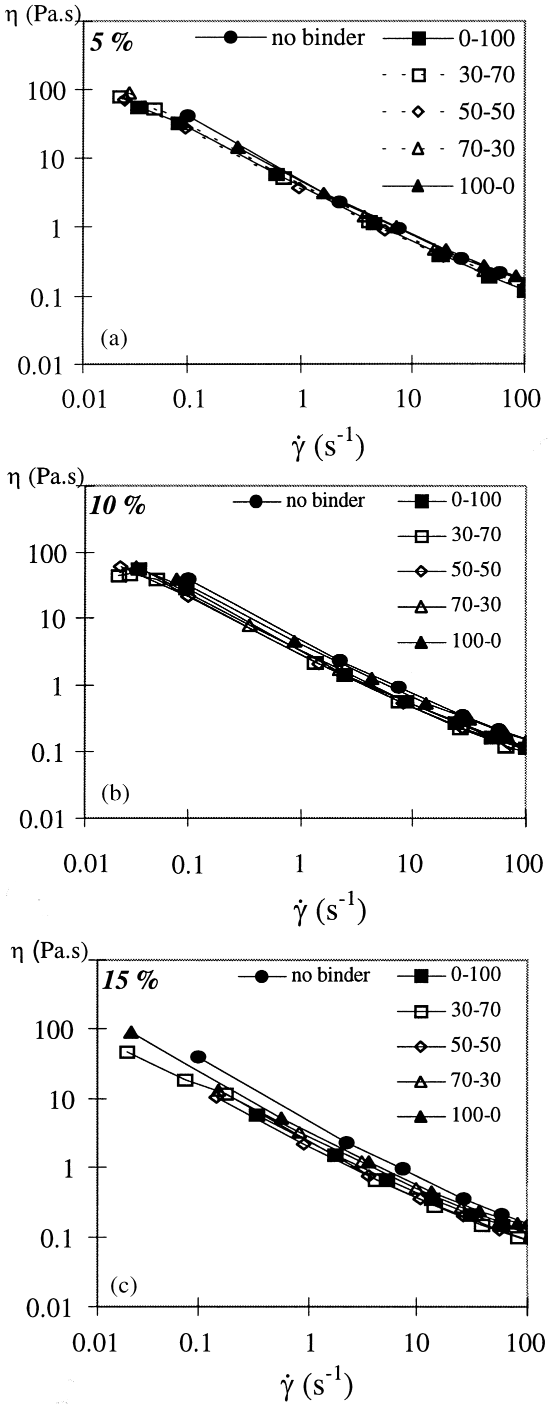
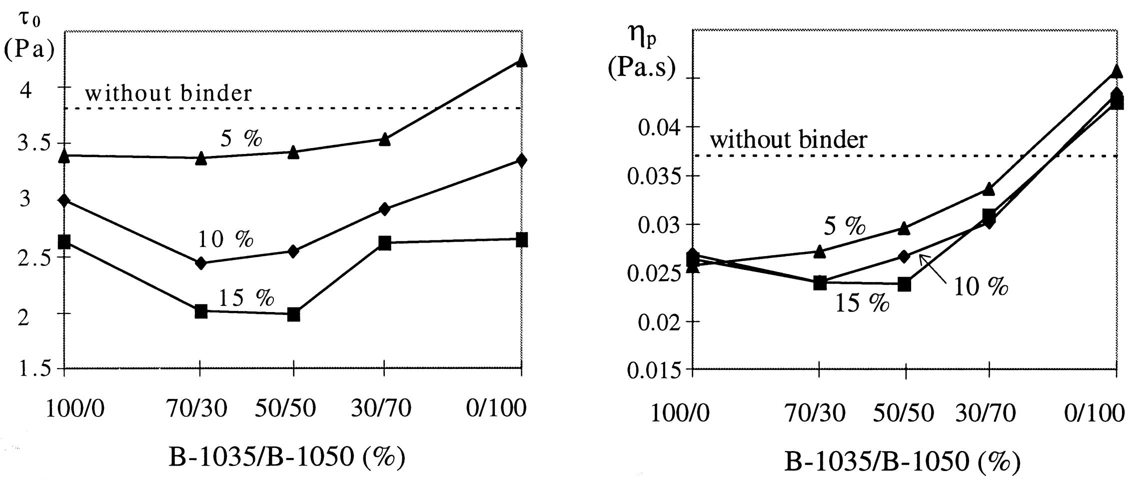


Fig. 4. Viscosity curves of slurries prepared with mixtures of the two binders (B-1035 and B-1050) in different ratios (100/0, 70/30, 50/50, 30/70, 0/100; the first number refers to the wt% of B-1035 and the second one to the wt% of B-1050) and for different active binder contents (5, 10 and 15 wt%) without solid loading adjustment (Table 2).

The effect of the binder composition on the rheological behaviour can be better appreciated from stress sweep experiments, expressed by plastic viscosity and Bingham (apparent) yield point (Fig. 5(a) and (b)). A combination of two binders leads to a minimum of viscosity, especially at high binder concentration (15 wt%). The highest plastic viscosity was obtained for the slurry prepared with pure B-1050 binder whereas the solid content slightly decreases because the B-1050 binder contains a lower concentration of latex particles than B-1035 (Table 1). This can be attributed to the crosslinkable structure of the B-1050 binder[14] that difficults its orientation in the flow direction and to its higher intrinsic viscosity than the B-1035 binder. The comparison of the characteristics of B1035 and B1050 binders (Table 1) suggests that the stabilizants used in these binders are different. Mixture of these binders in different proportions probably involved some changes in the interactions in this complex system among the various components, namely the different stabilizants of latex particles in B-1035 and B-1050 binders, the dispersant of the alumina particles (D-3005) and the alumina particles. A last parameter which could affect the viscosity of the suspensions and which can lead to a minimum of viscosity, observed for the suspension prepared with 50/50 B1035/B1050 binder, is the latex particle size distribution of the mixtures of the two binders possessing latex particles of different sizes and likely of different size distribution. As a result, we can assume that the changes in interactions and in latex particle size distributions could lead to a slurry with a minimum viscosity for a given binder composition.

To sum up the rheological investigations on this complex system in which numerous interactions could occur between the different components, the two following points could be underlined. First, at constant particle (latex + alumina) concentration into the suspension, the nature of the binder (B-1035 or B-1050) and its content (0 to 15 wt%) have small effects on the rheology of the system. Secondly, a mixture of B-1035 and B-1050 binders leads to a decrease of the suspension viscosity, especially at high concentration (15 wt%) of active binder, with a minimum for a B-1050/B-1035 ratio close to 1:1.



(a) (b)

Fig. 5. Plastic viscosity (η_p) and yield stress (τ_0) of the slurries prepared with mixtures of the two binders (B-1035 and B-1050) in different ratios (100/0, 70/30, 50/50, 30/70, 0/100; the first number refers to the wt% of B-1035 and the second one to the wt% of B-1050) and for different binder contents (5, 10 and 15 wt%) without solid loading adjustment (Table 2).

3.2 Tape casting and drying

A strong adherence was observed on the glass plate for all the compositions used. From the PET film, it was impossible to release properly the tapes containing 5 or 10% of binder (whatever the binder). For tapes containing 15% of binder it was possible to release them from this support, but it required many precautions to avoid tearing. Contrarily, in the case of PP film, all the tapes could be very easily released whatever the slip composition used. From a theoretical point of view, adhesion on a support of a dried tape containing polymer additives could arise from different mechanisms:[15] mechanical interlocking, interdiffusion of polymeric chains, electrical or chemical interactions. In our case, the three tested support (glass, PET, PP) exhibit almost the same smoothness. Mechanical interlocking is then unlikely as a mechanism to explain adherence on glass or PTE supports. During the drying, the latex particles coalesce to form a continuous matrix film between the ceramic particles. Therefore, interdiffusion of polymeric chains could not explain the adherence of the tapes on the PET plastic film. It remains two possible mechanisms (electrical or chemical interactions). According to the conclusions of Garbassi *et al.*[15] in their review about adhesion, electrostatic interactions can play a role in adhesion, but their contribution is generally less important than chemical interactions. Hence, we can assume that adhesion on the glass and PET film result from Lewis acid-base interactions. In agreement, these two supports exhibits polar surfaces whereas the PP film exhibits a quite non polar surface. Therefore, because of the weak adherence, the PP film was adopted for the whole study.

The drying is one of the most important processing steps in the tape casting manufacture. It enables to obtain a solid tape from a liquid slip. Specific investigations have been conducted to understand the mechanisms of tapes or films drying.[16–21] A two stage process was generally encountered: (i) a constant rate first stage, controlled by capillary migration of the solvent, and (ii) a second stage, controlled by the diffusion of the solvent through the solidified part of the film with a decreasing drying rate depending on the suspension composition. During the first stage, the solvent starts to evaporate from the top surface of the tape, allowing particles to approach each others. As a consequence, the curvature of the liquid/vapour 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:[21]

$$\Delta P = -2\gamma_{LV}/r \tag{1}$$

where γ_{LV} is the liquid/vapour interfacial energy (or surface tension) and r is the radius of curvature of the menisci. When the center of the curvature is in the vapour 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. At the beginning of the drying (first stage), the viscosity of the fluid phase is low enough to allow ceramic particle rearrangement, avoiding internal stresses. The contraction of the tape in the direction perpendicular to the casting plane involved by this rearrangement compensates the loss of solvent.

Therefore, the liquid–vapour interface remains at the surface of the tape.

Progressively as the evaporation proceeds, the liquid in the tape becomes enriched in polymeric binder. This involves an increase of the viscosity which changes the fluid flow within the pores and the evaporation feature. So in the second drying stage, the contraction rate can not more matches the evaporation rate. Therefore the surface of the tape solidifies and the liquid/vapour meniscus penetrates into the tape. The drying rate is now governed by the diffusion of the solvent and decreases in comparison to the drying rate in the first step.

During this second stage, internal stresses occur which could lead to cracking of the green tapes. The magnitude of these stresses result from the balance of two opposite phenomena: one tending to increase the stress level due to constrained volume shrinkage and the other tending to decrease the stress level due to the relaxation of the polymeric phase. The tape is constrained by the support and, hence, contraction (or shrinkage) could only occur perpendicularly to the surface, i.e. along the tape thickness. Therefore, the development of stresses in the tape appears to be unavoidable despite the relaxation that could occur in the polymer matrix.[22] In addition, the high viscosity reached by the fluid phase in the second drying step hinders particle rearrangement, giving rise to stresses. Consequently, it is suitable to have a first drying step as long as possible. Different authors[22,23] have shown that this step is very short in the case of tape-casting using organic media. We can assume that this step is longer in the case of water-based suspensions. Intensity of the drying stresses will depend, for a given system, on the tape geometry (thickness) and on drying conditions.

In order to avoid cracking, a critical casting thickness (CCT) value was introduced as the tape thickness that never should be exceeded. This CCT depends on the slurry composition and on the drying rate. Any accurate measurements of the CCT were carried out on our slurries dried under

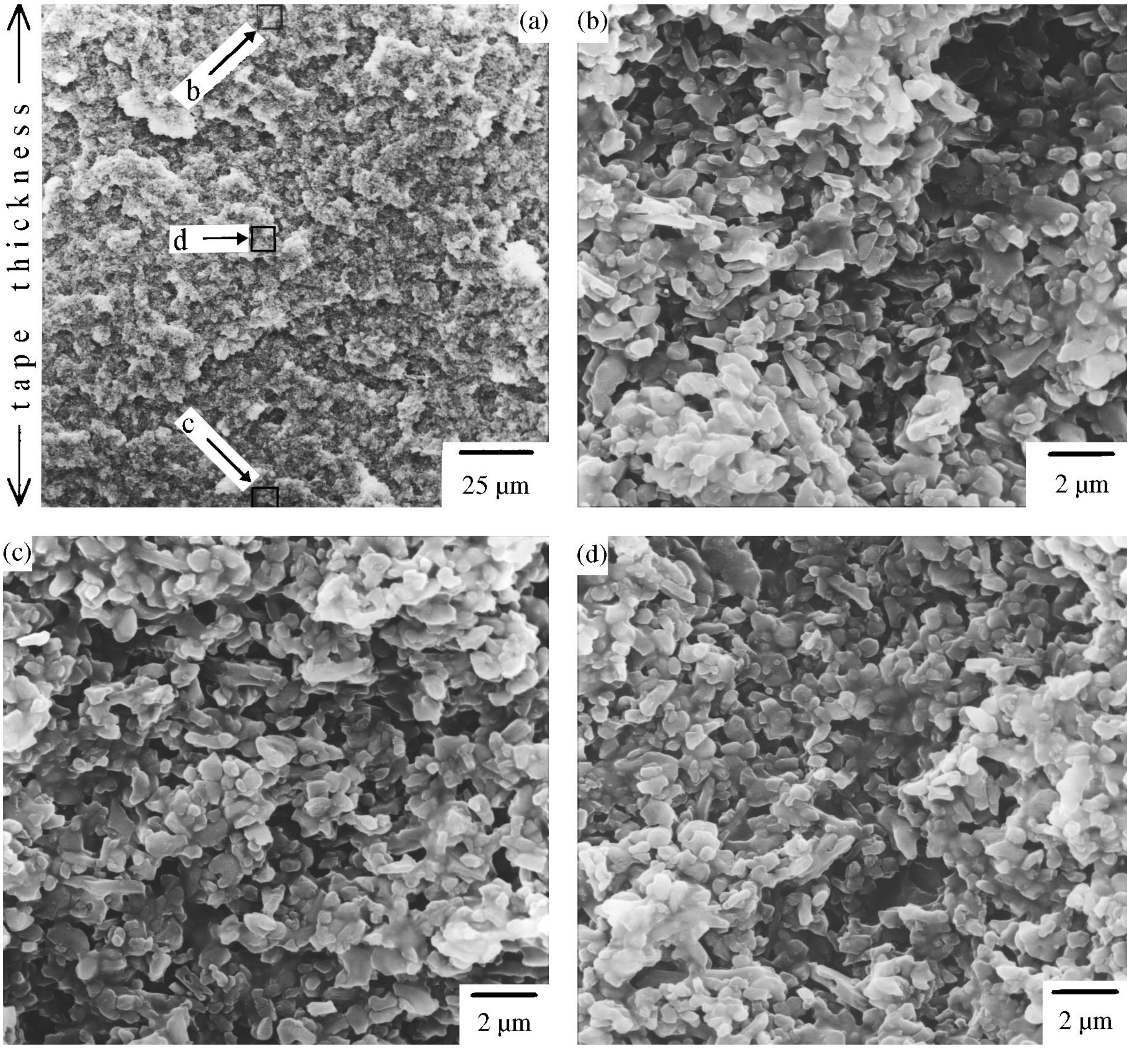


Fig. 6. (a) Cross-section of a green tape (15 wt%—B-1050 binder) along the whole thickness; (b) (c) and (d) micrographs correspond to the top surface, the enter and the bottom surface in contact with the casting support, respectively.

the above condition (i.e. air at room temperature). The CCT seems to be close to 500 μm for the slurry prepared with 15 wt% of the B-1050 binder (Tg = 10°C) and above 750 μm for the slurry prepared with 15 wt% of the B-1035 binder (Tg = −40°C). The B-1050 binder exhibits smaller latex particles (0·1–0·14 μm) than the B-1035 one (0·37 μm). On one hand, the mechanical efficiency (i.e. the bond between ceramic particles) of the high Tg B-1050 binder is greater than that of the low Tg B-1035 binder. On the other hand, the closure of the interparticle channels occurs quickly at the surface of the tape for the slurry containing small particles (in our case B-1050 latex particles) and for a binder leading to a strong bonding between ceramic particles (in our case B-1050 binder). Hence, the duration of the first drying stage is shorter in the case of the B-1050 binder, that increases the drying stresses during the second stage. Moreover, the higher Tg of the B-1050 binder leads to a lower relaxation of the polymeric phase than for the low Tg B-1035 binder. This suggests that the development of stresses during drying is enhanced in the green tapes prepared with the B-1050 binder, increasing the risk of cracking.

The duration of the drying step is a critical point in the case of industrial production where continuous tape casters are used. However, in our investigation, the duration of drying is less critical and we have chosen natural drying conditions with air at room temperature. For a tape containing 15 wt% of B-1050 binder, with a thickness of 350 μm just after casting, the complete drying time is estimated at 5 h. The complete removal of water has been confirmed by thermogravimetric analysis. A long drying time could be a drawback for low viscous suspensions because it could lead to settling of particles to produce green tapes with a non homogeneous microstructure. In our case, the homogeneity of the particle packing was preserved through the tape thickness (Fig. 6). This is likely due to the high solid content of the slurries and their flow properties characterized by a shear-thinning behaviour that allows the suspensions to return at a high level of viscosity after being sheared under the blade.

3.3 Properties of the green tapes

For the three binder contents, both sides of the tapes exhibited bright and very smooth surfaces and deairing step did not seem to be necessary in the slip preparation process.

Both the top surface and the bottom face in contact with the polypropylene film of the green tapes prepared with 15 wt% of the pure B-1035 binder then burned out at 500°C for 4 h present a similar microstructure, attesting the homogeneous particles packing in the green tape (Fig. 7). It clearly appears in Table 3 that increasing the binder content, slightly decreases the relative density of

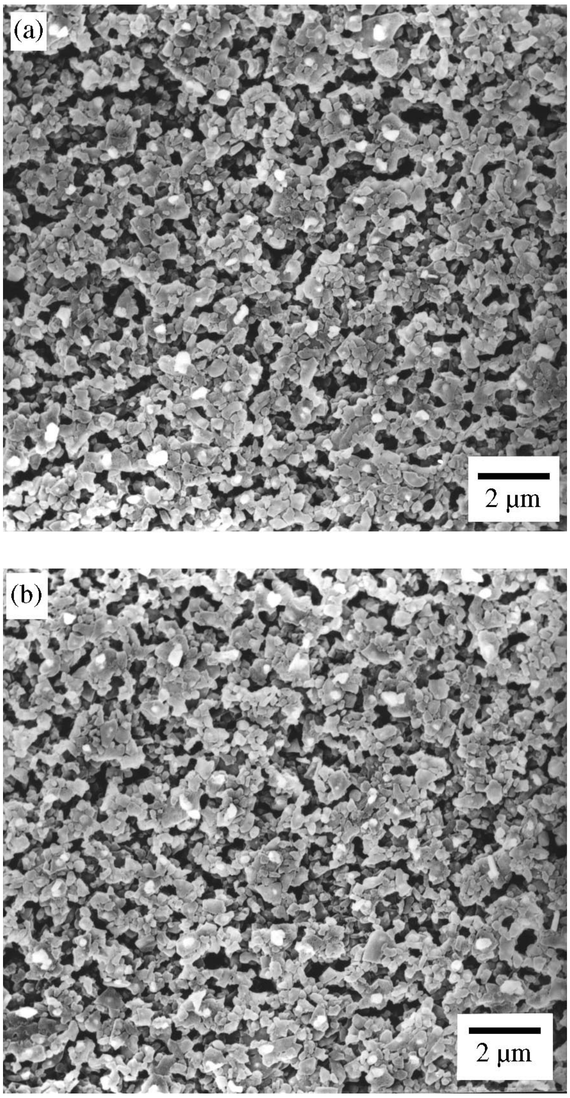


Fig. 7. Microstructure of both sides of a tape prepared with 15 wt% of pure binder after binder burning-out at 500°C for 4 h. (a) top surface in contact with air, (b) casting support surface.

Table 3. Relative densities of the green tapes (d_{exp}: experimental density, d_{r}: relative density, d_{a} average relative density for each binder content, dAl$_2$O$_3$: 3·98)

Binder content (wt%) and composition	d_{exp}	d_r	d_a
5% (100% B-1035)	2·23	56·03	
5% (70% B-1035 + 30% B-1050)	2·21	55·53	
5% (50% B-1035 + 50% B-1050)	2·22	55·78	56·03
5% (30% B-1035 + 70% B-1050)	2·24	56·28	
5% (100% B-1050)	2·25	56·53	
10% (100% B-1035)	2·08	52·26	
10% (70% B-1035 + 30% B-1050)	2·06	51·76	
10% (50% B-1035 + 50% B-1050)	2·09	52·51	52·16
10% (30% B-1035 + 70% B-1050)	2·07	52·01	
10% (100% B-1050)	2·08	52·26	
15% (100% B-1035)	2·01	50·50	
15% (70% B-1035 + 30% B-1050)	1·99	50·00	
15% (50% B-1035 + 50% B-1050)	2·00	50·25	50·30
15% (30% B-1035 + 70% B-1050)	2·00	50·25	
15% (100% B-1050)	2·01	50·50	

the green tapes. A larger amount of binder leads to a higher porosity after burning-out of organic components. Whatever the binder content, the relative green density is greater than 50% before lamination. These values are similar to values encountered with other aqueous systems.[24]

4 Conclusion

This work has shown the efficiency of acrylic emulsion binders (Duramax B-1035 and Duramax B-1050), associated with an ammonium polyacrylate dispersant (Duramax D-3005) to produce ceramic slurries suitable for aqueous tape-casting. The preparation of high concentrated suspensions is facilitated by (i) the dispersion of ceramic particles in water, compared to organic media, (ii) the low viscosity of the binders, and (iii) the absence of deairing step before casting. The shear thinning behaviour fits the tape-casting requirements and lead to green tapes with a high microstructural homogeneity and with a very good aspect of the surface.

The tape casting slurries containing the alumina particles, the acrylic emulsion binders and a dispersant are complex systems in which numerous interactions could occur between the different components. However, it appears that at constant particle (latex + alumina) concentration, the nature of the binder (B-1035 or B-1050) and its content (0 to 15 wt%) have small effects on the rheology of the system. Nevertheless, a mixture of the low Tg binder (B-1035) and the high Tg one (B-1050) leads to a decrease of the suspension viscosity, especially at high concentration (15 wt%).

The low Tg B-1035 binder allows to produce thicker tapes than the high Tg B-1050 one, without cracking during drying in air at room temperature. The 'soft' (lower Tg) latex particles reduce the internal stresses during drying and lead to higher critical cracking thickness than the larger size 'hard' (high Tg) particles.

The high concentrated suspension enables the production of homogeneous green tapes with a green density greater than 50%.

Mechanical properties of green tapes, lamination behaviour and sintering conditions are now being studied to determine the optimal composition of the tape casting slurry and will be presented in a further paper.

Acknowledgements

This work has been performed in the frame of a Human Capital and Mobility programme, contract no. CHRX CT94 0574. We want to thank the European Community for its financial support.

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