Journal of the European Ceramic Society 18 (1998) 241–247
Published by Elsevier Science Limited

PII: S0955-2219(97)00115-5
0955-2219/98/$19.00 + 0.00

Aqueous Suspensions for Tape-casting Based on Acrylic Binders

C. Pagnoux,[a] T. Chartier,[a]* M. de F. Granja,[b] F. Doreau,[b] J. M. Ferreira[b] and J. F. Baumard[a]

[a]LMCTS, CNRS UPRES A 6015, ENSCI, 47–73 avenue Albert-Thomas 87065 Limoges, France
[b]Glass and Ceramic Engineering Department, Universidade de Aveiro, 3810 Aveiro, Portugal

(Received 20 January 1997; accepted 30 May 1997)

Abstract

The use of water-based systems represents an interesting alternative to the widespread non-aqueous tape-casting but the low strength of water-based binders generally limits their applicability. A tape-casting slurry is a complex system where each organic component has a substantial effect on the rheological behaviour. In this study the effect of the dispersant and binders in alumina aqueous tape-casting slurries were characterized with electrophoretic mobility and rheological measurements. In aqueous medium, a 4,5-dihydroxy-1,3-benzenedisulfonic acid, was found to be a very effective dispersant for alumina. The amount of dispersant required to achieve a minimum of viscosity was equal to 0·2 wt%. Two aqueous emulsions of acrylic polymers were used as binders. These binders strongly affect the rheology of the suspensions. The best conditions to obtain a homogeneous stable slurry with a high powder loading suitable for tapecasting were determined in terms of order of component addition, rheological behaviour and ageing of the suspensions. Acrylic binders should act through a cohesive mechanism and lead to green tapes with good mechanical strength. Published by Elsevier Science Limited.

1 Introduction

Tape-casting is the prominent process used to produce thin and flat ceramic sheets mainly for the electronic industry.[1–3] Tape-casting, basically, consists of preparing a suspension composed of the ceramic powder dispersed in a solvent, with addition of dispersants, binders and plasticizers. 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 can be cut to the appropriate shape. After removal all organic components, green sheets or multilayer systems are sintered.

A tape-casting slurry is a complex system in which each component has a substantial effect on the rheological behaviour of the slurry. The major function of a solvent is to act as a dispersing vehicle and to ensure the dissolution of the organic components (i.e. dispersant, binders and plasticizers) which should be inert toward the ceramic powder (oxidation and hydrolyse). Homogeneous dispersion of ceramic particles in a highly loaded suspension is required to obtain a reliable production of high quality products. Using micron and submicron-size ceramic particles, a dispersing agent must be added to prevent the particle agglomeration caused by the strong electrostatic forces associated with the high surface area/mass ratio.[4] The selected binder, plasticizer and dispersant should be soluble in the chosen solvent.

Tape-casting systems may be classified according to the type of solvent used. Organic solvents are generally used for tape-casting.[5,6] Depending on the composition of the ceramic powder and on the thickness of the tape, a variety of non-aqueous organic solvents such as alcohols, ketones or hydrocarbons are commonly used to prepare highly concentrated suspensions with reproducible rheological properties and drying behaviour. Non-aqueous solvents have low boiling points and prevent the ceramic powder from hydration, but require special precautions concerning toxicity and flammability.

The low strength of water-based binders limits their applicability, while slow evaporation and agglomeration due to hydrogen bonding make water-based systems less attractive.[7] Until now, aqueous systems are used for non-critical applications where slow evaporation and high binder

*To whom correspondence should be addressed.

concentration can be tolerated. Nevertheless, water-based systems would be preferred in terms of toxicity, environmental consistency and price and the use of water-based systems represents an interesting alternative to the widespread non-aqueous tape-casting. A comparison of aqueous and non-aqueous slurries for tape-casting is reported by Nahass *et al.*[8] Compared with non-aqueous solvents, the variety of water-soluble binders and plasticizers systems is restricted.[9]

The technological advances in aqueous-based additives, especially aqueous-based acrylic binder emulsions, have allowed tape-casting of ceramic powders to be transposed from organic solvent-based to aqueous-based processes. The colloidal properties of polymer emulsions, specifically developed for ceramic applications, lead to formulations containing high solid contents in well-dispersed systems. Moreover, these emulsions have useful and unique characteristics such as internal plasticization and controllable crosslinking.[10] Such cross-linked polymers provide a good cohesion to the green sheet but with a low strain to failure. In order to produce green tapes with a good flexibility, the addition of a low glass transition temperature (Tg) emulsion binder could be beneficial.[11]

The aim of this study is to prepare high concentrated and well dispersed alumina aqueous suspensions for tape-casting technology. The effects of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate, $(HO)_2C_6H_2(SO_3Na)_2$, as dispersant and two selected acrylic polymers as binders on the properties of alumina slurries were investigated by using electrophoretic mobility and rheological measurements. A particular emphasis is given to the influence of each organic additive on the rheological behaviour of the suspension.

2 Experimental procedure

2.1 Starting materials

The powder used in this study was the Alcoa A-16SG alumina (Pittsburgh, USA) with an average particle size of 0·40 μm (Sedigraph 5100, Micromeritics) and a specific surface area of 8·1 m^2g^{-1} degased at 300°C during 2 h (N_2 BET).

The dispersant used was the 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate (Tiron, Aldrich). In aqueous solutions, ionic Tiron molecules dissociate into negative ions which act to produce the stabilising electrical double-layer according to the DLVO theory. Tiron was found to be a very effective dispersant for alumina powder in deionized water. The strong dispersing effect of Tiron is attributed to the adsorption ability of the phenolic OH groups and to the creation of surface charges by the deprotonated sulfonic groups.[12]

Two acrylic polymers were used as binders, a high Tg binder (Duramax® B-1050, Rohm and Haas, Tg = + 10°C) and a low Tg one (Duramax® B-1035, Rohm and Haas, Tg = 40°C). These binders are aqueous emulsions that contain 48 and 55 wt% of polymers, respectively. Their molecular weights are higher than 10 000.

2.2 Preparation of the suspensions

The standard procedure for preparing suspensions for viscosity or ESA measurements involved two steps. First, the deagglomeration of the alumina powder in the deionized water, with the dispersant, by ultrasonic treatment (pulsed, 3 min, 600 W, Vibra-cell ultrasonic desintegrator VC 600, Sonic & Materials, USA). Then after 12 h, binders were added and suspensions stabilised for 24 h by using a low-speed rotating roller.

2.3 Characterisation

2.3.1 Zeta-potential experiments

Electrokinetic measurements provide information on the magnitude of the electrostatic forces of repulsion between ceramic particles. Zeta potential values of the alumina particle charges in the suspensions were measured using an Electrokinetic Sonic Amplitude (ESA) measurement apparatus (Model ESA 8000 Matec).

This technique is based upon the acoustic wave which is generated by the respective motion of the electric double-layer ions and of the charged particles submitted to a high frequency alternating electric field (1 MHz). This motion generates a sound wave at the same frequency as the electric field with an amplitude proportional to the electrostatic potential at the shear plane where the zeta potential is defined, to the particle concentration and to the amplitude of the applied electric field.

The ultrasonic signal is detected and converted to a voltage (ESA) by a piezoelectric transducer. In the case of our suspensions, the ESA data are directly proportional to the zeta potential, then the curves of variations of the electrokinetic properties in function of pH and/or dispersant amounts will be presented with ESA values as the *Y* axis.

At the solid loading used, the relation between the magnitude ESA signal and the dynamic electrophoretic mobility μ_d of the particles is linear:

$$\mu_d(\omega) = ESA(\omega)/c\Delta\rho\phi \quad (1)$$

where ω is the angular frequency of the applied field, c the velocity of sound in the suspension, $\Delta\rho$

the difference of density between the particles and the liquid and ϕ the volume fraction of the particles.

The zeta potential ζ can then be calculated according to O'Brien's formula:[13]

$$\zeta = \mu_d(\omega)\eta G(\alpha)^{-1}\,\varepsilon^{-1} \quad (2)$$

where is the dielectric permitivity of the suspension, η the viscosity of the liquid and $G(\alpha)$ is a term which corrects for the inertia of the particle in the alternating field which acts to reduce the velocity amplitude of the particle motion for a given potential zeta. $G(\alpha)$ is dependent on ω, on the particle radius and on the kinematic viscosity of the liquid.

ESA signals are useful at high solid contents (up to 10 vol%) and are highly reproducible if careful control of temperature, dispersing conditions and solid content are ensured.

Slurries were prepared with a 3·5 vol% solid loading with the required amount of dispersant and/or binders. The ionic strength was previously adjusted with 0·01 M NaCl. During the ESA experiments, the pH was adjusted with HCl 1 M and NaOH 1 M. To maintain homogeneous dispersion during measurement, a magnetic stirrer is placed under the sample.

2.3.2 Adsorption curves

Slurries were prepared with 60 wt% solid loading with different amounts of Tiron. After 12 h to attain chemical equilibrum, the pH 9 was measured. Slurries were centrifugated and supernatants cloudy due to the well dispersed finest particles of alumina were removed. To clarify the supernatants, 2 g of NH_4Cl (> 99·99% Aldrich), an inert electrolyte, were added in each sample. The increase of the ionic strength leads to the compression of the electrical double layer around each particle and particles settled easily providing a clear supernatant. A second centrifugation was performed to remove clear supernatants. As Tiron is a salt of sodium, the sodium content in the supernatants was determined by inductively coupled, argon plasma, atomic emission spectrometry. The Tiron adsorption was calculated from the difference between the amount of Tiron added and that remaining in the supernatant.

2.3.3 Viscosity experiments

The viscosity was measured using a Controlled Stress Rheometer (Carri-med CSL 100, England) using a cone/plate configuration. The rheological behaviour of suspensions was modelled using the Herschel–Bulkey's equation:

$$\Gamma = \Gamma_o + K(D)^n \quad (3)$$

where Γ is the applied stress (Nm^{-2}), D the measured shear rate (s^{-1}), Γ_o the yield stress (Nm^{-2}), K a viscosity coefficient and n the shear rate exponent.

2.4 Tape-casting

Suspensions were cast onto a fixed Mylar carrier surface using a Doctor Blade equipment (Cerlim Equipment, Limoges, France). The casting speed was constant at $v = 1{\cdot}2\,cm\,s^{-1}$ and the gap between the blade and the support was adjusted at $h = 600\,\mu m$. The shear rate generated during casting is then evaluated at $20\,s^{-1}$. Then, the apparent viscosity of suspensions was taken into account at $D = 20\,s^{-1}$.

3 Results and Discussion

3.1 Effect of dispersant

The effect of Tiron on the state of dispersion was studied without binder addition. An A16SG alumina suspension exhibited a pH value of 9 and an ESA amplitude of $-0{\cdot}7$ mPa.m. V^{-1}. The zero point of charge (zpc) for alumina (Alcoa A16SG) was approximately pH 8 (Fig. 1). When an amount of 0·2 wt% of Tiron was added, the natural pH of the slurry did not change any more. The anion adsorbed to the surface of alumina and produced a negative surface charge with a high density, leading to a better dispersion. The zero point of charge shifted toward pH 4 where the negative charges produced by the anion were neutralized.

ESA data were recorded versus amount of dispersant (Fig. 2). A slurry was prepared for each concentration and no salt was added. After 24 h to achieve chemical and physical equilibrium, a pH 9 was measured whatever the amount of Tiron is.

The ESA data reached a high value ($-3{\cdot}9$ mPa.m V^{-1} corresponding to $\zeta = -53$ mV)

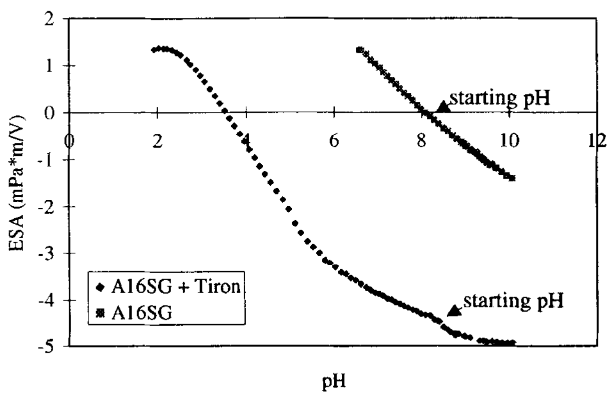

Fig. 1. ESA data versus pH for alumina slurries without deflocculant and with 0·2 wt% of Tiron with respect to alumina.

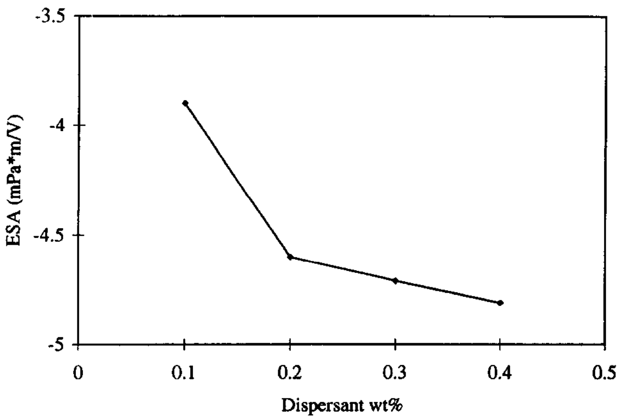

Fig. 2. ESA data of alumina suspension versus dispersant amount with respect to alumina (pH = 9).

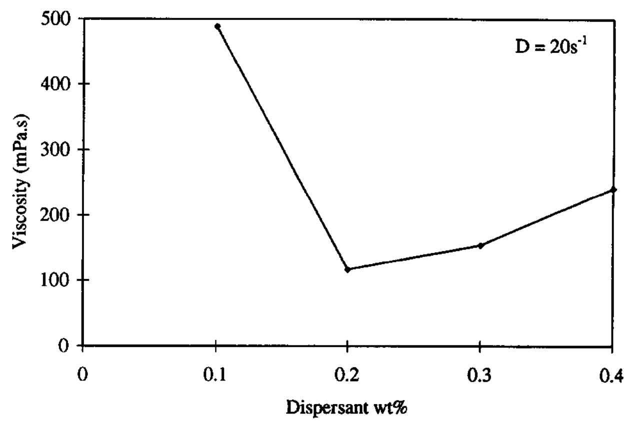

Fig. 4. Viscosity at $20\,s^{-1}$ of alumina suspension (80 wt%) versus amount of Tiron at pH = 9.

with an addition of a low amount of dispersant (0·1 wt%), suggesting a good state of dispersion. Then the value of ESA was almost constant ($-4{\cdot}8$ mPa.m.V^{-1} corresponding to $\zeta = -71$ mV) for amounts of dispersant ranging from 0·2 to 0·4 wt%.

The adsorption curve of Tiron on A16SG alumina particles is shown in Fig. 3. For 0·2 wt% of Tiron introduced, 50% (0·18 mg m^{-2}) of dispersant was chemisorbed and 50% remained in solution. For initial amounts of Tiron higher than 0·2 wt%, the quantity chemisorbed increased slowly and the amount of dispersant which remained in the solution was more and more important. Tiron is an ionic and hydrophilic compound and had a low affinity for the surface of alumina particles and a large quantity of dispersant remained in the solvant.

In order to optimize the quantity of Tiron corresponding to the best state of dispersion, slurries were prepared with 80 wt% solids loading with different amount of Tiron for viscosity measurements.

Viscosity decreased with Tiron addition until a minimum value (116 mPa.s) was reached for 0·2 wt% of Tiron (Fig. 4). Further additions resulted

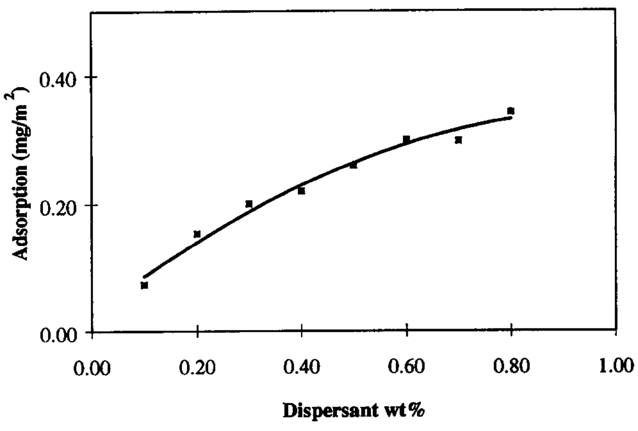

Fig. 3. Adsorption isotherm of Tiron on alumina.

in an increase in viscosity. A low viscosity (about 100 mPa.s) achieved a rather high powder loading (80 wt%) demonstrating that Tiron is an efficient dispersant for alumina powders in aqueous media.

The magnitude of the ESA signal increased very fast with addition of deflocculant up to 0·2 wt% of Tiron and reached a plateau for higher concentrations. The minimum of viscosity and the beginning of the plateau of the surface charge were reached for the same value of dispersant (i.e. 0·2 wt%). This suggests that a low amount of Tiron involved a significant contribution of the electrostatic mechanism to the repulsion between alumina particles.

Gauckler *et al.*[14] reported that an organic molecule of phenol with one phenolic group in ortho position chemisorbs onto the surface of alumina. The sulfonate groups ionised at pH 9·0 developed negative charges at the surface of the alumina particles. For amounts of Tiron higher than 0·2 wt% the viscosity of slurries increases because of ions concentration and then the ionic strength increase. The diffuse electrical double layer around each particle is compressed by the ions and the repulsive potential is reduced. This effect is observed on rheological measurements but not on ESA measurements. This suggests that the viscosity is much more sensitive to small changes in the dispersant concentration. Thus, in order to evaluate the required amount of Tiron for the slurry, the viscosity measurement was chosen.

3.2 Effect of binder

The binder content of the suspension was expressed as the dry weight base of the binder (latex particles) with respect to alumina.

Alumina particles in the suspension prepared with the B-1035 binder or the B-1050 binder exhibited the same amplitude of the ESA signal for pH in the range 6–10 as particles in suspension

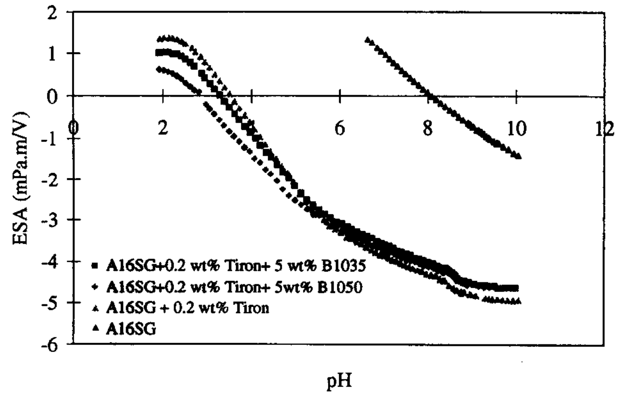

Fig. 5. ESA data versus pH for alumina slurries.

prepared with only the dispersant (Fig. 5). Then binders seem to have no influence on the charge density of alumina particles dispersed with Tiron. Both binders emulsions (B-1050 and B-1035) containing about 50 vol% of active latex particles exhibited a very weak amplitude of the ESA signal (ESA = $-0{\cdot}4$ mPa.m. V^{-1}) at pH 9. This suggested that binders did not seem to involve a significant contribution to electrostatic repulsion between alumina particles and did not affect the efficiency of Tiron on this.

Nevertheless, binders strongly affect the rheological behaviour of the liquid phase (without powder) and of the suspensions, increasing the viscosity and changing the characteristics from Newtonian (for pure water) to shear thinning in most cases. The shear-thinning behaviour of suspensions is desirable in many colloidal processing methods, including tape-casting of ceramics. During the casting process, slurry viscosity decreases under the shear stresses generated by the doctor-blade. Immediately after the shear is released (and during storage), the slurry viscosity returns to a high level. This avoids any settling of the particles and preserves a homogeneous distribution of the ceramic particles and of organic components in the tape by reducing the mobility of the constituents.

In order to better understand the contribution of each component on the rheological behaviour of the system, the viscosity of slurries (71·7 wt% Al_2O_3) was measured after addition of each binder and after addition of a mixture of binders with different sequences of introduction, i.e. simultaneous addition or with addition of a second binder, B-1035 or B-1050, 24 h after introduction of the first one.

The yield values, shear rate exponent and apparent viscosity values calculated by Herschel–Bulkey's equation are reported in Table 1.

Addition of binders to the slurry imparts a high shear-thinning flow behaviour showed by the values of shear rate exponent ($n<1$). The slurry prepared with only the B-1050 binder exhibited a high viscosity ($\eta=6$ Pa.s at 20 s^{-1}) and a high yield stress value comparing with the effect of the B-1035 ($\eta=0{\cdot}48$ Pa.s at 20 s^{-1}). Binders have similar density and size of latex particles but their chemical composition and their Tg were different. These aqueous emulsions consist of latex particles which are stabilized with a deflocculant agent. Depending on the nature of the stabilizing agent and on the chemical composition, each binder may affect differently the rheological behaviour of Al_2O_3 suspensions.

Whatever the sequence of binder addition, slurries with a mixture of the two binders showed similar rheological behaviour (values of viscosity, shear rate exponent and yield stress) and exhibited intermediate values between the slurries prepared with pure B1035 and pure B1050 binder.

Binders are added to slips in order to enhance the strength of the green tape after the solvant has evaporated. With a high molecular weight ($>10\,000$) and a low glass transition temperature (Tg = +10°C), the B-1050 should be an efficient binder. Furthermore, tapes prepared from organic slurries are more easily thermocompressed when the amount of binder increases. The binder ensures a good strength between the sheets and good quality interfaces in multilayer structures.[15,16]

To confer sufficient flexibility to the green tape for easy handling and storage, a plasticizer should be added in the tape-casting slurries. The most important effect of the plasticizer is to reduce the Tg at room temperature or less. The B-1035 polymer with a low Tg reduces the viscosity of the

Table 1. Values of apparent viscosity (20 s^{-1}), yield stress, shear rate exponents of suspensions with 71·7 wt% alumina, 0·25 wt% Tiron (Al_2O_3 + T + H_2O) and with 10 wt% solid binders. (B-1035 + B-1050): simultaneous addition, (B-1050) + B-1035: B-1050 added first, then 24 h later, introduction of B-1035. (B-1050/B-1035 = 0·7)[11]

Slurries (71·7 wt% Al_2O_3) T≡Tiron	η *(D = 20 s−1)* Pa.s	*Yield stress* Γ_o *(Nm^{-2})*	*Shear rate exponents* n
Al_2O_3 + T + H_2O	0·025	0·3	0·96
(Al_2O_3 + T + H_2O) + B-1035	0·48	1·1	0·50
(Al_2O_3 + T + H_2O) + B-1050	6	10·0	0·20
(Al_2O_3 + T + H_2O) + (B-1050 + B-1035)	1·37	1·8	0·35
(Al_2O_3 + T + H_2O) + (B-1050) + B-1035	1·37	1·8	0·35
(Al_2O_3 + T + H_2O) + (B-1035) + B-1050	1·40	1·5	0·37

system and then acts as a plasticizer. According to the results of the Table 1, the slurry with B-1035 (Tg = −40°C) exhibits the lower viscosity over the classical shear rate used for tape-casting (10–30 s^{-1}) but the necessary addition of the binder B-1050 (Tg = + 10°C) increases the viscosity of the slurry restricting the solid's content.

To tape-cast a slurry in the optimum conditions, the viscosity of the suspension at 20s−1 should be in the range of 1000–1500 mPa.s. In our system, this experimental conditions were achieved using a slurry with 71·7 wt% alumina solid loading. According to the results presented in Table 1, the binders will be added simultaneously in the tape-casting slurries for the ageing study.

3.3 Ageing

Previous studies[6,17] showed that addition of binders could desorb the dispersant during time and that the optimum amount of dispersant needed to achieve a minimum of viscosity for the complete suspension was higher than in the powder/solvent/dispersant system.

The effectiveness of the Tiron in the solvent/dispersant/powder system is a strong function of the amount adsorbed. To determine if this result applies to the entire system, the viscosity of suspensions with two amounts (0·2 and 0·3 wt%) of dispersant was measured as a function of ageing time.

Just after preparation, the apparent viscosity of the two suspensions are very close. Binders were the organic additives which strongly influenced the rheological behavior, and a small difference between two amounts of Tiron (from 0·2 to 0·3 wt%) which led to a 50 mPa.s viscosity increase in the powder/solvent/Tiron system (Fig. 4) did not significantly influence the apparent viscosity at 20 s^{-1} of the complete suspension with a viscosity of about 1400 mPa.s (Fig. 6).

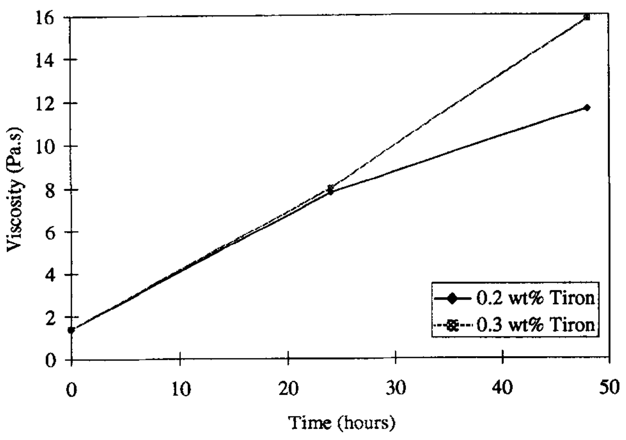

Fig. 6. Apparent viscosity of alumina slurries (71·7 wt%) with binders (10 wt%; B1050/B1035 = 0·7) (simultaneous addition) for 0·2 and 0·3 wt% of Tiron versus ageing time.

During the first 24 h, viscosity increased in the same way for the two suspensions. For longer ageing time, the viscosity increased more quickly for the slurry containing 0·3 wt% of Tiron.

In order to interpret the interactions between powder, Tiron and binders, two hypotheses can be avanced. In the first hypothesis, acrylic binders did not adsorb onto the surface of alumina and acted mostly through a cohesive mechanism rather than through an adhesive one. The latex particles were chemically bonded together forming a 3D network and creating a matrix around alumina particles. The relatively large and expanded polymer chains bridged alumina particles. When the two binders were added, they created a mix matrix where both binders contributed at the same time to the viscosity of the slurry.

In the second hypothesis a chemical equilibrium can be established for adsorption between the dispersant and the binders and there was no preferential adsorption.

On the other hand, the ESA signal amplitude, ionic conductivity and pH of a slurry prepared with 0·2 wt% Tiron and a 10 wt% mixture of the two binders (B1050/B1035 = 0·7) remained constant during 24 h, indicating that binders did not desorb Tiron from the surface of alumina particles and did not affect the efficiency of the dispersant during time.

As discussed earlier Tiron had a low affinity for the alumina surface and according to the fact that Tiron was not desorbed by binders, the acrylic binders used did not seem to adsorb onto the alumina surface and probably acted through a cohesive mechanism. The constant values of ESA signal amplitude, ionic conductivity and pH during time confirmed that no chemical interactions between dispersant and binders were effective.

During time the mix matrix created by the two binders should become more viscous, in another way emulsions should be destabilized. This can be attributed to the cations produced by the decomposition reaction into water of some oxides which are contained in alumina powder as impurities.[18] For instance, A16SG alumina contains 0·06 wt% of Na_2O and at pH 9 the decomposition of this oxide was effective and led to a Na^+ concentration of 1500 mg per liter of fluid according to the tape-casting formulation. In the same time, the Na+ concentration due to the non-adsorbed Tiron was about 460 mg l^{-1} for an initial addition of 0·2 wt%. Cations may interact with binder and lead to a gelation of the matrix. Gelation was more important when the amount of Tiron, and then the concentration of Na^+, were high. This interpretation was supported by the fact that the viscosity of a suspension with the same composition but prepared with a high purity alumina (AKP30, Sumitomo, Japan purity > 99·99%) did not vary during time. Ions released from the surface of A16SG powder actually interact with the acrylic binders used and can be detrimental to the rheological behavior when suspensions are submitted to ageing for instance for de-airing prior tape-casting.

Just after preparation slurries were tape-cast, the green bodies were easily removed from the Mylar surface and no cracks were detected but samples were brittle. These first tests of casting showed the necessary addition of the binder with a low Tg to enhance the workability of the tape.

4 Conclusion

Tiron has proved to be a very efficient dispersant for alumina. A low amount (0·2 wt%) allows to achieve a high density surface charge ($\zeta = -70$ mV) in a large range of pH. Acrylic binders used did not reduce the repulsive potential due to the dispersant and should not be adsorbed onto the surface of particles but should create a mix matrix around particles of alumina. They probably acted through a cohesive mechanism. Due to no adsorption of the binders onto Al_2O_3 particles, slurries exhibited the similar rheological behaviours whatever the sequence of addition aqueous emulsions. During time, this polymeric matrix became more and more viscous. Aqueous emulsions of latex particles should be destabilized by the cations produced by the decomposition of some oxides present as impurities in the alumina powder.

Further work will concern the effect of the total concentration of binders and of the relative concentration between the two binders on the rheological behaviour. The aim will be to find the best agreement between the green density and the mechanical strength of the green bodies.

Acknowledgements

This work was supported by the European Commission CEC Human Capital and Mobility Programme, Contract CHRX-CT94-0574, 'Application of fundamental principles of colloid and interface science and rheology to ceramic forming processes.'

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