Derivatives of Biomacromolecules as Stabilizers of Aqueous Alumina Suspensions

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ABSTRACT: The stabilization of alumina suspensions is key to the development of high-performance materials for the ceramic industry, which has motivated extensive research into synthetic polymers used as stabilizers. In this study, mimosa tannin extract and a chitosan derivative, that is, macromolecules obtained from renewable resources, are shown to be promising to replace synthetic polymers, yielding less viscous suspensions with smaller particles and greater fluidity, that is, more homogeneous suspensions that may lead to better-quality products. The functional groups of tannin present in mimosa extract and *N,N,N*-trimethylchitosan (TMC) are capable of establishing interactions with the alumina surface, thus leading to repulsion between the particles mainly due to steric and electrosteric mechanisms, respectively. The stabilization of the suspension induced by either TMC or mimosa tannin was confirmed by a considerable decrease in viscosity and average particle size, in comparison with alumina suspensions without stabilizing agents. The viscosity/average particle size decreased by 49/84% and 52/87% for suspensions with TMC and mimosa tannin, respectively. In addition, the increase in the absolute zeta potential upon addition of either TMC or mimosa tannin extract, especially at high pHs, points to an increased stability of the suspension. The feasibility of using derivatives of macromolecules from renewable sources to stabilize aqueous alumina suspensions was therefore demonstrated. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 58–66, 2010

Key words: mimosa tannin; *N,N,N*-trimethylchitosan; renewable resources biomacromolecules; aqueous alumina suspension stability

INTRODUCTION

Ceramic materials have found applications in ceramic coating, biomaterials, electronic, and semiconductor materials, to name a few. Most applications require that colloidal particles, such as alumina, remain dispersed in aqueous suspensions. One of the main questions involved in the use of colloidal suspensions of alumina is to identify processes to prevent aggregation.[1–3] The aqueous alumina suspensions used in ceramic processing have a large number of solid particles, and their dispersion may be assisted by the addition of other species. The latter may be, for instance, polyelectrolytes, that is, polymers with charged groups or which can acquire charges due to ionization, depending on the pH of the medium. The polyelectrolyte molecules can interact with the surface of alumina, hindering the approach of other particles, and upon such interactions depends the ability of polymers to stabilize colloidal suspensions.[3,4]

Steric and electrosteric mechanisms are normally responsible for the stabilization of colloidal systems. Electrostatic stabilization is based on the mutual repulsion of like electrical charges that can be generated when particles are dispersed in a polar medium. The steric stabilization occurs due to the adsorption of a macromolecular layer on the particles, thus preventing them from close contact with each other. Stabilization is reached when the thickness of the coating is sufficient to keep particles separated by steric repulsions. The electrosteric stabilization is a combination of the two previous mechanisms: steric and electrostatic stabilization.[4–9]

Through the control of parameters such as viscosity and particle size the physicochemical properties of the ceramic suspensions can be controlled. In aqueous solutions, the net surface charge of alumina depends on the pH, with the reactions involving hydrated alumina particles, which in a simplified way can be represented as follows:

Acid solution:

$$x[H_3O^+] + [-O-Al-]_n(OH)_x \rightleftharpoons [-O-Al-]_n(OH_2^+)_x + x\,H_2O \quad (1)$$

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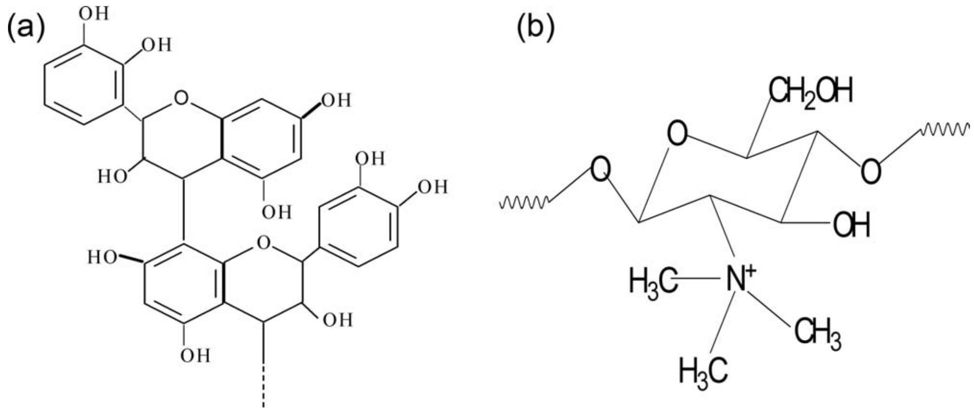

Figure 1 Partial structure of: (a) mimosa tannin; (b) *N,N,N*-trimethylchitosan, (TMC).

Alkaline solution:

$$x\mathrm{OH}^- + [-\mathrm{O}-\mathrm{Al}-]_n(\mathrm{OH})_x \rightleftharpoons [-\mathrm{O}-\mathrm{Al}-]_n(\mathrm{O}^-)_x + x\,\mathrm{H_2O} \quad (2)$$

At a specific pH, the number of negative and positive charges is equal, that is, the point of zero charge (pcz).

Polyelectrolytes may adsorb on the alumina particles and promote steric repulsion between particles. In fact, the interactions between polyelectrolytes and alumina particles are complex, for there is a compromise between attraction and interparticle repulsion, which is affected by small changes in the parameters of the system.[10,11] Several macromolecules have been used as stabilizing agents for alumina suspensions, including sodium polyacrylates.[1,2,7,8,12–15]

In this work, a macromolecule obtained from renewable resources and a derivative of a natural polysaccharide, namely mimosa tannin and *N,N,N*-trimethylchitosan (TMC) (Fig. 1), respectively, were used to stabilize alumina suspensions. Mimosa tannin extracts are water soluble polyphenolic-based compounds that exist in a variety of plants.[16–18] In aqueous alkaline media, they are negatively charged due to phenoxide rings [$-\mathrm{C_6H_4O}-$] originating from deprotonation of phenolic groups [$-\mathrm{C_6H_4OH}$]. The interest in mimosa tannin as stabilizers of aqueous alumina suspensions arises from these structural characteristics.

Chitosan is obtained by partial deacetylation of chitin, a polysaccharide extracted from the exoskeletons of crustaceans, mainly crabs and shrimps. In the deacetylation process, the acetamide groups ($-\mathrm{NHCOCH_3}$) of the repeating units of chitin are converted into amino groups ($-\mathrm{NH_2}$) via alkaline hydrolysis.[19,20] If at least 40–60% of the acetamido groups are hydrolyzed the resulting product is called chitosan, a polymer soluble in acidic aqueous media ($\mathrm{pH} < 6.0$) due to protonation of its amino groups ($\mathrm{p}K_\mathrm{a} \approx 6.5$).[19,21,22] Therefore, chitosan is soluble in weak acid aqueous solutions, but it is insoluble in neutral and alkaline media, a serious drawback for many applications.[23] Among the strategies adopted to overcome this limitation, the preparation of chitosan derivatives with improved solubility has been proposed.[19,24] For instance, the extensive methylation of chitosan results in *N,N,N*-trimethylchitosan (TMC), a macromolecule (Fig. 1) containing permanently charged groups (quaternized nitrogen atoms) which is hydrosoluble in a wider range of pH when compared with the parent chitosan.[20]

The action of TMC and mimosa tannin as stabilizing agents was investigated here with measurements of viscosity, average particle size, and zeta potential. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If the particles have a large negative or positive zeta potential, they will repel each other leading to dispersion stability. On the other hand, aggregation of the particles occurs at low zeta potential values, leading to dispersion instability, as a consequence of weak or inexistent repulsive forces. Zeta potentials higher than +30 mV or –30 mV normally correspond to stable suspensions.[14,25,26] The effects from incorporation of mimosa tannin or TMC on the morphology of the alumina suspensions are also discussed.

EXPERIMENTAL

The alumina samples, kindly supplied by Treibacher Schleifmittel Brazil Ltda., São Paulo, Brazil, have a surface area of 2.4 $\mathrm{m^2\ g^{-1}}$ (determined by BET) and average particle size 1.0 μm, as informed by the producer.

The extensive methylation of chitosan for preparing *N,N,N*-trimethylchitosan was carried out according to the following procedure: to the suspension containing 3.0 g, (0.0176 mol) of chitosan Fluka (200,000 g $\mathrm{mol^{-1}}$ as average mass molecular weight, as informed by the producer) in 150.0 mL of *N*-methyl-2-pyrrolidone, 25.8 mL of NaOH (0.0361 mol), 33.84 g of iodomethane (0.238 mol), and 5.4 g of NaI (0.036 mol) were added and stirred for 3 h at 36°C. Then, the chitosan derivative was isolated by filtration and submitted to dialysis (Viskase Corporation –21 mm membrane diameter; cut-off 12,000–16,000 gmol) for 3 days against aqueous NaCl 0.1*M*. After exhaustive rinsing, the *N*,*N*,*N*-trimethylchitosan chloride (TMC) was filtered and vacuum dried. The TMC was characterized with ^{1}H NMR spectroscopy using a spectrometer Brucker AC 200. The sample was dissolved in a D_2O/HCl mixture (100/1v/v) at a concentration of 10 g $L^{-1\cdot}$ The parameters for the acquisition of ^{1}H NMR were as follows: pulse 90° corresponding to a pulse width of 8.2 μm; LB = 0.3 Hz; NS = 16.

Mimosa tannin extract is based on polyphenolic compounds, but also contains carbohydrates oligomers and monomers,[16] and was kindly donated by TANAC SA (Montenegro, Rio Grande do Sul, Brazil). The average molar weight mass of mimosa tannin was determined by size exclusion chromatography (SEC) using a Shimadzu SCL-10A system controller connected to a LC-10AD pump, CTO 10 column oven, and RID-6A refractive index detector. The column system consisted of a 5 μm mixed PLgel [preceded by a 10 μm (50 × 7.5mm) PLgel guard column] with *N*-methyl-2-pyrrolidinone (NMP) (Aldrich HPLC grade) as mobile phase. The system was calibrated using pullulan with the following molar masses: 1.6×10^6, 3.8×10^5, 2.12×10^5, 1.0×10^5, 4.8×10^4, 2.37×10^4, 1.22×10^{-4}, and 5.8×10^{-3} g mol^{-1}. Before being injected into the SEC system, the solution was filtered through a 0.45 μm PTFE membrane filter. The mimosa tannin extract concentration injected was 0.0020 g mL^{-1} in NMP. The chromatogram showed two peaks (figure not shown) assigned to weight average molar masses (M_w) of near 44,700 and 4,700 g mol^{-1} (less intense peak). The SEC average molar masses does not correspond to absolute values and the results have to be referred to as pullulan-equivalent molar mass. Then, the low pullulan–equivalent weight average molar mass fraction can be assigned to non-or less-aggregated mimosa tannins macromolecules, as indicate by the low polydispersity index (M_w/M_n near 1.1). The high weight average molar mass fraction (M_w/M_n near 1.4) is a consequence of aggregation involving tannin-tannin and tannin-carbohydrates molecules.[16]

Aqueous alumina suspensions (60 wt %) were prepared with 220 mL distilled water and 402 g alumina powder, stirred for 1 h, in a 500 mL glass beaker. The viscosity measurements were then performed with a rotational Brookfield Viscometer–model DVII, cylindric geometry, using spindle 3 and 3 rpm, at room temperature. The rotating spindle is immersed in the beaker of suspension and, under this condition, the applied shear rates are not constant within the measurement chamber. Previous studies showed that under these conditions the stirring is enough for observing the electrostatic stabilization, which results from the mutual repulsion of like-electrical charges on the alumina surface, when no stabilizer is present. Therefore, these conditions were chosen in order to better observe the effective action of the stabilizer, in a pH range that includes those at which the electrostatic stabilization previously mentioned is present, as will be discussed latter. Mimosa tannin extract and TMC were weighted and added into alumina suspensions directly as powder. The pH of aqueous alumina suspensions was adjusted with the addition of HCl 1 mol dm^{-3} and NaOH 1 mol dm^{-3} solutions.

For zeta potential and particle size measurements, 2.0 wt % alumina suspensions were used. The average particle size and zeta potential were measured using a ZETA PALS equipment from Brookhaven Instruments Corporation.

The scanning electron microscopy (SEM) analysis was carried out with a Zeiss-Leica apparatus, model 440, with an electron acceleration of 20 kV. For this, a drop of the alumina suspensions was placed on a solid support which was then inserted in an oven at 60°C until the evaporation of water was complete. Electrical contact with the sample was made with silver paint and a gold coating to make the sample conductive. The same procedure was used for preparing the samples of alumina and alumina/mimosa tannin; alumina/quaternized chitosan suspensions.

As mimosa tannin extract is predominantly based on polyphenols, for the sake of simplicity in the next section the results are discussed mainly considering the interactions involving tannin and alumina. It must be again emphasized that the mimosa tannin extract was added into alumina suspensions directly as powder, which probably minimizes the possibility of tannin-tannin and tannin-carbohydrates aggregation, because the large amount of alumina particles in the aqueous suspension favors the interaction alumina-mimosa tannin. In addition, even considering the aggregate tannin-carbohydrate, the interaction with alumina surface probably involves functional groups of the tannin moiety, which predominate in the bulk of the aggregate.

RESULTS AND DISCUSSION

The interaction between tannin present in mimosa extract or quaternized chitosan (TMC) and the alumina surface involves mainly electrostatic and H-bond interactions, as depicted in the Scheme in Figure 2. However, as can be inferred from the

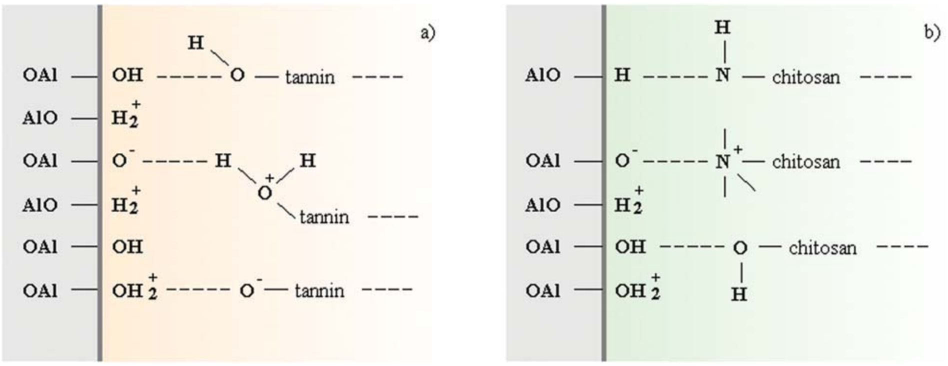

Figure 2 Schematic representation of the possible interactions between groups of: (a) mimosa tannin and (b) TMC and alumina surface in aqueous medium. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

structures in Figure 1, the macromolecule of tannin is stiffer than that of TMC. Upon interacting with the surface of alumina particles, mimosa tannin can generate a steric barrier that prevents the approach of other particles, even though mimosa tannin may not cover the particles. TMC, on the other hand, can at least partially cover the surface of the particles as its molecules are chains, then more flexible than mimosa tannin, that exhibit positive charges. The TMC used in this work had 55% of the amino groups trimethylated, according to the ^{1}H NMR analysis (spectrum not shown). In addition to interactions with the negative charges on the alumina surface, other interactions may occur such as those involving the chitosan hydroxyl groups [Fig. 2(b)]. The mimosa tannin can have negative or positive sites depending on the pH, which can interact with the alumina surface [Fig. 2(a)], as their pK_a is near 10.[27] At this pH, $\sim$ 50% of phenolic hydroxyl groups are dissociated, generating phenolate ions. In the suspension of alumina, the negative charges on the surface of the particles affect the dissociation of phenolic hydroxyls. Therefore, the value of pK_a can be considered only to estimate the interactions that can occur. The alcoholic hydroxyl is less acidic than the phenolic one, therefore alkoxide groups are present only at high pH values.

The viscosity of the alumina suspension decreased upon addition of mimosa tannin extract or TMC, until saturation was reached, as shown in Figure 3(a,b). The measurements were performed at pH 10.0, for which the alumina surface possesses a significant amount of negative charges that may interact with the $-N(CH_3)_3^{(+)}$ groups from TMC [Fig. 2(b)] and nonionized hydroxyl groups [as $-C_6H_4OH$] of mimosa tannin [Fig. 2(a)]. Figure 3(a,b) also shows that upon addition of about 0.06 of TMC and 0.01 wt % of mimosa tannin extract, the viscosity of the suspension decreased near ten times. These amounts of mimosa tannin and TMC were then considered in further experiments to investigate the influence of pH on the stability of the suspension. Significantly, the suspension can be stabilized using a smaller amount of mimosa tannin extract than TMC. As already mentioned, the interactions of mimosa tannin with the surface of alumina particles probably introduce a steric barrier preventing the approach of other particles. With such an efficient barrier, a small amount suffices to promote stabilization of the suspension.

At low pH values, between 3 and 5, the suspension is stabilized by the repulsive interactions between the positive charges on the alumina surface, at first with no need of a stabilizing agent. This is why the viscosity remains low, regardless of the addition of TMC or mimosa tannin extract, as shown in Figure 4. Above pH 6.0, however, the negative and positive charges at the surface of the particles lead to attractive interactions and then aggregation of alumina particles, which in turn leads to an increase in viscosity. For pH $\geq$ 7.0, the viscosity of the aqueous alumina suspensions is very high, as the point of zero charge (pcz) is near pH 7.0, as will be shown later with zeta potential measurements (Fig. 8).

The effect from TMC and mimosa tannin is then apparent for pH $\geq$ 6.0, as evidenced in Figure 4, with large reductions in viscosity upon introduction of these macromolecules in the solution. The stabilization is probably electrosteric due to the adsorption of charged macromolecules on the alumina surface. The adsorption of mimosa tannin on the alumina surface probably occurs via interactions involving ionized and nonionized hydroxyl groups of the macromolecule and sites of the alumina surface, mainly through hydrogen bonds. For the positively charged TMC, the interactions probably involve mainly the negative sites on the alumina surface, especially in alkaline medium.

The average size of the particles in the alumina suspension was strongly affected by adding of TMC, from pH 6.0 to 8.0 as shown in Figure 5(a). From pH

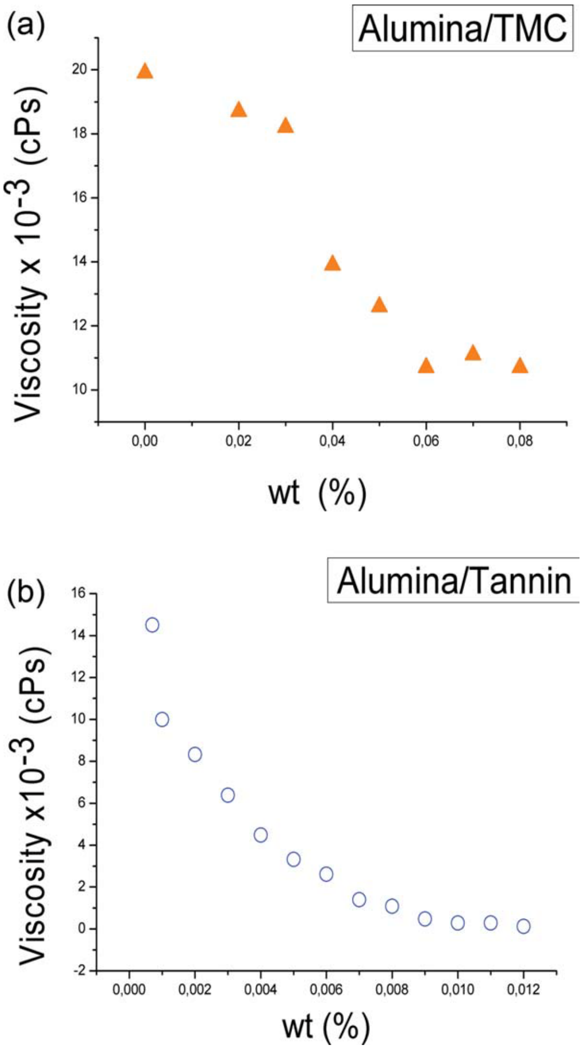

Figure 3 Viscosity of alumina suspension as a function of wt % of: (a) TMC, (b) mimosa tannin extract; 25°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

3.0 (ca. 140 nm) to 5.0 (ca. 300 nm) and from 8.5 (ca. 400 nm) to 10.0 (ca. 150 nm) the particles are small, even in the absence of the stabilizing agent owing to repulsion between sites of like charges on the alumina surface.[12,13] Indeed, with high alumina concentrations, as in the viscosity experiments, the stabilizing effect due to repulsion of negative charges up to pH 10[3,11,12] is not observed, and the viscosity is maintained constant above pH near 7.0 [Fig. 4(a,b)]. For pHs between 6.0 and 8.0, in the absence of TMC particle aggregation leads to larger average size (maximum value of 1315 nm, at pH 7.0) as illustrated in Figure 5(a). In contrast, when TMC is present, the average particle size remains practically unaltered (ca. 120 nm) for the whole pH range mentioned.

Upon addition of mimosa tannin extract, the particle size in the suspension also decreases sharply from pH 6.0 to 8.0. The average size for the particles with no stabilizing agent was about 1000 nm, with sedimentation being visually observed. The addition of a small amount of mimosa tannin (0,01 wt %), however, decreases the particle size (ca. 140 nm) [Fig. 5(b)], and no sediment was observed.

Figure 6 shows size distribution curves for particles in alumina suspensions, including those containing mimosa tannin extract and TMC. The pHs chosen were 4.0, 7.0, and 8.0, that is, including the pcz [near pH 7.0, Fig. 8(a)] where the alumina particles have higher tendency to aggregate owing to the strong electrostatic attraction of oppositely charged particles. In the absence of the macromolecules, at pH 7.0, and mainly at pH 8.0, the distribution curve is broader, thus indicating higher polydispersity, in addition to exhibiting

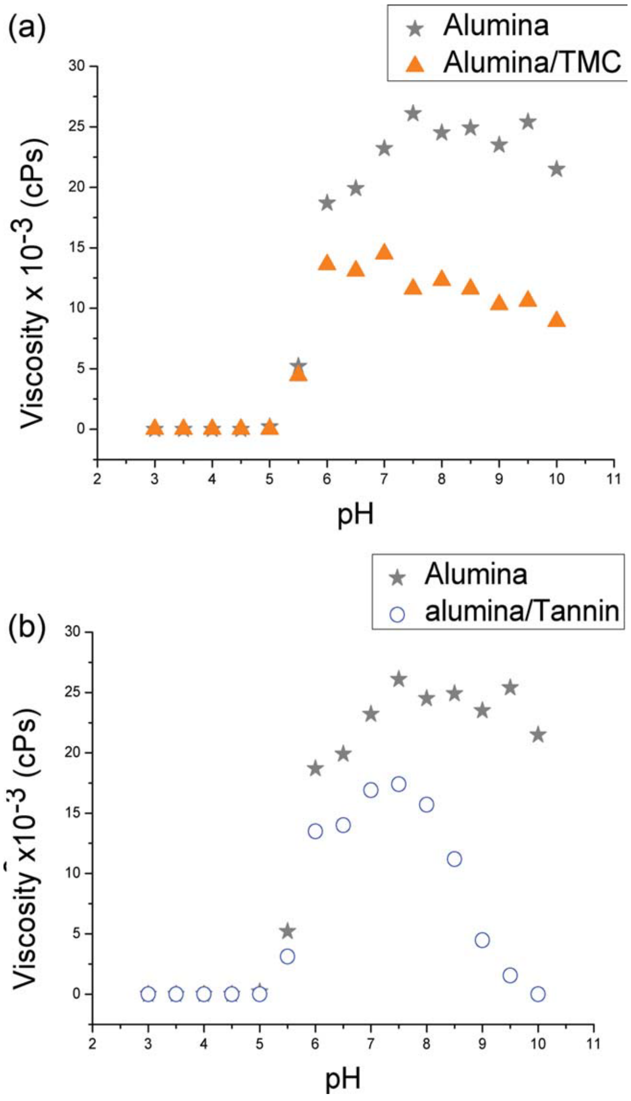

Figure 4 Viscosity of the aqueous suspension vs. pH: (a) TMC; (b) mimosa tannin extract. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

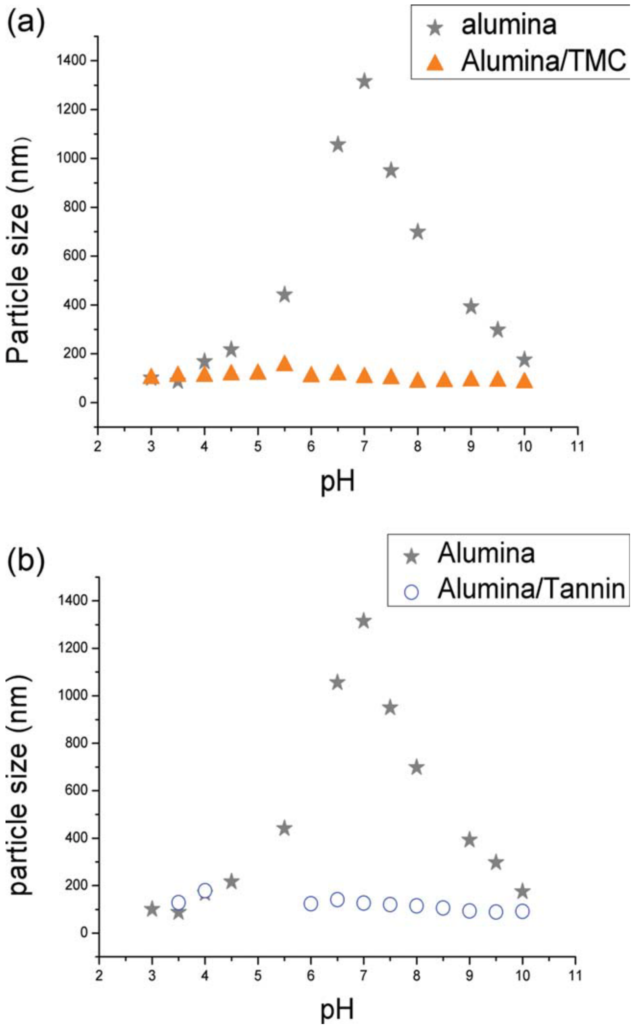

Figure 5 Average particle size vs. pH for aqueous alumina suspension: (a) TMC; (b) Mimosa tannin extract. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

larger particle sizes (near 1200 and 1010 nm, respectively, as values at the maximum, Fig. 6) than the suspensions containing either mimosa tannin (near 50 and 110 nm, respectively, as values at the maximum) or TMC (near 50 and 100 nm, respectively, as values at the maximum), which display a narrow distribution with average particle sizes below 300 nm.

At pH 4.0, the differences between the curves with (near 50 nm as values at the maximum, Fig. 6) or without (240 nm as value at the maximum, Fig. 6) stabilizing agent are less drastic when compared with those at pHs 7.0 and 8.0. This can be explained by the fact that at pH 4.0, the suspension is inherently stable owing to the large number of positive charges, because the hydrated alumina surface is protonated at this pH, which leads to repulsive interactions and hinders aggregation between the particles.

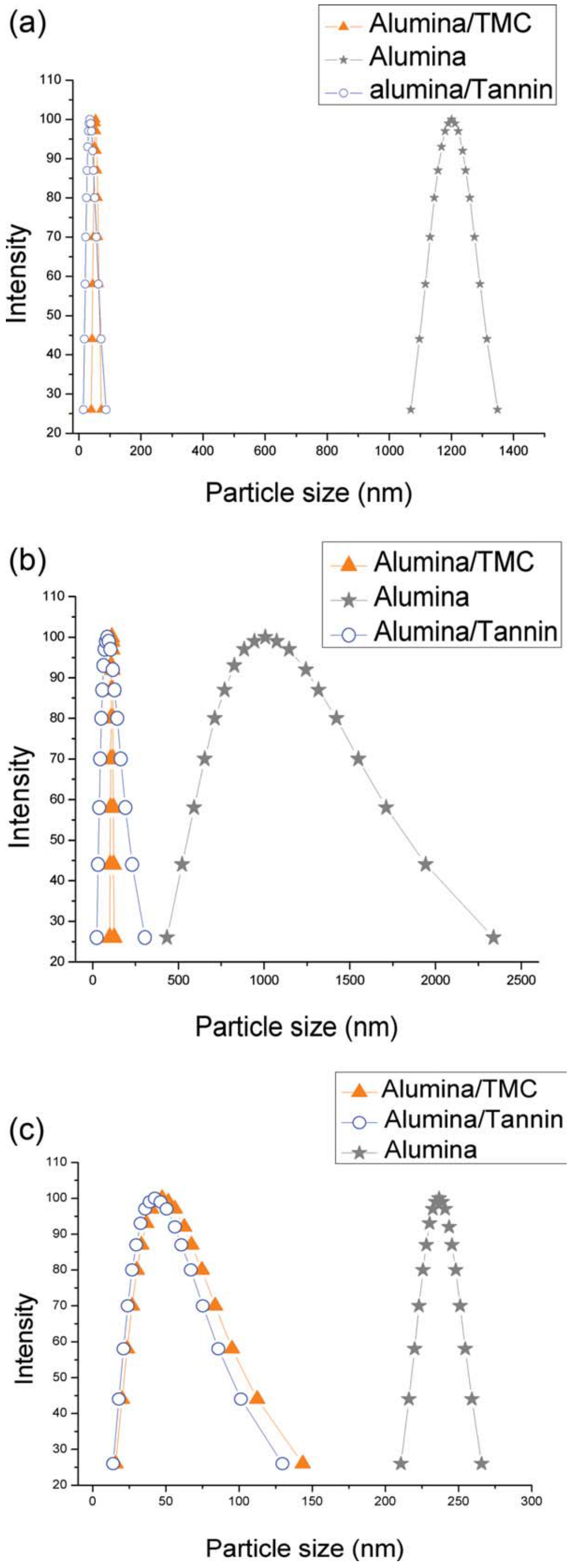

Figure 6 Distribution of the particle size: alumina suspensions with mimosa tannin extract and TMC, (a) pH 7; (b) pH 8.0; (c) pH 4.0. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

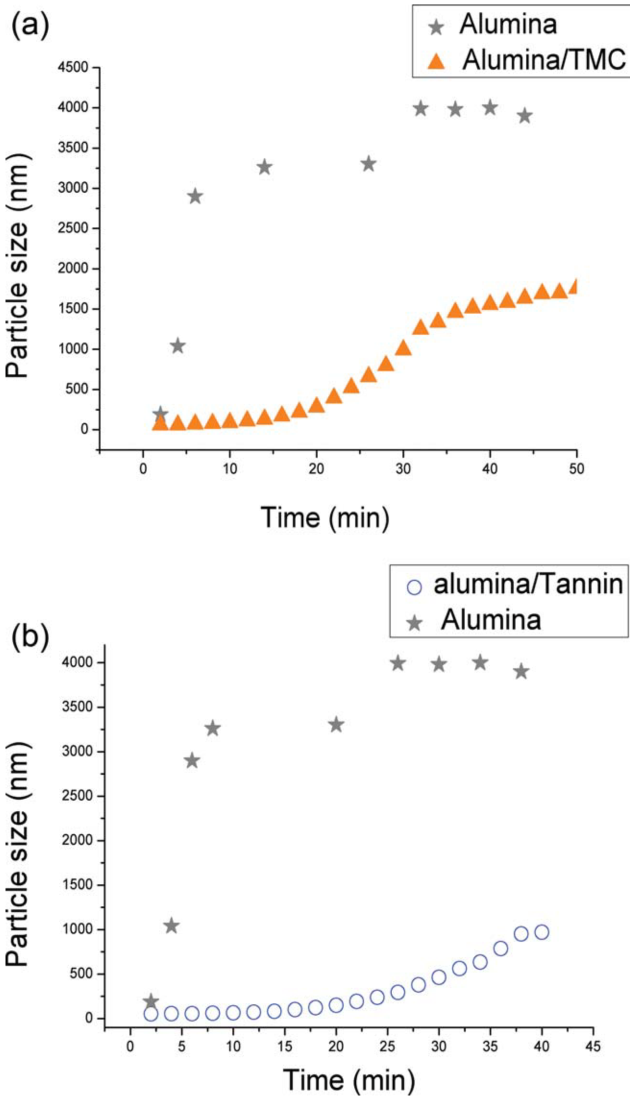

Figure 7 Average particle size vs. time for alumina suspensions without stabilizing agent and with: (a) TMC; pH 6.0; (b) mimosa tannin extract, pH 8.0. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 shows the change in particle size in the alumina suspensions as a function of time. Within 10 min, with no stabilizing agent, the suspension tends to aggregate (average particle size near 3100 nm). On the contrary, Figure 7(a,b) indicate that with TMC and mimosa tannin aggregation is observed only after 30 min. However, even after aggregation the particle sizes are considerably lower when TMC or mimosa tannin extract are added (average particles sizes near 1000 and 450 nm, respectively), when compared with the aqueous suspensions of alumina [Fig. 7(a,b)].

The addition of stabilizing agents causes changes in the electrical double-layer around the alumina particles. The adsorption of such agents on the alumina surface may screen the surface charges, depending on the pH and degree of dissociation of the functional groups on the alumina surface and of the agents.[15,27–29] After addition of TMC, the zeta potential for the alumina suspensions is positive for the whole pH range, as shown in Figure 8(a). In alkaline media, the interaction between the positive sites of TMC and the negative sites on the alumina surface lead to net charge positive, although the values are lower than those of pH 3.0 to 5.0, in contrast to the particles in an aqueous solution without stabilizing agent. The "free" positive sites of TMC predominate, thus resulting in a small positive zeta potential. These results are consistent with the viscosity and average particle size data discussed previously and confirm that quaternized chitosan is an efficient stabilizing agent.

The addition of mimosa tannin extract also changes the zeta potential of the aqueous alumina suspension, as shown in Figure 8(b). Although the

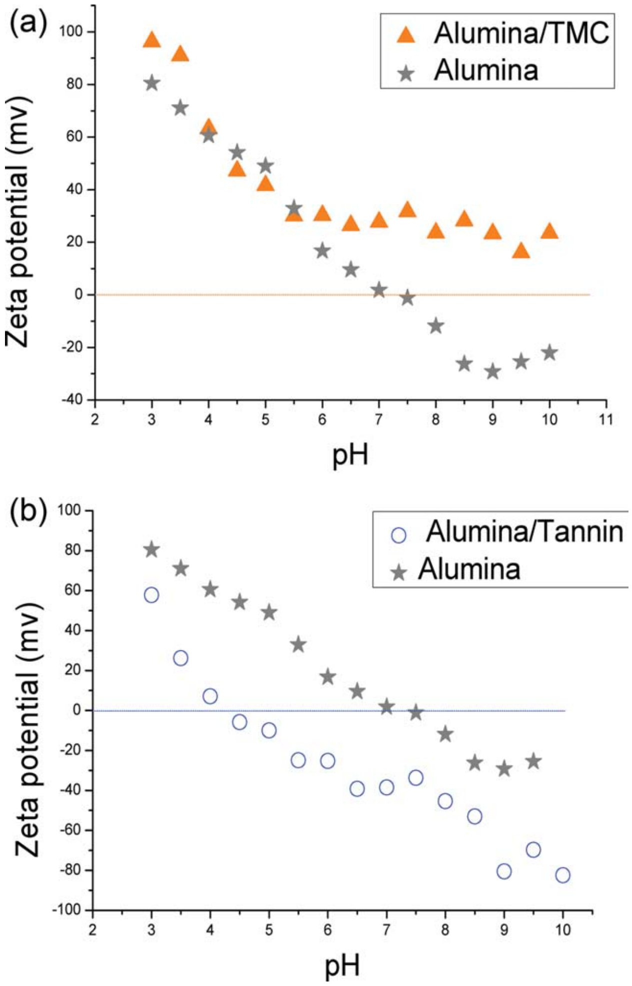

Figure 8 Zeta Potential for the alumina suspension vs. pH in the absence and presence of stabilizing agent: (a) TMC; (b) mimosa tannin extract. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

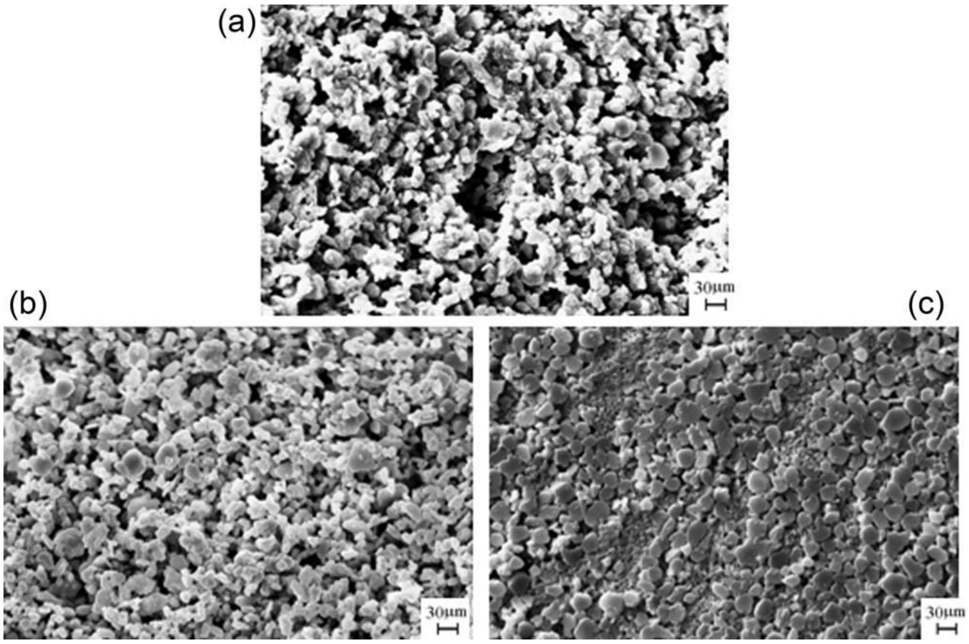

Figure 9 SEM image obtained for the particles sedimented from aqueous alumina suspension: (a) without stabilizer; (b)TMC; (c) Mimosa tannin extract, pH near 9; magnification ×5000.

decrease in zeta potential has no importance for low pHs, because the alumina suspensions are already stable, it is especially relevant at high pHs, for which a significant decrease in the zeta potential was observed [Fig. 8(b)]. As already indicated in the viscosity measurements, the incorporation of mimosa tannin is beneficial for stabilizing the suspensions at such high pH.

The micrographs shown in Figure 9 can be taken as an indication of the morphology of the particles in suspension. The suspension was submitted to drying and therefore the images observed must be considered only as an indicative of the state of the particles in the suspension. In any case, the morphology of the sedimented particles should somehow resemble that of the suspended particles. Figure 9(a) shows an irregular morphology with agglomerates and spaces between particles sedimented from suspensions with no stabilizing agent. These interstitials probably store water molecules that generate voids when the sample is dried, which decreases the quality of the final product. When either mimosa tannin or TMC were added in the suspension, the particles are better packed, as indicated in Figure 9(b,c).

It can be pointed out that even at pH near 9, where the alumina suspension is somewhat stabilized by the repulsion between negative charges at the surface of the particles, the incorporation of mimosa tannin and TMC leads to a more homogeneous system (Fig. 9).

CONCLUSIONS

The results presented here demonstrated that quaternized chitosan (TMC) and mimosa tannin extract acted as efficient stabilizing agents for aqueous alumina suspensions, particularly at pH > 7, as shown with viscosity, zeta potential, and particle size measurements. The stability of average particle size as a function of time is promising, because time stability is crucial for processing the material. This work points to the viability of replacing synthetic polymers normally used as stabilizing agents in aqueous ceramic suspensions with polymers obtained from renewable sources.

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