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Influence of surfactant addition sequence on the suspension properties and electrophoretic deposition behaviour of alumina and zirconia

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Abstract

A well-known polyelectrolyte salt, ammonium polymethacrylate (Darvan-C) is used to stabilise ethanol-based Al_2O_3 and $Ce-ZrO_2$ suspensions with butylamine addition. The sequence in which n-butylamine and Darvan-C are added to the suspension greatly affects the properties of the wet deposit obtained by electrophoretic deposition. To investigate this effect, electrical conductivity of the suspension and the shear rate dependence of its viscosity are investigated. When n-butylamine is added first, the equilibrium in the suspension is almost immediately reached and a plastically deformable wet deposit is obtained over a large n-butylamine/Darvan-C ratio. The suspension has a shear-thinning viscosity and the deformable deposit is characterised by a high solvent content, which allows the rearrangement of particles during drying. When Darvan-C is added before the n-butylamine, the wet deposit is smooth and rigid. The suspension has a lower viscosity and a near-Newtonian behaviour is observed. A similar behaviour is observed for Al_2O_3 and $Ce-ZrO_2$ suspensions. The green density of the dried deposits is not influenced by the addition sequence and higher green densities are obtained for Al_2O_3 when compared to $Ce-ZrO_2$.
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1. Introduction

Electrophoretic deposition (EPD) can be used for the fabrication of advanced ceramics in the form of coatings, thin walled objects, laminates, functionally graded materials and others.[1] It is a colloidal processing technique, often based on non-aqueous suspensions in order to avoid the hydrolysis of water at the electrodes. In order to properly control the process, more knowledge is needed on the structure of the suspensions used and its relationship to the characteristics of the deposit and the deposition process. In this work we have studied the EPD process in ethanol-based suspensions of alumina and zirconia. We have studied the role of a polyelectrolyte Darvan-C (ammonium polymethacrylic acid, NH_4^+-PMA) and an organic base (n-butylamine) which

is used to adjust the acid/base character of the suspension.

In colloidal processing of ceramic powders, polyelectrolytes have a double role of particle charging and electrosteric stabilisation of the suspension. Depending on the functional groups of the polyelectrolyte, the pH is adjusted in the acid or base range, to enhance their dissociation. The stabilisation of water-based ceramic powder suspensions with Darvan-C has been widely studied. Highly stable aqueous suspensions have been reported for different powders such as: Al_2O_3,[2–4,7] ZrO_2,[5] TiC,[6] and TiO_2.[3] The adsorption mechanism in water is well understood and the plateau concentration depends on the pH of the suspension. At pH < iep, a high adsorption is observed, due to electrostatic forces between positively charged particles and $-COO^-$ groups.[2–4] By increasing the pH > iep the charge on the particles and on the polyelectrolyte have the same sign and the plateau concentration decreases. The pH of the suspension plays also a role on the configuration of the adsorbed Darvan-C.

By increasing the pH, the increasing number of dissociated functional groups of the Darvan-C creates repulsive forces and opens the configuration from the coiled to the tailed form.[2–4,8,9] In this paper the electrophoretic deposition behaviour and stability of ethanol-based suspensions of Al_2O_3 and $Ce\text{-}ZrO_2$ are studied as a function of sequence in which *n*-butylamine (BA) and Darvan-C (DC) are added to the suspension.

2. Experimental procedures

The powders used in this study are $\alpha\text{-}Al_2O_3$ (Baikowski grade SM8), with an initial average particle size of $0.6 \mu m$ and a BET of $10 m^2/g$ (supplier data), and 12 mol% CeO_2-stabilised ZrO_2 (Daiichi grade CEZ12) with an initial average agglomerate size of $0.35 \mu m$ and a BET of $12 m^2/g$ (supplier data). The powders are stored in a desiccator. The particle size distribution in ethanol, after 1 h of ultrasonic dispersion (Telsonic Ultrasonics, TPC-120) is determined using a Malvern Mastersizer Plus.

The solvent used is anhydrous ethanol (Merck pro-analysis) and the organic base is *n*-butylamine (Across 99% purity). The ammonium salt of polymethacrylate (Darvan-C, R.T. Vanderbilt Co., USA), with a molecular weight of 10,000–16,000, is used. The polymer is a water-based solution, with an active polymer content of 25 wt.%. The measured pH of the polyelectrolyte stock solution is 7.2. Fig. 1 presents the FTIR signature (Thermo Nicolet equipment) of the polyelectrolyte used.

The amount of *n*-butylamine is expressed in weight percent, relative to the dry powder content in suspension. The polyelectrolyte content is expressed in microlitre of the Darvan-C stock solution per gram of dried powder.

The viscosity measurements are performed using a Physica MCR 300 rheometer. A double wall Couette geometry is used. Temperature is controlled by a Peltier system and kept at $25 \,^{\circ}C$, and a solvent cage is used to limit the evaporation of the ethanol. The conductivity measurements are realised with an InoLab conductivity meter.

The electrophoretic deposition is performed in a vertical cell electrode. The distance between the stainless steel electrodes is 3.5 cm. The surface of the deposition electrode is $9 \, cm^2$. During the experiments, the voltage is kept constant at 100 V and the current as function of time is monitored. The suspension is continuously stirred in the deposition cell, in order to prevent any sedimentation during deposition. The rotation speed during the experiment is kept constant.
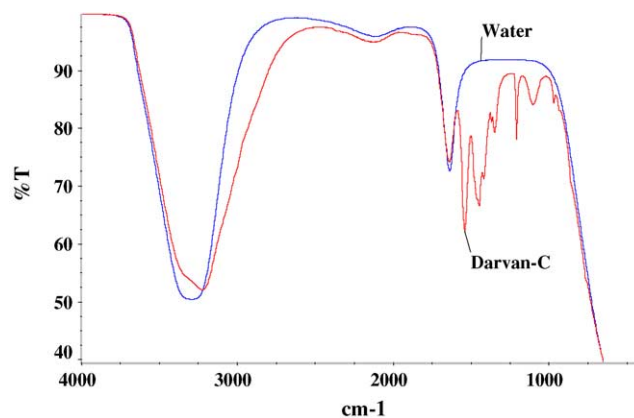

Fig. 1. FTIR spectrum of water and Darvan-C.

3. Results and discussion

3.1. Powder characterisation

The particle size characteristics of the Al_2O_3 powder dispersed in ethanol, summarised in Table 1, reveal significant agglomeration of the Al_2O_3 stock supply. Ultrasonication, however, proves to be very efficient in de-agglomerating the alumina suspension, as illustrated by the important decrease of the d_{90} from 40 to $1.5 \mu m$. A narrow particle size distribution, which is preferred for a homogeneous deposit, is obtained after 1 h of ultrasonic treatment. The size distribution of the $Ce\text{-}ZrO_2$ particles, however, does not change even after 1 h of ultrasonic treatment in ethanol, as can be deduced from Table 1. Comparing the suppliers' average particle size data and the actual measurements, leads to the conclusion that the $Ce\text{-}ZrO_2$ powder has stronger agglomerates than the Al_2O_3 powder.

3.2. Suspension conductivity

Ethanol, an organic solvent with high dielectric constant, is chosen in order to obtain a highly charged polyelectrolyte. The powders are ultrasonically dispersed in ethanol for 1 h followed by magnetic stirring. The suspensions contain a constant amount of powder (100 g/l), corresponding with 2.5 vol.% Al_2O_3 or 1.5 vol.% $Ce\text{-}ZrO_2$, and different concentrations of *n*-butylamine and Darvan-C. In this study, *n*-butylamine has the role to dissociate the Darvan-C and to charge the ceramic particle surface. After each addition of *n*-butylamine (BA) or Darvan-C (DC), the suspensions are

Table 1
Particle size distribution before and after ultrasonic dispersion in ethanol

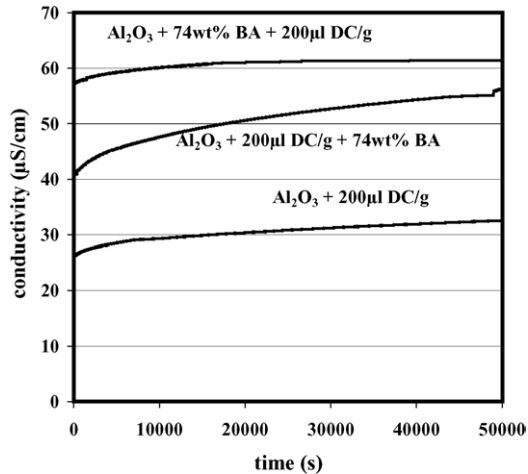|		$d_{10} (\mu m)$	$d_{50} (\mu m)$	$d_{90} (\mu m)$
Al_2O_3	Before ultrasonic dispersion	0.3	0.7	40
	After ultrasonic dispersion	0.25	0.5	1.5
Ce-ZrO_2	Before ultrasonic dispersion	0.2	0.8	3
	After ultrasonic dispersion	0.2	0.8	3

Fig. 2. Conductivity of Al_2O_3 suspensions (74 wt.% n-butylamine and 200 µl/g Darvan-C) as a function of the adsorption sequence and time.

magnetically stirred for 30 min in order to obtain a homogenous distribution of the compounds.

The steady state conductivity in the Al_2O_3 suspension obtained by the addition of 74 wt.% of n-butylamine followed by 200 µl/g Darvan-C is almost immediately reached (Fig. 2). The suspension conductivity is high with a small initial increase as function of time. The first added n-butylamine charges the powder surface negatively. Upon addition of Darvan-C to this suspension, the polyelectrolyte dissociates and obtains a negative charge due to the base nature of the suspension. Since the particles are also charged negatively, the polyelectrolyte adsorption is not favoured and the amount of free polymer in the suspension is high. According to literature, and assuming that the behaviour of the polyelectrolyte in water can be extrapolated to its behaviour in ethanol, the adsorption of the polyelectrolyte in this case is of the "low affinity" type.[10]

Without base addition, Darvan-C is not completely dissociated. Ethanol is a slightly acid solvent and the Al_2O_3 particles in ethanol are slightly positively charged. The adsorption mechanism is by electrostatic attraction between the $-COO^-$ groups and the positively charged surface hydroxyl sites of alumina. According to the literature, in this case the adsorption is of the high affinity type and the polyelectrolyte will be adsorbed on the surface until saturation.[10]

The conductivity measurements show that when the first added compound is BA, the degree of dissociation of Darvan-C is much higher (Fig. 2) than when the first added compound is DC.

3.3. Suspension viscosity

The suspensions are prepared as described above and mixed for 30–45 min before viscosity measurements. In order to avoid a significant influence of the evaporation of ethanol on the small amount of sample analysed (5 ml), the
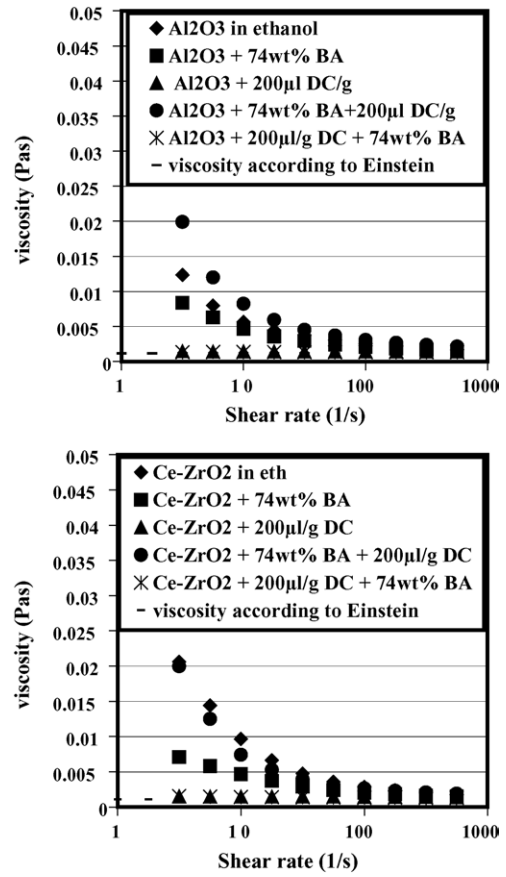

Fig. 3. Flow curve of Al_2O_3 ($\phi = 0.025$) (a) and Ce-ZrO_2 ($\phi = 0.015$) (b) suspensions in ethanol.

tests are limited to 600 s. The results of the viscosity analysis are summarised in Figs. 3–6, presenting the suspension viscosity as a function of the shear rate. The 2.5 vol.% Al_2O_3 and 1.5 vol.% Ce-ZrO_2 suspensions used in the present study are in the dilute regime. Einstein's law of viscosity predicts a suspension viscosity η_S equal to $\eta_{Ethanol} (1 + 2.5\phi)$, where ϕ is the volume fraction calculated based on the core
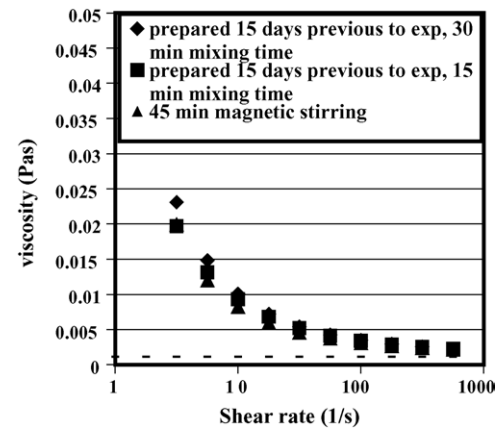

Fig. 4. Flow curve of ethanol-based Al_2O_3 suspension with 74 wt.% n-butylamine and 200 µl/g Darvan-C as a function of mixing and stirring time ($\phi = 0.025$).
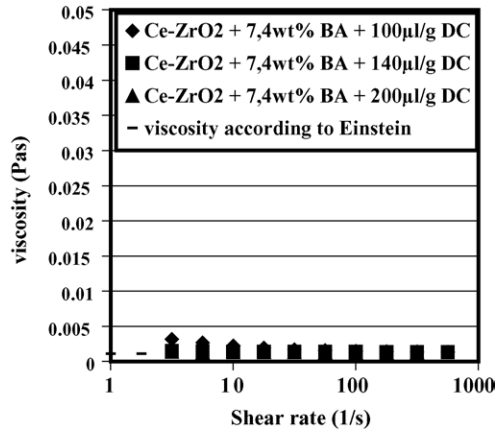
Fig. 5. Flow curve of ethanol-based Ce-ZrO$_2$ suspensions stabilised with 7.4 wt.% n-butylamine and different amounts of Darvan-C ($\phi = 0.015$).

diameter of the particles (see Figs. 3–6). For the suspensions stabilised with n-butylamine (74 wt.%) and Darvan-C (200 µl/g), their addition sequence has a strong influence on the suspension behaviour (Fig. 3). If Darvan-C is the first added compound, the suspension is essentially stable, as inferred from the small viscosity, independent of the shear rate, similar to the suspension stabilised by Darvan-C only. The adsorption of the negatively charged Darvan-C on the slightly positively charged particles is due to electrostatic interactions. Only in the case of a completely covered surface, are repulsive forces generated between particles to effectively stabilise the suspension in an electrosteric way.[10] The addition of n-butylamine to the suspension stabilised with Darvan-C does not change the viscosity. When butylamine is added the Darvan-C only dissociates further, increasing the electrosteric stability. This Newtonian behaviour with a value very closed to the value predicted by Einstein shows that the particles are not interconnected, so the effective diameter remains small. The ionic concentration in the suspension wi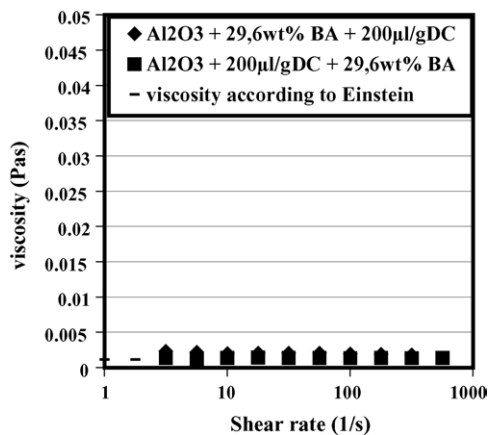ll increase with time as indicated by the conductivity experiments (Fig. 2). This process, however, is rather slow and the viscosity is measured after 30 min of magnetic stirring, when complete dissociation of the polyelectrolyte is not yet reached.

When n-butylamine is the first added compound, the viscosity of the suspension is higher than the viscosity obtained for the suspensions stabilised with only n-butylamine or Darvan-C (Fig. 3). In this case, according to previous studies,[8,9] the adsorption of the polyelectrolyte on the particles will be realised in the tailed configuration. The amount of free polymer in the suspension is higher than in the case where the first adsorbed compound is DC.[8,10,11] The free polymer can form bridges with the adsorbed polymer on the particles and flocculate the suspension.[12] Flocculation will lead to a more pronounced increase of the effective volume fraction, due to an interconnected network. In such cases, especially the low shear viscosity increases and the suspension is observed to become shear-thinning.[13] Similar behaviour is observed for the Al$_2$O$_3$ and Ce-ZrO$_2$ suspensions.

The viscosity of the Al$_2$O$_3$ suspension with n-butylamine (74 wt.%) and Darvan-C (200 µl/g), added in this order, is studied as a function of shear rate for different preparation histories, as presented in Fig. 4. The viscosity of the freshly prepared suspension and the suspension after ageing for 15 days is comparable, indicating a behaviour independent of time. The absence of any effect of mechanical stirring on the flow curve indicates that the flocculation in the sample is reversible (or weak).

In the case of Ce-ZrO$_2$ suspensions, lowering the n-butylamine content from 74 (Fig. 3) to 7.4 wt.% (Fig. 5), while keeping the amount of Darvan-C at 200 µl/g, results in a reduction of the viscosity to a near-Newtonian behaviour. Lowering also the Darvan-C content from 200 to 100 µl/g hardly influences the viscosity at 7.4 wt.% n-butylamine (Fig. 5). The quantity of the polymer adsorbed on the surface should be higher when adding a lower amount of n-butylamine and the configuration is expected to be intermediate between the coiled and the tailed form.[9]

Comparing Fig. 3a and Fig. 6 illustrates that the same trend is observed for Al$_2$O$_3$ suspensions, stabilised with 29.6 wt.% n-butylamine and 200 µl/g Darvan-C. In this case, the addition sequence of n-butylamine and Darvan-C has only a minor influence on the flow curve. The suspensions have a low viscosity independent of the shear rate. It can be concluded from Figs. 3–6, that the viscosity of the alumina and zirconia suspensions is sensitive to the addition sequence of BA and DC in the case of a high amount (74 wt.%) of n-butylamine addition. The viscosity is observed to be higher and displays shear-thinning when butylamine is added first. The viscosity, however, decreases with decreasing n-butylamine content. At lower levels of n-butylamine, the suspensions have a low viscosity and a near-Newtonian behaviour, independent on the addition sequence suggesting better stabilised dispersions.

Fig. 6. Flow curve of ethanol-based Al$_2$O$_3$ suspensions stabilised with 29.6 wt.% n-butylamine and 200 µl/g of Darvan-C, as a function of the addition sequence ($\phi = 0.025$).

3.4. Electrophoretic deposition behaviour

Since the powders are negatively charged by the adsorption of $-COO^-$ groups on the particle surface and by the addition of butylamine, deposition took place at the anode. Experimental observation revealed that the addition order of *n*-butylamine and Darvan-C to the Al_2O_3 and Ce-ZrO_2 powder dispersed in ethanol determines the deformability of the wet deposit. The property of deformability is tested by placing a zirconia ball of 2 cm diameter on the wet deposits and observing whether the ball penetrated the deposit or stayed on the surface. The observations on deformability as function of the preparation of the suspension are summarised in Table 2.

When *n*-butylamine is the first added compound, the alumina and zirconia deposits are plastically deformable as shown in Fig. 7 (top) over a large *n*-butylamine/Darvan-C ratio. In addition, these deposits also changed shape under their own weight on the vertical electrode in the deposition cell and their drying time is long (see further about drying below). With BA as the first added compound, the Darvan-C is completely dissociated and the $-COO^-$ groups adsorbed on the particle surface lead to a high surface charge. The suspension conductivity (Fig. 2) and the current during the EPD process (Fig. 8) are consistent with a high degree of dissociation of the Darvan-C in this case. The high degree of dissociation of the adsorbed Darvan-C and its associated expanded form could explain the formation of the deformable deposit. The more open structure of the flocks (see viscosity measurements Fig. 3) evidently lead to a more open deposit which even deforms under its own weight thus leading to an irregularly formed deposit which sags to the bottom of the electrode.

On the contrary, the deposits are rigid and their surface is smooth when the first adsorbed compound is Darvan-C (see Fig. 7, bottom). In this case, the degree of dissociation of Darvan-C is lower, as proven by the lower suspension conductivity (Fig. 2) and the current during EPD (Fig. 8). The adsorption of Darvan-C on the particles in a less expanded form could explain the tighter packing of the particles and the rigid character of the deposit. By decreasing the amount of BA, the suspensions are more stable, but the deposit properties do not change (Table 2).
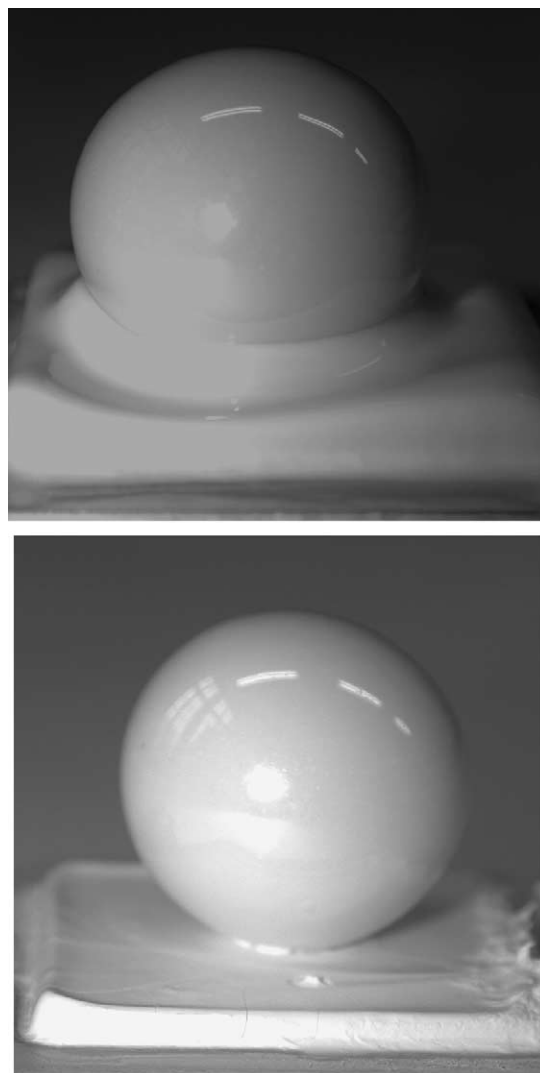

Fig. 7. Top: Deposit deformed under the weight of a 20 mm zirconia ball. Bottom: Example of a rigid deposit under the same conditions.

3.5. Drying

Fig. 9 presents the weight loss during drying, due to solvent evaporation. For the same deposit composition, the drying time is longer with a BA/DC addition sequence (de-

Table 2
Observations on deposit deformability as function of suspension preparation history

| Powder	First added compound	Second added compound	Viscosity (Pa s) at $3.16\,s^{-1}$	Deposit characteristics
Al_2O_3	74 wt.% BA	200 µl/g DC	0.0199	Deformable
Al_2O_3	200 µl/g DC	74 wt.% BA	0.0013	Rigid
Ce-ZrO_2	74 wt.% BA	200 µl/g DC	0.0199	Deformable
Ce-ZrO_2	200 µl/g DC	74 wt.% BA	0.0015	Rigid
Al_2O_3	29.6 wt.% BA	200 µl/g DC	0.0023	Deformable
Al_2O_3	200 µl/g DC	29.6 wt.% BA	0.0013	Rigid
Ce-ZrO_2	7.4 wt.% BA	100 µl/g DC	0.0031	Deformable
Ce-ZrO_2	7.4 wt.% BA	140 µl/g DC	0.0015	Deformable
Ce-ZrO_2	7.4 wt.% BA	200 µl/g DC	0.0013	Deformable
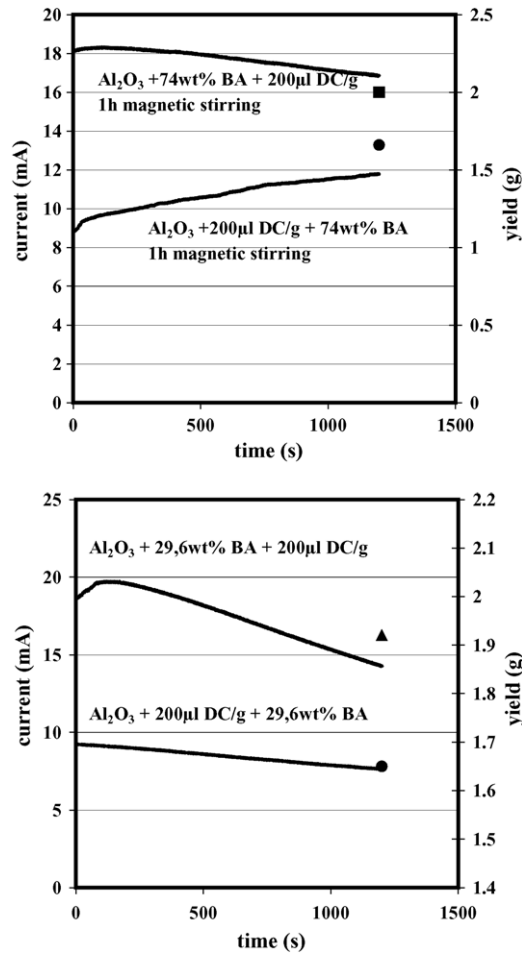
Fig. 8. The current evolution as a function of time for a constant applied voltage of 100 V and the Al_2O_3 electrophoretic deposition yield after 1200 s.

Fig. 9. The drying curves (weight loss) of Al_2O_3 and Ce-ZrO_2 deposits.

formable deposit) than for the DC/BA sequence (rigid deposit). It is observed that the volume of the deformable deposit decreases about 50% during drying. In this case, more solvent is bonded to the DC adsorbed in the tailed form compared to the less extended polyelectrolyte configuration in the other addition sequence. For the Ce-ZrO_2 suspensions with 7.4 wt.% n-butylamine, the drying time increases with increasing amount of Darvan-C, directly correlating the quantity of polymer to the amount of bonded solvent (Fig. 9).

In the case of deformable deposits, the distance between the particles in the wet state is higher than in the case of a rigid deposit. This difference in interparticle distance can be explained by the interconnected network formed between particles (high viscosity) and the ethanol bridges formed between particles (drying curves).

It should be remarked that the green density of the alumina deposit after drying is similar (∼40%), regardless of the adsorption sequence. The relative density of dried zirconia deposits is much smaller, ∼20%, and also independent on the addition sequence of BA and DC. The differences in green density appear to be related to the intrinsic packing density of both powders.
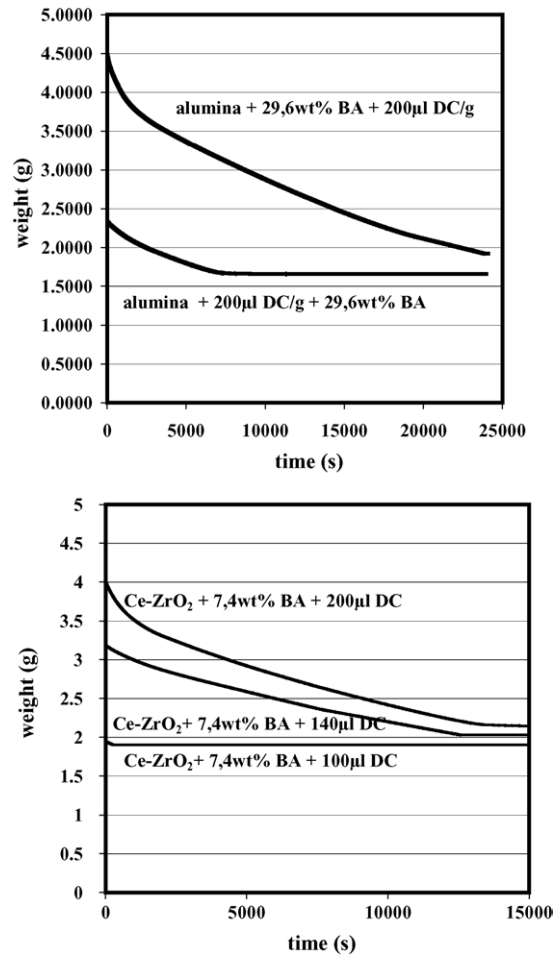
4. Conclusions

The properties of the EPD deposits obtained from alumina and zirconia suspensions stabilised with Darvan-C and butylamine depend markedly on the sequence of addition of the surfactants.

When the first compound added to the suspension is butylamine the deposit is deformable in the sense as defined in Fig. 7. It deforms also under influence of its own weight during deposition; it is subject to long drying times and substantial shrinkage during drying. With the assumption that the behaviour of the polyelectrolyte in ethanol is similar to its published behaviour in water, the viscosity and conductivity data of the suspension indicates that the polyelectrolyte is highly charged and adsorbs on the surface of the particles in an extended "tailed" form, which leads to a low volume concentration of particles in the wet deposit. In viscosity measurements, this leads to a shear thinning behaviour, at least at the highest concentration of butylamine used in this work. Lower concentrations of BA and of DC lead to lower viscosities and to essentially Newtonian behaviour. The deformable characteristic of the wet EPD deposit remains, however, the same.

On the contrary if Darvan-C is the first added compound, then the wet deposit is rigid with a much higher volumetric concentration of particles, as evidenced by the drying curves. The viscosity in this case is always low and Newtonian. The polyelectrolyte is thought to be absorbed on the particle surface in a more "coiled" form.

A similar behaviour is observed for Al_2O_3 and $Ce-ZrO_2$ suspensions. The green density of the dried deposits is not influenced by the addition sequence and higher green densities are obtained for the Al_2O_3 powder when compared to the $Ce-ZrO_2$.

Acknowledgments

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