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Coagulation of mixed organic systems and alumina particles for paste production

Cécile Pagnoux *, Marion Mougenot, Pascual Garcia Perez, Thierry Chartier, Jean-François Baumard

SPCTS, ENSCI, 47 Avenue Albert Thomas, 87065 Limoges Cedex, France

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Abstract

Pastes of alumina with plastic properties were prepared by direct coagulation casting (DCC) of concentrated suspensions (≥50 vol%). Two polyelectrolytes were used to produce mixed systems of organic and mineral particles. An anionic polymer, bearing both sulfonate and carboxylate functions, was used to disperse efficiently alumina powder in water. A cationic polymer, the chitosan (CT), which complexes with the anionic one was added into the stable suspension to form an organic network dispersed into the ceramic matrix. The sequence of addition of the chitosan in the suspension appears to be a significant parameter in order to optimise the suspension formulation. After in situ coagulation, cylinders were extruded.

Keywords: Suspension; Coagulation; Al_2O_3; Paste

1. Introduction

The preparation of ceramic pastes with a high solid loading is of a great interest for extrusion or injection molding. The paste has to exhibit a degree of plasticity to enable it to be deformed and to maintain that shape. For advanced ceramic components, organic additives such as binders and plasticizers have to be added to confer to the paste suitable rheological properties for extrusion or injection moulding. Usually all the components (powder, solvent, additives) are mechanically mixed. The main problems addressed to this method are (i) the homogeneity of the organic phase in the ceramic network; (ii) the reproducibility of the mixing from one batch to another; and (iii) the contamination of the mixture due to the abrasive properties of the powder used.

To overcome these problems, colloidal way seems to be promising because it offers the ability to provide stable systems with a high solid loading. A paste can then be achieved by controlling the destabilisation of the suspension with an adjusted formulation. Ceramic shaping by destabilisation of aqueous suspensions has been much investigated in the past 10 years and in particular the direct coagulation casting (DCC) process. This method needs the preparation of a concentrated suspension which is poured into a non-porous mould and destabilised by a time delay reaction. The fundamental studies on DCC[1–4] made it possible to determine the key parameters which control the two steps of this process, i.e. dispersion and coagulation of the suspension to obtain cohesive green parts. It is possible to transpose this knowledge to other raw material/organic additive systems, in particular, to confer plastic properties to the destabilised suspension.

This idea has been already developed. Prabhakaran et al.[5] have prepared extrudable paste from an alumina suspension electrostatically dispersed and coagulated by acetic anhydride addition. One percent of PVA is necessary to enhance the mechanical strength to prevent deformation. Davies and Binner[6,7] carried out an overall study of the coagulation of an alumina suspension electrostatically dispersed by salt addition. They conclude that it is essential to achieve a high state of dispersion before system destabilisation to obtain a homogeneous paste. The influence of the ions on the lubricating effect has also been discussed. The ability of the counter ion, in particular NH_4^+, to structure the water molecule network when the particles approach each other should play an important role

* Corresponding author. Tel.: +33 555452222; fax: +33 555790998.
E-mail address: c_pagnoux@ensci.fr (C. Pagnoux).

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to give plasticity to the destabilized system. These two studies show that a homogeneous paste can be obtained with a system presenting low viscosity with at least 50 vol% of solid loading. An adsorbed polymeric layer on the particle surface is also beneficial to lubricate the interface of mineral particles.

To induce lubrication between alumina particles without binder addition, the presence of a network of non soluble organic particles between the mineral ones could make it possible to obtain a coagulated ceramic with plastic properties and without deformation. It is possible to prepare colloidal suspensions of organic particles by complexation reaction between an anionic and a cationic polymer. A condensation reaction occurs and a neutral core is obtained which can be surrounded by the polyelectrolyte in excess.[8,9] Our objective was to synthesize colloidal organic particles stabilised with the same dispersant as the alumina powder. Cationic polymers are scarce and are ionised under acidic conditions. One biopolymer, chitosan (CT) was chosen because of its variety of properties, biocompatibility, antibacterial and environmental friendly nature, and also because the influence of its chemical properties on its complexation with some anionic compounds has been studied.[8–11] In order to enhance electrostatic attraction between the chitosan and an anionic polyelectrolyte in acidic media, sulfonate functions are preferable, and in order to obtain a strong adsorption on the alumina surface, carboxylate functions are essential. Then we have chosen a copolymer, bearing the two functions. Firstly, the dispersion of concentrated alumina suspensions using the anionic copolymer was studied. Secondly, a stable colloidal suspension of organic particles dispersed with this anionic polymer has been synthesised. Then, mixed organic mineral systems have been prepared by two ways. The first way is to complex the two polymers in water and then to add the powder. In the second way, chitosan complexes with the anionic polymer already adsorbed on the alumina particles. The electrokinetic and rheological properties of the suspensions proved to be powerful techniques to characterize each system and to optimise the formulation. Finally, solid and coagulant agent concentrations have been determined to obtain a paste sufficiently stiff able to be extruded.

2. Experimental procedure

2.1. Starting materials

The powder used in this study is an α-alumina prepared by the Bayer process (P172SB, Péchiney-Alcan, Canada). Concentrations of Na_2O, SiO_2, CaO, Fe_2O_3, and MgO are 600, 900, 600, 120, and 900 ppm, respectively. MgO was added to act as a grain-growing inhibitor for a finer microstructure of the sintered ceramic. The specific surface area is equal to $8\,m^2\,g^{-1}$ once degased at 300 °C for 2 h, (N_2 BET). The particle size distribution is large with a medium size of 0.4 μm (Fig. 1). The average size is in agreement with that obtained with the Mastersizer 2000 and the particle shape is far from spherical. This powder is not self-dispersible in water and it flocculates immediately in water.

The anionic polymer was obtained from Alco Chemical (USA). Versaflex One® (VO) is a proprietary composition containing multiple sequential anionic and non-ionic groups. It is an additive used in industrial water treatment to disperse particles. As no information about the chemical composition of the compound are available from the supplier, we have carried out titration and chemical analysis of VO. VO is an aqueous solution containing the acidic form ($d = 1.21$, 40 wt%, pH 4.3, $\eta = 75$ mPa s (25 °C Brookfield)). The Na and S content are 2.2 and $4.6\,mol\,l^{-1}$ of commercial solution, respectively. The presence of sulfur should correspond to SO_3^- functions. The concentration of COOH groups, obtained by titration, is equal to $4.3\,mol\,l^{-1}$ of commercial solution corresponding to $9 \times 10^{-3}\,mol\,g^{-1}$ of polymer ($pK_a = 5.3$). We can assume that the chemical structure of this copolymer contains as many sulfonate functions as carboxylate. A comparison has been made with a salt of polymethacrylic acid (PMA) (Aldrich, $M_w = 5000$ by GPC, average $M_n = 4000$, 30 wt% in water, $50 < \eta < 175$ mPa s (25 °C Brookfield)). The COOH concentration is $8.5 \times 10^{-3}\,mol\,g^{-1}$ of polymer ($pK_a = 5.8$). To compare the viscosity, we assumed that the VO solution is Newtonian and its viscosity is proportional to the polymer content. It should be around 55 mPa s for a solid loading of 30 wt% and then in the same range as for PMA. This suggests that VO shows similar behavior to that of PMA and is a low molecular weight polymer.

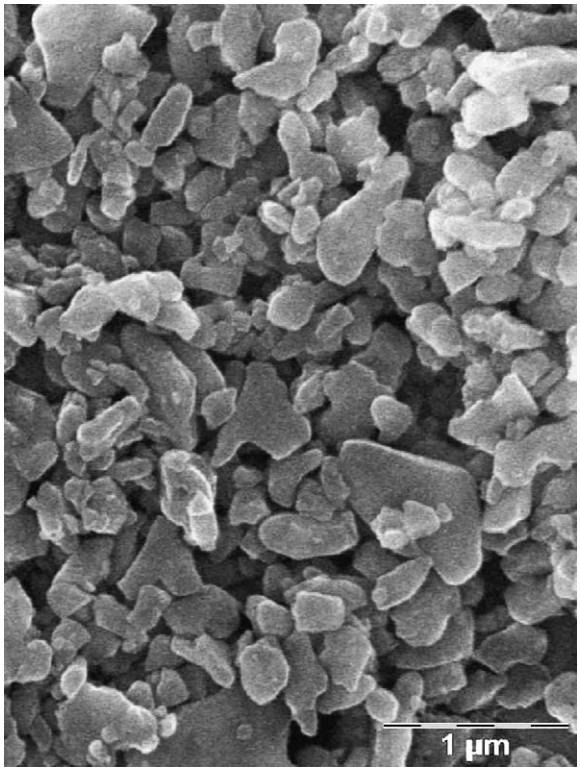

Fig. 1. SEM micrograph of particles of P172SB powder.

The cationic polymer, the chitosan, was obtained from France Chitine (France). It is a whitish ivory powder, with a deacethylation degree of ≥90%. The viscosity of a solution (1 wt% of chitosan, solvent: acetic acid solution (1%)) measured as follow ($T = 25$ °C, Brookfield LV spindle no. 1, 12 rpm) falls within the range 20–100 mPa s. From the viscosity values, the molecular weight is estimated to be between 3.3 and $5 \times 10^6\,g\,mol^{-1}$. This

polyelectrolyte leads to a more viscous solution compared to the Versaflex one. It is a linear cationic polymer readily soluble in acidic solution. The powder (0.3 g) is dissolved with 1.8 ml of HCL (1 M) and 10.2 ml of water. A viscous solution is obtained and the concentration of amino groups was determined by titration at 5.4×10^{-3} mol g^{-1} of CT. Ten percent of HCl added for the solubilisation are in excess. For pH >6, the polyelectrolyte precipitates.

2.2. Suspension and paste preparation

Polyelectrolyte complexations were performed at room temperature using VO as starting solution. Under constant magnetic stirring, very small volumes of CT solution were added. A qualitative analysis that consisted of an estimation of the sedimentation rate of the particles permitted the adjustment of the following parameters: polyelectrolyte concentration, starting pH of the CT solution, and the ratio VO/CT.

Two ways, which differ by the order of polyelectrolyte addition, for the suspension preparation before the coagulation were used. The flow charts of Fig. 2 summarizes the two processes. The first one consists of an addition of a stable suspension of organic particles, a VO amount necessary to disperse the alumina powder and then the powder. The mixture is deagglomerated by ultrasonic treatment. The second one consists of an addition of CT in a stable alumina suspension dispersed with VO. Assumption has been made that VO and CT react together to form organic particles at the interface of the mineral ones. The values given in italics in Fig. 2 are the parameters which were optimised with the present study.

These systems have been coagulated by adding a powder of hydroxyaluminium diacetate. This compound has been used to develop a new way of internal coagulation of alumina suspension dispersed with Tiron.[4] This nanopowder (50 nm) decomposes itself in water to release Al^{3+} ions which firstly decreases the suspension pH toward the IEP, reducing the interparticle repulsive potential. Secondly, trivalent ions production strongly contributes to the decrease in repulsive potential by increasing the ionic strength in the suspension and then by compressing the diffuse electrical double layer. The kinetic of the decomposition reaction can be controlled by temperature. $Al(CH_3COO)_2OH$ is added homogeneously into the suspension and the mixture is poured when it is still fluid into the cylindrical dye of the extrusion system to avoid bubbles formation.

After suspension destabilisation, the paste was forced through a stainless steel cylindrical dye ($d = 10$ mm) by a piston. The extrusion force was imposed by a mechanical testing machine (Lloyd Instrument, England) and measured by a 20 kN load cell (precision 1%). The speed of the piston can be accurately controlled.

2.3. Characterization

Particle size distributions were performed by using static light scattering granulometer (Mastersizer 2000, Malvern Instrument).

Zeta potential values of the alumina particles in the various prepared slurries were measured by using an electrokinetic sonic amplitude (ESA) measurement apparatus (Model ESA8000 Matec, Northborough, MA, USA).[12] Measurements were carried out with slurries containing a 3 vol% solid loading. To measure the zeta potential values over a large pH range, two suspensions were used, one from the natural pH to acidic pH and one for basic pH. Ionic strength was fixed at 10^{-2} mol l^{-1} with NaCl. Solutions of NaOH (1 M) and HCl (1 M) were used as titrants. The data recorded with the ESA analyser correspond to the measured ultrasonic signal converted to a voltage (ESA). According to the O'Brien model,[13] ESA

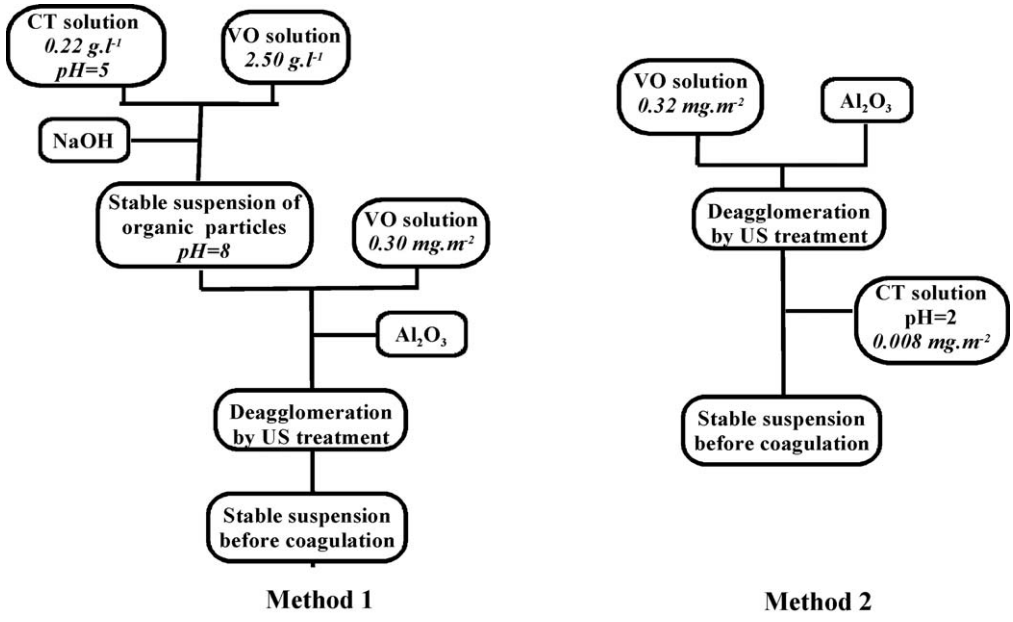

Fig. 2. Flow charts of suspension preparation before coagulation.

voltages were converted to zeta potentials. The relationships which permit the calculations are reported in another article.[14]

The flowing properties of suspensions were examined with a controlled stress rheometer (Carri-med CSL 100, England) using a cone/plate configuration (diameter: 4 cm; angle: 2°). The experimental procedure consisted of applying a linear ramp of stress and finally of decreasing the linear stress to 0 N m^{-2}. High solid concentration suspensions (≥50 vol%) showed shear thinning behaviour; a dynamic viscosity was calculated in the linear part of the curve.

3. Results and discussion

3.1. Dispersion of alumina powder with VO

Fig. 3 gives the influence of VO addition on the particle size distributions of P172SB powder. Without additive, the average size of agglomerates is 3 μm. A concentration of 0.21 mg m^{-2} of VO is sufficient to remove all the agglomerates of the powder and to decrease the mean particles size to 0.4 μm. The broader distribution of deagglomerated particles is in agreement with that obtained by the supplier.

Fig. 4 reports, versus VO concentration, both the zeta potential variations of diluted suspension (3 vol%) and the dynamic viscosity variations of concentrated suspensions (50 vol%). At the natural pH (8.5), the zeta potential of the particles is measured at a low value of −5 mV. The powder is not self-dispersible and it immediately flocculates in water. An addition of 0.5 mg m^{-2} of VO makes it possible to drastically decrease

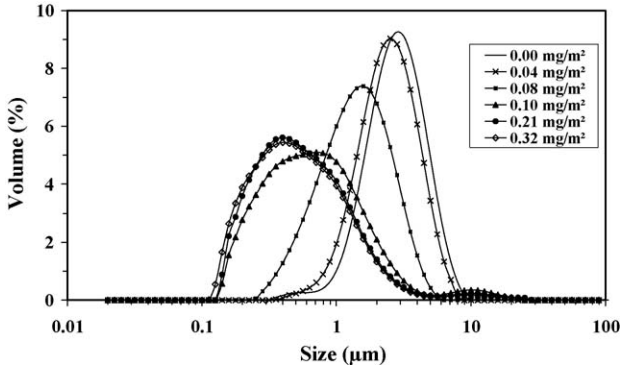

Fig. 3. Size distribution of P172SB particles in suspension vs. VO concentration.

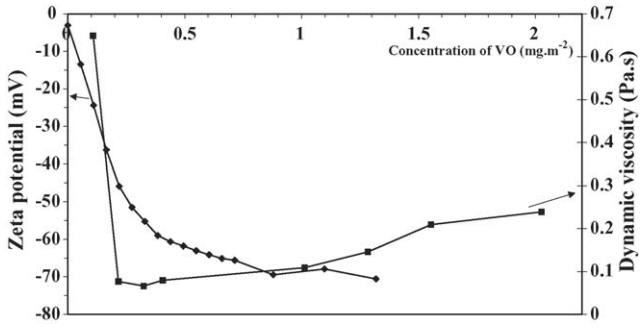

Fig. 4. Zeta potential (♦) of a diluted P172SB suspension (3 vol%) and dynamic viscosity (■) of concentrated suspensions (50 vol%) vs. VO concentration.

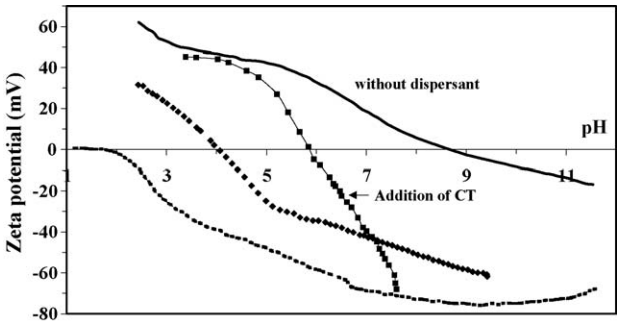

Fig. 5. Electrokinetic properties of alumina suspension without dispersant and with 0.5 mg m^{-2} of PMA (♦), with 0.32 mg m^{-2} of VO (–),with VO in which CT solution is added (■).

the potential to −60 mV (pH 7.5). Further additions of VO up to 1.5 mg m^{-2} permits to reach a lower potential of −70 mV (pH 6.3); it demonstrates that this polyelectrolyte adsorbs on the alumina surface and that the free ionisable groups create a high density of negative surface charge. As VO is an acid, the suspension pH decreases but not enough to induce alumina solubility. The minimum value of the dynamic viscosity of concentrated suspension is obtained for an addition of 0.32 mg m^{-2}. We can note that this concentration leads to a zeta potential of −55 mV that is not a high value to be reached. This suggests that this polyelectrolyte disperses the powder with not only an electrostatic effect but also with a steric one. Further additions of VO result into more viscous suspensions because of the non-adsorbed polymer, which increases the ionic strength that destabilizes the suspensions.

In order to make a comparison with a salt of polymethacrylic acid, a well-known dispersant of alumina, the electrokinetic properties of suspension dispersed with VO and PMA versus pH have been compared (Fig. 5). The IEP of a P172SB suspension without additive is measured at pH 8.6. For pH < IEP, the zeta potential increases linearly up to pH 5.4 and a maximum value of +60 mV is obtained in acidic media showing that this powder can be dispersed with a strong acid addition. For pH > IEP, the zeta potential does not follow the linear variation obtained for 5.4 < pH < 8.6 and is very low in this pH range (less than −20 mV). Bivalent ions such as Ca^{2+} and Mg^{2+}, present in the P172SB, which strongly structure the network of water molecules are very efficient to approach the surface and to screen the electric charge. PMA addition does not change the natural pH anymore but the adsorption of the molecule makes it possible to develop a negative repulsive potential (−60 mV) between the particles. As the pH decreases, the absolute value of the potential decreases to reach the IEP at pH 4. Two phenomena occur, the neutralisation of the carboxylate groups ($pK_a = 5.3$) and the protonation of the free hydroxyl surface groups. The surface coverage by this polymer is not complete because the potential becomes positive for pH < IEP. The adsorbed layer should undergo a configuration change on the surface. It should change from an extended chain, when anionic repulsion between carboxylate groups is maximum, to a loop configuration, when no repulsion occurs that diminishes the surface coverage. On the contrary, the copolymer covers the alumina surface better

because in acidic media the potential does not become positive. The structure of this polymer should contain both sulfonate and carboxylate groups. SO_3^- groups are ionised in all the pH range and the hydrophobic monomer, which composes the chemical structure, should permit a very strong adsorption on alumina surface that involve a high concentration of hydroxyl surface groups. The polymer remains negatively charged in acidic media and the protonation of a few concentration of OH surface groups is not sufficient to obtain a positive potential for pH < IEP measured at 2.4. The potential is less than −40 mV for pH >4.5, that is beneficial to electrostatically attract a cationic polymer as chitosan. The amplitude of the repulsive potential is higher than the one created by PMA and for pH >9, the potential remains constant. As VO is a complexant agent of Ca^{2+} and Mg^{2+} ions, these ions cannot disturb the ionisation properties of OH surface groups and does not neutralise the density of charge. This study demonstrates that a copolymer bearing both sulfonate and carboxylate groups can be an efficient dispersant of alumina powder. A solid loading of 57 vol% can be achieved in the suspensions which are suitable to develop a colloidal process. In addition, it is expected that this kind of polymer can disperse also numerous oxides such as TiO_2, ZrO_2, etc.

3.2. Preparation of colloidal suspensions of organic particles

Our objective was to prepare organic particles stabilised with the same dispersant as the alumina powder. Complexation between an anionic and a cationic polymer can lead to the precipitation of a solid. Previous works showed that this reaction is enhanced by strong electrostatic attractions, hydrophobic and Van der Waals interactions.[8,9] A reaction of condensation occurs between the acidic and the basic groups and at low ionic strength, counter ions are released and a solid precipitates. Several parameters influence the size distribution of the particles: the polyelectrolyte concentration, the pH of the starting solutions, the ratio between the two polymers, the order and the rate of the addition, the ionic strength, and the chemical nature of the ions added. Usually, polyelectrolyte complexation is studied in order to better understand different biological phenomena. But various useful fields involving interpolymer complexation imply numerous investigations such as the synthesis of membranes or capsules. Applications are powerful such as chemical filtration or controlled drug delivery. In this present study, the complexation between two polyelectrolytes is used for a different goal. Nevertheless, it is necessary to determine the parameters influencing the complexation.

To obtain a stable colloidal system bearing a negative charge, we choose to add a CT solution into a VO solution because the anionic functional groups are always in excess and are neutralised as well as the CT is added. No salt was added because as organic suspension will be mixed with alumina powder, ions could destabilise concentrated ceramic suspensions.

All formulations investigated are listed in Table 1. The polyelectrolyte concentrations, the ratio between the anionic and cationic functions (n^-/n^+) and the pH of the starting CT solution are the studied parameters. The pH of the final suspension and the observations made about the system stability are also mentioned in Table 1. Firstly, the ratio n^-/n^+ (nos. 1–3) and the polyelectrolyte concentrations (nos. 4–6) were tested without changing the pH (2) of the starting solution of CT. From the first set of experiments (1–3), a ratio $n^-/n^+ = 38.64$, with a large excess of anionic polymer was selected because it leads to the precipitation of flakes, dispersible with US treatment and not to a large agglomerate unbreakable. From the second set of experiments (nos. 4–6), a minimal polyelectrolyte concentration was fixed at 2.5 g l^{-1} of VO and at 0.22 g l^{-1} of CT. We can note that Schatz et al.,[8] with a system composed by Dextran sulfate and chitosan, have also determined a critical concentration of polyelectrolytes to obtain particles.

In a third set of experiments (nos. 7–10), the variation of the CT solution pH makes it possible to increase the pH of the final suspension and in the same time to decrease the size of the particles. When the pH of the CT solution is fixed at 5.5, a stable system is obtained and no sedimentation occurs after one week. For higher values of pH, the polymer precipitates. We can attribute this pH dependent behaviour to the ionisation of COOH groups ($pK_a = 5.3$). In the 3.5–4.8 pH range, the anionic polymer bears a higher density of negative charge than at pH 2. When condensation occurs, the repulsion should impede agglomeration of

Table 1
Compositions used for synthesis of organic particles suspensions

Number	VO concentration (g l^{-1})	CT concentration (g l^{-1})	n^-/n^+	nSO_3^-/nNH_3^+	pH of CT solution	Suspension pH	Observation
1	1.25	0.44	9.66	5.00	2.0	2.2	Large agglomerate
2	2.5	0.44	19.32	10.00	2.0	2.2	Large agglomerate
3	5.0	0.44	38.64	20.00	2.0	2.2	Flakes (rapid sedimentation)
4	2.5×10^{-2}	2.2×10^{-3}	38.64	20.00	2.0	2.0	Solution
5	2.5×10^{-1}	2.2×10^{-2}	38.64	20.00	2.0	2.0	Solution
6	2.50	0.22	38.64	20.00	2.0	2.2	Flakes (rapid sedimentation)
7	2.50	0.22	38.64	20.00	3	3.0	Flakes (rapid sedimentation)
8	2.50	0.22	38.64	20.00	4	3.5	Small flakes (rapid sedimentation)
9	2.50	0.22	38.64	20.00	5	4.5	Low sedimentation
10	2.50	0.22	38.64	20.00	5.5	4.8	Stable system, no sedimentation
11	1.25	0.22	19.32	10.00	5.5	4.8	Low sedimentation
12	0.625	0.22	9.66	5.00	5.5	4.8	Small flakes (rapid sedimentation)

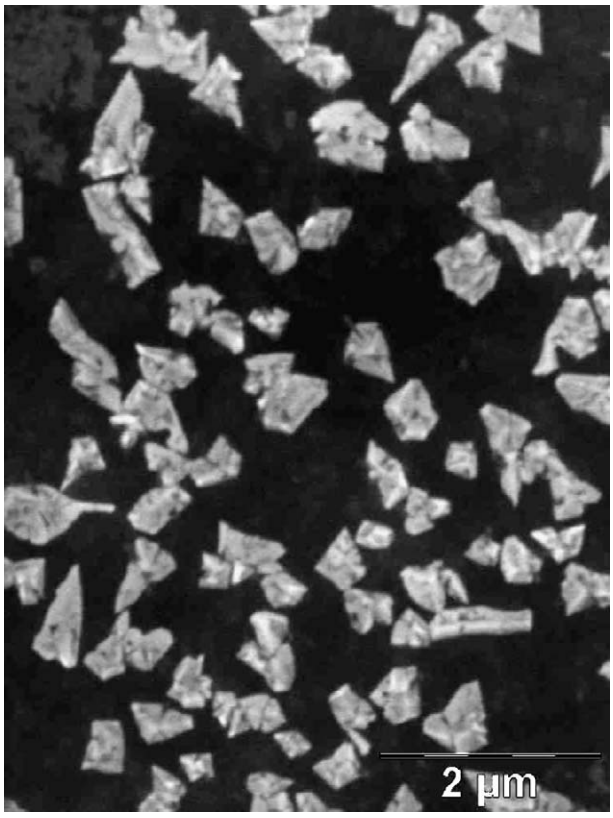

Fig. 6. Organic particles obtained with the formulation 10, the pH has been fixed at 8.

organic particles and should limit any increase of the size. This assumption was verified by increasing the pH with NaOH of the final suspension (no. 10). The size of the particles decreases down to pH 8 as the COOH functions are fully ionised. Under acidic conditions, interactions occurs mainly between SO_3^- and NH_3^+, although SO_3^- are in excess, the concentration is too low to disperse the particles. As pH increases, both SO_3^- and COO^- interact with NH_3^+, as negative functions are in large excess, some of these permit the dispersion and the stabilisation of the system. Under basic conditions, it was shown that the complex does not become stable as the amino groups are neutralised, the cationic polymer precipitates.[8] A SEM picture (Fig. 6) shows particles obtained at pH 8. The shape is far from spherical and the average size is about 0.5 μm. This formulation was chosen to be mixed with alumina suspension.

By adjusting some parameters, we are now able to control the preparation of a stable system in which organic particles are stabilised with the same dispersant than alumina particles and in the same pH range.

3.3. Preparation of mixed suspensions

3.3.1. Mixture of organic particles with alumina (method 1)

The organic suspension obtained previously was mixed with alumina powder (Fig. 2). The concentration of VO and CT in the organic suspension are 0.09 and 0.008 mg m^{-2} of powder, respectively. To optimise the stability of the alumina suspension, an extra amount of VO has to be added to the mixture. This

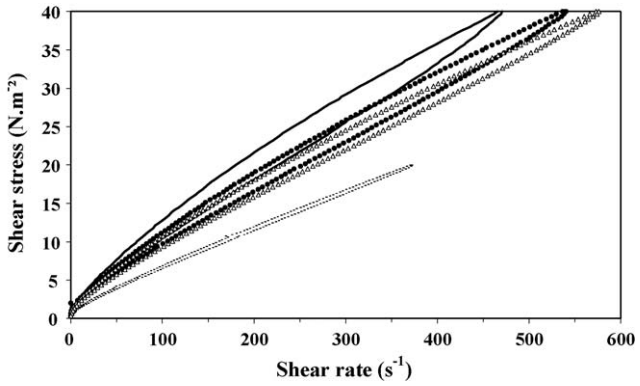

Fig. 7. Curves τ (N m^{-2}) = $f(\gamma$ (s^{-1})) of mixed organic/alumina suspensions (50 vol%) with different amounts of VO (–, 0.27), (●, 0.30), (△, 0.33) mg m^{-2}. Curve obtained with the alumina suspension stabilised with 0.32 mg m^{-2} of VO has been added (—) for comparison.

concentration has been determined by studying the rheological properties of concentrated suspensions (50 vol% of Al_2O_3) prepared with different amounts of VO. The rheogramms τ (N m^{-2}) = $f(\gamma$ (s^{-1})) presented in Fig. 7 show shear thinning properties of the suspensions without yield stress. Whatever the VO concentration, the flowing properties of the suspensions are very similar. These suspensions are more viscous than alumina suspension well dispersed with only 0.32 mg m^{-2} of VO. For the coagulation experiments, the VO concentration has been fixed at 0.30 mg m^{-2}. Then, the total amount of VO into the suspension reaches a value of 0.39 mg m^{-2}. Using this method, it is not possible to prepare suspension with a solid loading of alumina larger than 50 vol% because dilatancy properties are observed. Organic particles contribute to increase the solid concentration into the suspension. We can assume that organic particles are well dispersed in the ceramic network and do not form cluster. But the ratio between the mineral and organic particles number would be a relevant parameter in order to know if the concentration of organic particles is sufficient to ensure the lubrication between the minerals.

3.3.2. Addition of CT into an alumina suspension stabilised with VO (method 2)

The process of this method is summarised in Fig. 2. Fig. 8 shows the rheogramms of alumina suspensions (0.32 mg m^{-2} of VO) with and without CT addition. The first CT concentrations tested are included in the range used to obtain the stable organic suspension. Even thixotropy is observed, the CT addition up to 0.008 mg m^{-2} ($n^-/n^+ = 136$) enhances the flowing properties of the suspension. Larger concentrations, 0.04 and 0.08 mg m^{-2} destabilise the suspension. For an alumina concentration of 50 vol% and with optimised concentrations of additives, the sequence of CT addition influences the flowing properties of the suspensions. Compared to the suspension stabilised with only 0.32 mg m^{-2}, the first method leads to more viscous suspensions. The interpolymer complexation does not likely occur in the same way and when the VO is adsorbed on the alumina surface, its configuration is not the same than in solution. The pH of a concentrated P172SB alumina suspension is about 8.5, VO is strongly ionised. CT is electrostatically attracted by the

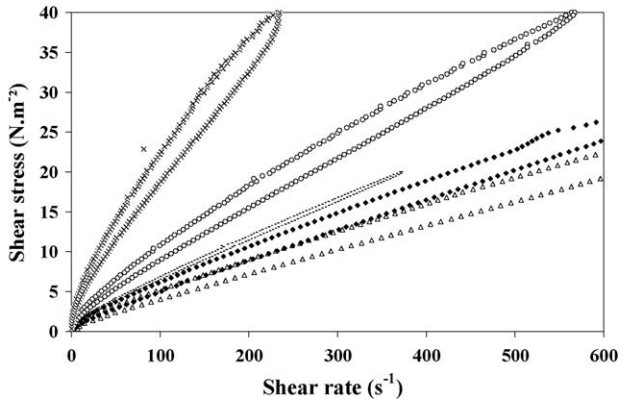

Fig. 8. Curves τ (N m^{-2}) = $f(\gamma)$ (s^{-1})) of alumina suspensions (50 vol%) stabilised with 0.32 mg m^{-2} of VO and in which with different amounts of CT were added (–, 0.00), (♦, 0.004), (△, 0.008), (◯, 0.04), (×, 0.08) mg m^{-2}.

surface and should react with VO. We can expect that a layer of polymer can be formed between the particles that lubricate the interface. As a result, a suspension prepared by method 2 with 52 vol% of alumina shows similar properties than the optimised suspension (50 vol%) prepared with the method 1.

Fig. 9 reports the zeta potential and the pH of an alumina suspension dispersed with 0.32 mg m^{-2} of VO in function of the CT concentration and the zeta potential versus pH is plotted on Fig. 5. Up to 0.008 mg m^{-2}, CT addition does not decrease anymore the zeta potential and then does not influence the repulsive forces between the particles. Indeed, only 0.7% of negative functions or 1.4% of COOH functions is involved to react with amino groups. Addition of 0.04 and 0.08 mg m^{-2} lead to a zeta potential of −28 and −20 mV, respectively showing that CT reacts with VO to form organic particles either in the solution or on the alumina surface. In the two cases, negative charge created by the VO adsorption is neutralised that destabilises the suspension. The quantity of anionic polymer necessary to disperse the powder becomes insufficient. As the pH decreases, the size of organic particles should increase (cf. paragraph 2) because the neutralisation of the COOH groups and their dispersion in the ceramic network becomes less homogeneous. A concentration of 0.175 mg m^{-2} of CT is then necessary to overall compensate the negative potential.

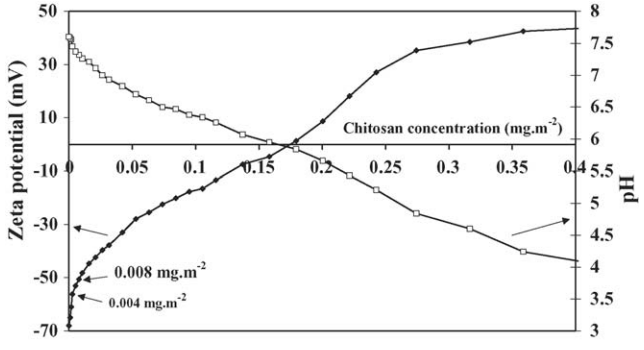

Fig. 9. Zeta potential (▲) and pH (□) variations vs. CT addition of an alumina suspension (3 vol%) dispersed with 0.32 mg m^{-2} of VO.

As CT is added, the pH decreases. Fig. 5 shows that the zeta potential becomes positive for additions higher than 0.175 mg m^{-2} and reaches the value obtained at pH 4 without additive for an amount of 0.4 mg m^{-2}. We can conclude that CT desorbs VO from the alumina surface and as the pH becomes acidic, the free OH groups are protonated. In concentrated suspensions (≥50 vol%), the pH remains constant at 9 and we can assume that with an addition of 0.008 mg m^{-2} of CT, CT and VO form organic particles or organic layer very well dispersed in the ceramic network that makes possible the lubrication between the particles.

This study shows that the rheological properties of the suspension depend on the sequence of addition of the cationic polymer. The reaction of condensation between the two polyelectrolytes should not lead to the same objects (shape and size) if the anionic polymer is in solution or if it is adsorbed on the alumina surface.

3.4. Coagulation and extrusion

All formulations investigated for coagulation are listed in Table 2. The suspensions are prepared according to the second method. Alumina and coagulation agent concentrations were tested likewise. The concentration of VO and CT added are 0.32 and 0.008 mg m^{-2}, respectively. When the coagulated ceramic was able to be extruded, the duration from the $Al(CH_3COO)_2OH$ addition to the extrusion was mentioned in the last column. The speed of extrusion was fixed at 10 mm min^{-1}.

The release of Al^{3+} ions into such suspensions firstly decreases the pH near the IEP that diminishes the interparticles potential and secondly increases significantly the ionic strength. These two phenomena contribute to destabilize the system and to bring the particles closer each other. Nevertheless, the concentration of $Al(CH_3COO)_2OH$ tested (12–16 mg ml^{-1} of solution) is very low compared to the one used for DCC (70 mg ml^{-1}).[4] The coagulant agent amount has to be minimized to control the destabilisation step.

Firstly, without organic particles (formulation 1), a cohesive part is obtained; CT addition is essential to obtain an extrudable paste. Secondly, the coagulation kinetic is alumina and coagulant agent concentrations dependent. For plastic formed by extrusion, a compromise has been found with 52 vol% of alumina and 16 mg of $Al(CH_3COO)_2OH$ ml^{-1} of solvent. The coagulated ceramic exhibits plasticity when sufficiently loaded with powder. With a 55 vol% of alumina, the organic particles concentration is not enough to ensure a complete lubrication of the mineral network. The coagulant agent concentration was adjusted to permit its homogeneization in the suspension and to maintain a still fluid suspension for casting into the dye while reducing the coagulation kinetic. The presence of organic particles at the interface of the ceramic ones allows particles to move and gives plasticity properties of the coagulated ceramic which can be shaped before drying. After drying at room temperature (25 °C), a small (1%–2%) shrinkage is observed and the green density is in the 50%–52% range. The thermal treatment at 1600 °C leads to parts sin-

Table 2
Compositions used for coagulation and extrusion

Number	vol% of solid	$[Al(CH_3COO)_2OH]$ (mg ml^{-1} of solvent)	Observations
1	50	16	No plasticity of the coagulated ceramic
2	50	12	No cohesion, suspension with a high viscosity
3	50	14	Extrusion at $t = 2$ h, 45 min, deformation under its own weight
4	50	16	Extrusion at $t = 1$ h, 10 min, deformation under its own weight
5	52	12	Extrusion at $t = 1$ h, 30 min, deformation under its own weight
6	52	14	Extrusion at $t = 1$ h, 15 min, no deformation
7	52	16	Extrusion at $t = 1$ h, 10 min, no deformation
8	55	14	Very difficult extrusion at $t = 0$ h, 35 min, low plasticity properties

tered at 98% of the theoretical density with homogeneous microstructure.

4. Conclusion

This study shows that it is now possible, by using the DCC process, to give properties of plasticity to the coagulated ceramic without binder addition. As this process separates the two steps such as casting and consolidation of the suspensions, the coagulation kinetic can be controlled by adapting the suspension formulation. That presented in this paper makes it possible to synthesize the lubricant directly on their surface. This new formulation of concentrated ceramic suspension obtained by adding both a cationic and an anionic polymer where the negative one is both the powder dispersant and the complexant of chitosan offers the possibility by destabilising the suspension to prepare a paste with plasticity properties. Organic particles obtained by complexation between the two polyelectrolytes and homogeneously dispersed in the ceramic matrix lubricate the interface between the mineral particles. The better dispersion state of the mixed system is achieved when chitosan complexes with the anionic polymer previously adsorbed on the alumina surface. It could be interesting to extend this concept to other ceramic powders such as Si_3N_4 or SiC and to others formulations of cationic and anionic polyelectrolytes. This present work demonstrates that colloidal way represents a solution to prepare, with reliability, extrudable paste without hard agglomerates and with a few concentration of organic additives; that represents large advantages compared to the traditional methods.

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