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The rheological behavior and surface charging of gelcasting alumina suspensions

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Abstract

Aim of this work is to investigate the effect of monomers containing either carboxylate (ammonium acrylate) or acrylamide (hydroxymethylacrylamide) functional groups on the surface charging and rheological behavior of alumina suspensions. The rheological behavior was investigated by changing the concentrations of dispersant (ammonium polyacrylate) and monomers in the suspensions. The zeta potential of alumina suspensions containing each of the different monomers was measured as a function of dispersant additions. The suspension rheological behavior varied significantly depending on the monomer type, which could be explained in terms of repulsive forces, pH changes and additive interactions.

Keywords: A. Suspension; Gelcasting; Monomer; Rheology; Zeta potential

1. Introduction

Several studies have focused on the development of low-cost techniques to produce reliable high-strength ceramic bodies [1]. Most of these techniques are based on innovative concepts of handling and molding high solids loading ceramic suspensions that change to a stiff gel resulting in a rigid green body with the required shape (near net shaping) [2–5]. Among these techniques, the gelcasting process was rapidly adopted in industries due to its versatility and the necessity of small changes in common process plants [6].

The gelcasting process is based on gelling a ceramic suspension by means of *in situ* polymerization of water-soluble monomers. Recent work investigated the applicability of several kinds of monomers for this process [7,8], and it has been reported that some of them may strongly affect the rheological behavior of ceramic suspensions having important consequences in terms of the processing route and defect control. The increase in viscosity of suspensions has been associated to specific adsorption of some classes of monomer on ceramic particles. Nevertheless, further studies related to this phenomenon are still lacking.

The aim of this work is to investigate how the carboxylate and acrylamide groups, which are commonly found in several water-soluble monomers used in the gelcasting process, influence the rheological behavior of aqueous alumina suspensions and the zeta potential of alumina particles in the presence of ammonium polyacrylate as a dispersant. The relationship between these properties is expected to be the key to understand the role of monomer functional groups in the rheological behavior of ceramic suspensions.

2. Materials and experimental procedure

As-received alpha-alumina powder (Almatis, A1000-SG, U.S., $d_{50} = 0.9\ \mu m$, surface area = $10\ m^2/g$) was used in all experiments. Ammonium polyacrylate (Dispex A-40, 30 wt% aqueous solution, Ciba) was selected as a dispersant. Ammonium acrylate (40 wt% aqueous solution, Allied

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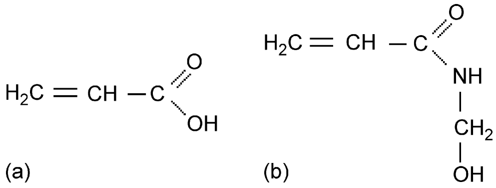

Fig. 1. Molecular structure of (a) acrylic acid and (b) hydroxymethylacrylamide.

Colloids) and hydroxymethylacrylamide (48 wt% aqueous solution, Merck), labelled AA and HMAM, respectively, were the monomers which were evaluated. Fig. 1 shows the molecular structures of these monomers.

Suspensions containing 40 vol.% solids were prepared for the rheological tests by adding the powder to a premix consisting of 25 wt% aqueous solution of monomer and varied concentrations of dispersants. The samples were ultrasonically dispersed and submitted to rheological tests, which consisted of measuring the shear stress as a function of the shear rate in the range between 0.22 and 55 s^{-1}. The sets of data were fitted to Casson's model giving Casson's viscosity and yield stress as a function of dispersant concentration. The experiments were carried out using a Brookfield LV DV-III viscometer with the R-13 small sample adapter.

The electrokinetics sonic amplitude (ESA) method was used to study the change in the surface charge of alumina particles when adding monomers or dispersants to the suspension. This technique provides the zeta potential of ceramic particles based on the measured electrophoretic mobility. The tests were carried out using a ESA MATEC 8000, which can simultaneously record the zeta potential, ionic conductivity, pH and temperature of the suspension. As a first step, these parameters were obtained by adding diluted monomer solutions (0.025 g/mL) into alumina aqueous suspensions containing 1 vol.% of solids. The addition rate of the monomer was 0.05 mL each 30 s. As a second step, the effect of adding dispersants to the monomer-containing suspensions was studied using the same suspensions, containing either HMAM or AA, after finishing the previous experiment. A 2 mg/L polyacrylate solution was introduced into the system at the rate of 0.05 mL each 30 s. A third set of experiments was carried out to evaluate the effect of adding the monomer to the zeta potential of polyacrylate-containing aqueous suspensions with 0.015 g polyacrylate/m^2 of alumina. This concentration was based on the rheological measurements.

3. Results and discussion

Fig. 2 shows the effect of the polyacrylate dispersant addition on the rheological behavior of alumina suspensions prepared either with a monomer solution (HMAM or AA) or with distilled water. The rheology of the suspensions was described well by Casson's model:

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta_C \dot{\gamma}} \qquad (1)$$

where τ is the shear stress, τ_0 the yield stress, η_C the Casson's viscosity and $\dot{\gamma}$ is the shear rate.

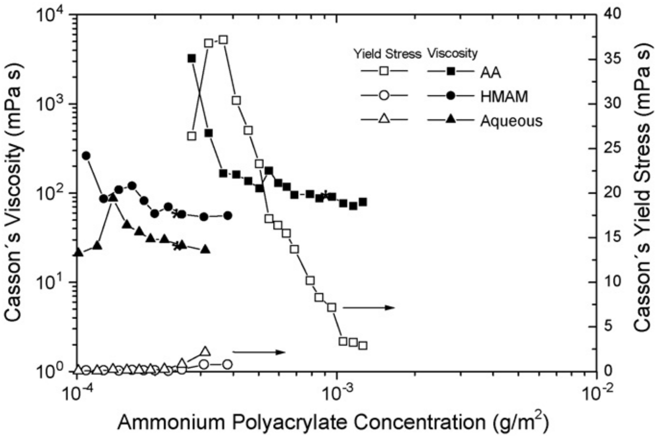

Fig. 2. Casson's viscosity (full symbols) and yield stress (hollow symbols) of alumina suspensions prepared either in plain water or with monomer solutions, as a function of dispersant additions. The star symbols correspond to optimum dispersant concentration.

Adding HMAM caused a small increase in Casson's viscosity and slightly changed the yield stress, compared to the aqueous suspension. This behavior indicates that this kind of monomer might not affect the efficiency of ammonium polyacrylate as a dispersant for alumina particles. A similar behavior was previously reported when acrylamide was used in the gelcasting process [9].

A different behavior was observed with suspensions containing AA solution: Casson's viscosity and yield stress values were significantly higher than those observed for both HMAM or aqueous suspensions. Additionally, the deflocculant concentration required to disperse the AA-containing suspension was nearly four times higher than that used in the other suspensions. This behavior suggests that some interaction between AA molecules and the alumina surface might occur before adding the ammonium polyacrylate, affecting the dispersion mechanism.

These results can be understood first based on the chemistry of monomers. In fact, each AA molecule has a carboxyl functional group which is well known to have great affinity to alumina surface [10]. Amino groups present in HMAM molecules, on the other hand, usually present more affinity to acidic surfaces [11] and a weaker interaction with an alumina basic surface should be expected.

Fig. 3 shows the apparent viscosity ($\eta_{app} = \tau/\dot{\gamma}$) of suspensions containing the optimum deflocculant concentration (depicted with stars in Fig. 2) as a function of the shear rate. As observed, even after complete dispersion, the apparent viscosity of suspensions containing AA was higher than the values observed for HMAM and aqueous suspensions in the measured shear rate range.

The differences in rheological behavior could be related to the powder dispersion, which was affected by the interaction between monomers and powder surface. The measurement of the particles zeta potential was used to investigate this interaction. Initially, the effect of monomers on the surface charges was evaluated and, thereafter, the effect of the dispersant and monomer association.

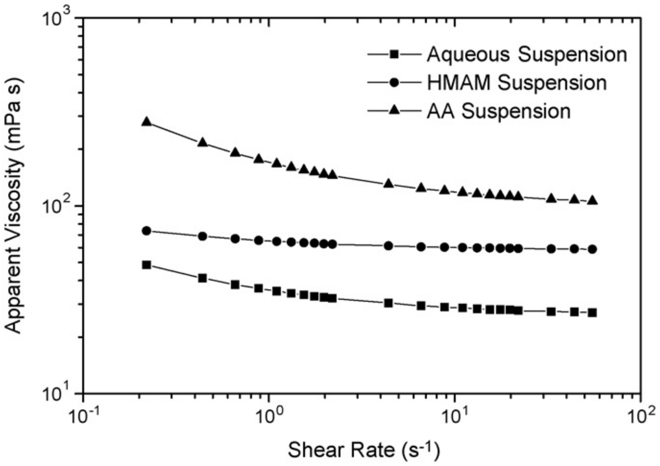

Fig. 3. Apparent viscosity as a function of shear rate of alumina suspensions containing the optimum dispersant concentration.

Fig. 4 shows how the different monomers affect the suspension's pH and zeta potential of alumina particles. Note that by adding HMAM to the suspension caused a negligible change in the zeta potential value, which remained close to zero in the evaluated range. The pH also remained constant, around 8.4 during the experiment. As HMAM has a basic character, it rarely dissociates in water in this pH range. Therefore, pH 8.4 may be considered a good approximation of the isoelectric point (IEP) for the Al_2O_3 used in this work. Conversely, the addition of AA monomers caused a small change in the zeta potential, which varied from zero to −4.6 mV, whereas the pH decreased from 8.4 to 5.4. The change in zeta potential occurred mostly at small AA concentrations. For monomer additions above 0.5 g (dry weight basis), the zeta potential leveled around −4.5 mV, but the pH still decreased from 6.5 to 5.4.

This behavior may be understood based on the specific adsorption of the acrylate group on the alumina surface. As shown in Fig. 4, the zeta potential is negative in spite of the pH changing to values below the IEP of alumina. This is not common behavior for oxides [12,13], which are normally positively charged below their zero charge point as a result of a reaction such as

$$MO + H^+ \rightarrow MOH^+ \quad (2)$$

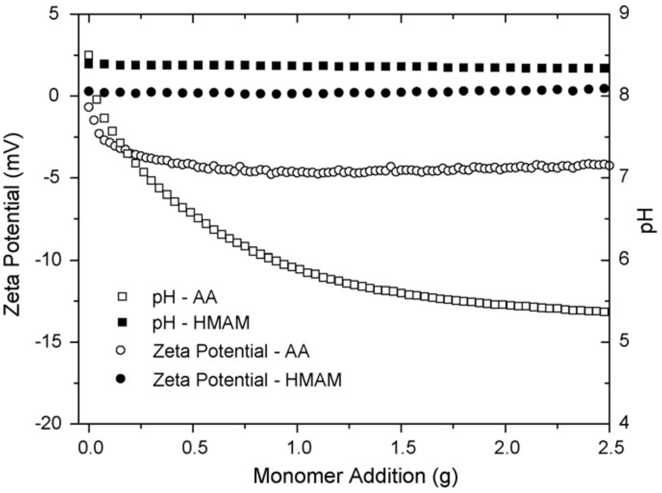

Fig. 4. Zeta potential of alumina particles and pH suspension as a function of monomer addition (dry weight basis).

Therefore, it is likely that as the particles surface was covered with AA monomers, the adsorption of H^+ ions was inhibited, which prevented the positive charges in the evaluated pH range from developing. This means that the monomer adsorption on the powder surface might have changed alumina pK_a as previously observed in a couple of materials [14,15]. Nonetheless, the adsorption of monomers does not explain the development of negative surface charges below the IEP. In fact, it has been shown that the ability of the adsorbate in changing the particles surface charge increases with the number of dissociable groups and that molecules with only one functional group would not be able to change the surface charge [10]. Although each acrylic acid molecule has only one carboxylate group, it is expected that some dimers and/or oligomers are found in the monomer solution. These molecules with additional carboxylate groups might induce a small negative surface charge in a pH range below the IEP.

Similar behavior is expected to take place when a dispersant is introduced into a monomer-containing suspension. Fig. 5 shows the zeta potential and pH of alumina suspensions containing HMAM and AA as a function of ammonium polyacrylate addition.

By adding a dispersant to the suspensions containing HMAM resulted in a zeta potential of −24 mV, even at small deflocculant concentrations. This behavior indicates that the interaction between the alumina particles surface and HMAM monomers was negligible, as expected from the rheological results and chemistry hypothesis.

The behavior of AA-containing suspension was quite different. Small additions of dispersant (<0.005 g) decreased the zeta potential (in modulus), but further additions increased its value (in modulus), which leveled around −10 mV. During this experiment, the pH slightly changed from 5.4 to 5.6. This behavior seems to confirm that AA adsorbs specifically on the alumina surface. At small deflocculant concentrations the adsorption of polyelectrolyte macromolecules was hindered by monomers, which completely covered the particle surface. At this stage, the only effect of adding polyelectrolyte was a reduction in the dissociation of carboxylate groups which were not involved in the attachment of dimers and oligomers to the surface, increasing the nondissociated (R–COOH) fraction. As the deflocculant concentration increased, its activity became high enough to withdraw the monomers from the alumina surface, which were replaced by the polyelectrolyte. Consequently, the zeta potential changed from −3 to −10 mV, as the polyelectrolyte has a larger number of dissociable groups compared to the removed species. However, since the polyelectrolyte dissociates only partially in this pH range (∼5.5) [13], the dispersing effectiveness is limited, and higher charges are not expected. In addition, a large fraction of the alumina surface sites is positively charged in this pH range, counterbalancing part of the polymer negative charges. Higher zeta potential values would

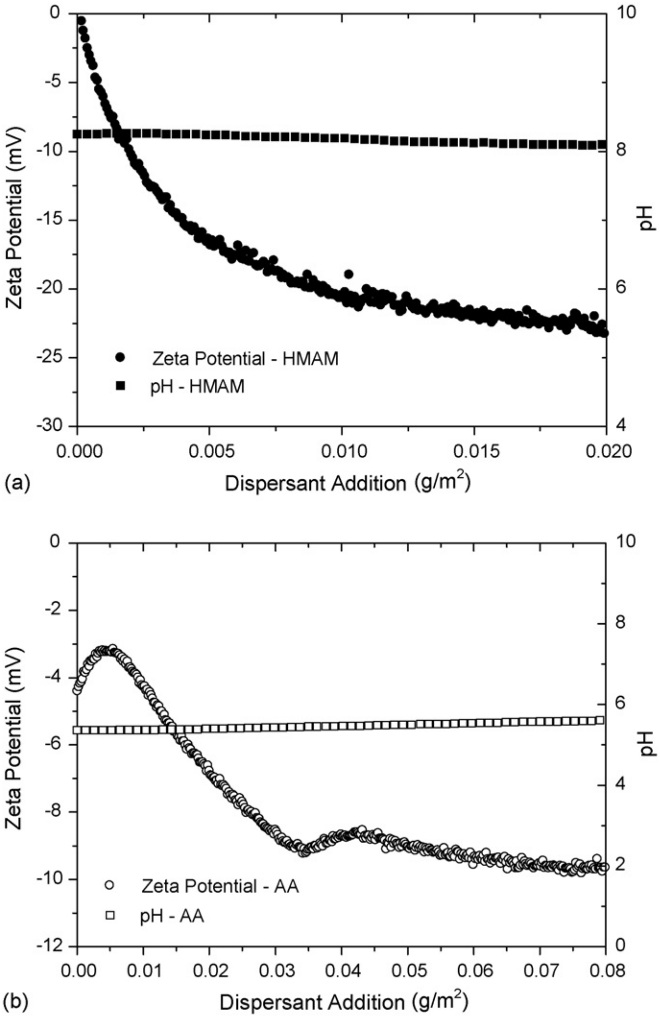

Fig. 5. Zeta potential and pH of alumina suspensions containing (a) HMAM and (b) AA as a function of dispersant addition.

be expected if the pH were increased. Nonetheless, the higher ionic strength would limit the zeta potential, comparatively to the values observed in suspensions prepared with either HMAM or plain water.

Fig. 6 shows the zeta potential and pH values of alumina suspensions containing previously added dispersant as a function of monomer addition (dry weight basis). It is clear that the addition of HMAM to the suspension did not affect the zeta potential of the system, which remained almost constant around −24 mV. Comparing the results with those in Fig. 4, one notes that the zeta potential reached the same value, regardless of the sequence of adding additives, because the activity of this monomer on an alumina surface is almost negligible.

The addition of AA monomers, however, changed the pH value from 8.5 to ~5.5, similarly to the behavior observed in Fig. 5. It also reduced the zeta potential (in modulus) from −23 to −12 mV, which is slightly higher than the plateau value attained in Fig. 5. This behavior may be basically attributed to the effect of the pH change, which reduced the polyelectrolyte dissociation, and not to the desorption of deflocculant molecules.

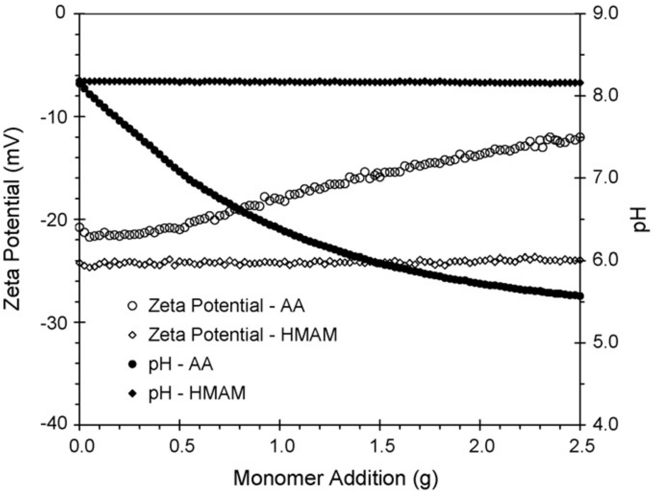

Fig. 6. Zeta potential of alumina particles and suspension's pH as a function of monomer addition (dry weight basis) to suspensions containing a dispersant.

The results also indicate that the attachment of polyacrylate on an alumina surface is stronger than that of monomers. Even when dealing with AA, which has higher specific adsorption energy than HMAM, the polyacrylate surface coverage is more stable, provided that its concentration is high enough to withdraw AA molecules from the alumina surface. This behavior is compatible with a previous work [10] which shows that the adsorption of short molecules containing a single carboxylate group on an alumina surface is weak and does not impart a significant surface charge. As the number of carboxylate groups per molecule increases, both the adsorption and surface charge increase, with clear effects on the zeta potential and, therefore, on the rheological properties.

4. Conclusions

The experiments showed that the rheological behavior of alumina suspensions containing monomers may be strongly influenced by the chemistry of the monomers. Powder dispersion using polyacrylate as a deflocculant was not affected by hydroxymethylacrylamide (HMAM) monomers, which showed a negligible interaction with the alumina surface due to chemical incompatibility between the oxide and the amide group in the evaluated pH range. As a result, high zeta potential values were attained after adding the dispersant and the rheological behavior of the HMAM-containing suspension was quite similar to that prepared with plain water.

On the other hand, suspensions containing acrylic acid monomers (AA) showed a higher yield stress and Casson's viscosity, and required a polyacrylate concentration roughly 10 times higher than that used to reach the minimum viscosity in the other suspensions. This behavior occurred because AA adsorbs specifically on the alumina surface. Therefore, a higher concentration of polyacrylate is required in order for its activity to become high enough to withdraw the adsorbed monomers from the powder surface and replace them with the polyelectrolyte. In the pH range near the IEP, a high ionic strength arises from the high concentration of dissociable carboxylate groups present in both the monomer and the dispersant. As a result, the apparent viscosity of the suspension becomes higher than that observed in the suspensions prepared with either aqueous HMAM solution or plain water.

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