Carboxymethyl lignin as stabilizing agent in aqueous ceramic suspensions

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Identifying new uses for residues of industries that process large quantities of biomass, as in bioethanol production, is essential for a sustainable development with reduced impact on the environment, which is the reason why many efforts have been devoted to find noble uses for lignins. In this study, a lignin obtained from sugarcane bagasse in a bioethanol producing plant was carboxymethylated to yield the water-soluble carboxymethyl lignin (CML), which was then used as stabilizing agent in aqueous alumina (Al2O3) suspensions. CML had a degree of substitution 0.46 ± 0.01, in relation to the C9 unit of lignin, and behaved as a polyelectrolyte in a large pH range owing to the dissociation of carboxylic groups. The action of CML as stabilizing agent of alumina aqueous suspensions was investigated using viscometry, zeta potential, and photon correlation spectroscopy (PCS) measurements, mainly as a function of pH and time. Overall, the results showed that CML had a good performance as a deflocculating agent, because it led to dispersions with low viscosity and small change in particle size as a function of time. The positive effect from the addition of CML was confirmed in the morphological features of the material obtained from the alumina suspensions after elimination of water, as indicated by scanning electron microscopy. The stabilization of alumina suspensions afforded by CML opens the way for similar applications of modified lignins, whose electrical and structural properties may be tuned for specific uses in various industries, including the ceramic industry.

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1. Introduction

The new technologies for producing bioethanol with enhanced efficiency hold great promise for generating energy with reduced impact to the environment (Mousavioun and Doherty, 2010; Trindade et al., 2005; Lepitre et al., 2004). In Brazil, sugarcane is the most suitable material for a low-cost production of bioethanol. In fact, sugarcane has been an important commodity in the country for many years, and it has become even more so recently because of the production of ethanol as fuel for automobiles. The large quantities produced and the extensive agricultural land occupied by sugarcane plantations now require new technologies for increasing the uses of byproducts and residues (Sun, 2004; Liu et al., 2006; Li and Hsieh, 2006; Shaikh, 2009) Furthermore, a rational use of these byproducts is crucial for a favorable energetic balance to be achieved. In the sugarcane bagasse, lignin comprises near 20% of the total weight, being extracted using for instance organosolv or alkaline processes (Mousavioun and Doherty, 2010; Frollini et al., 2004; Ramos et al., 2005; Hoareau et al., 2006). Lignin is the second most abundant vegetal macromolecule in Earth, after cellulose. Because the lignin composition varies from one species to another, it should be considered as a class of similar materials (Kubko and Kadla, 2005; Notley and Norgren, 2008).

The use of lignin has been reported, for example as a substitute for phenol in resins, in application as an adhesive in the production of particleboards (Hoareau et al., 2006; Çetin, 2002), in pharmaceutical (Majeti and Kumar, 2000; Chiellini et al., 2001), concrete additives, films, adhesives, agricultural chemicals (Gosselink et al., 2004; Lepitre et al., 2004), as a source of renewable aromatic chemicals (Binder et al., 2009), to derive polyurethanes (Ignat et al., 2011; Vanderlaan and Thring, 1998).

A pioneering process to extract lignin and saccharify cellulose has been used to obtain ethanol from sugarcane bagasse, which involved a rapid hydrolysis (Hilfst, 1997, 2007; Oliverio and Hilfst, 2004). The resulting cellulose and hemicelluloses are hydrated to yield sugars that are fermented to produce ethanol. Lignin is mostly burnt to deliver energy. In the present study, an attempt is made of finding other noble use for this extracted lignin, using a modified lignin as stabilizing agent for aqueous suspensions of alumina.

Obtaining stable suspensions is crucial for the ceramic industry, particularly when advanced materials are sought.
Ceramic materials have found applications in ceramic coating, biomaterials, electronic and semiconductor materials, to name a few. The fabrication of improved ceramic materials requires increasing control of processes involving powders with particles that may even be of nanometric dimensions and due these new processing techniques became necessary to meet the quality requirements. Most applications require that colloidal particles, such as alumina, remain dispersed in aqueous suspensions (Yokosawa and Frollini, 2002; Tari et al., 2000; Vasconcelos et al., 2005). These suspensions have a large number of solid particles, and several procedures have been used to minimize aggregation (Vincent, 1974; Cerrutti et al., 2010). Two requirements must be fulfilled for this purpose: (i) understanding of the physicochemical properties of the materials in the suspension, which ultimately define characteristics such as particle size; (ii) addition of materials to interact with alumina in order to prevent aggregation (Yokosawa et al., 2002; Bimal et al., 2004).

Dispersion of particles may be assisted by the addition of other species, increasing stability. These species can be polyelectrolytes (polymers with charges) that interact with the surface of alumina particles, hindering the approach of other particles (Yokosawa and Frollini, 2002; Surve et al., 2007).

Steric and electrostatic mechanisms are normally responsible for the stabilization of colloidal systems. Electrostatic stabilization referred a mutual repulsion of electrical charges that can be generated when particles are dispersed in a polar medium like water.

The surface oxide, as alumina, acquires negative, positive surface sites when in contact with a liquid (normally aqueous) through the reaction of the hydroxyl group of its surface. When the ions that determine the surface potential are $\text{H}^+$ and $\text{OH}^-$, the surface net charge depends on the $pH$ of the environment. Reactions can be represented in a simplified way as follows:

**Acidic aqueous medium:**

$$[1] x[H_3O^+] + [O-Al-O]_n(OH)_y = [O-Al-O(OH)_2^+]_y + x\text{H}_2\text{O}$$

**Alkaline aqueous medium:**

$$[2] x\text{OH}^- + (O-Al-O)_n(OH)_y = (O-Al-O)_n(O^-)_y + x\text{H}_2\text{O}$$

The steric stabilization occurs due to the adsorption of a macromolecular layer on the particles, thus preventing them from close contact with each other. The electrosteric stabilization is a combination of the two previous mechanisms: steric and electrostatic stabilization (Yokosawa et al., 2002; Surve et al., 2007; Palmqvist et al., 2006; Tavacoli et al., 2007).

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 (Hordern, 2004; Cruz et al., 2005). Several macromolecules have been used as stabilizing agents for alumina suspensions, including sodium polyacrylates (Tari et al., 1997, 2000; Vasconcelos et al., 2005; Vincent, 1974; Palmqvist et al., 2006; Bimal et al., 2005).

In this study a previously prepared carboxymethyl lignin (CML) was used as stabilizing agent in aqueous alumina ($\text{Al}_2\text{O}_3$) suspensions.

### 2. Materials and methods

The lignin used was kindly supplied by Dedini SA (Piracicaba, São Paulo, Brazil) (Hilst, 1997, 2007; Oliverio and Hilst, 2004). This lignin was extracted from sugarcane bagasse by the organosolv process, using ethanol/water as the solvent and sulfuric acid as a catalyst. Before use, the lignin was washed with hot water (70 °C).
for 30 min under mechanical stirring to remove residual sugars and impurities. The suspension was filtered and the lignin was dried in
an oven at 105 °C, until constant weight. The organosolv lignin was
then chemically modified through a carboxymethylation reaction
using monochloroacetic acid as reagent. The carboxymethylation
reaction starts with the alkalization of the lignin by sodium
hydroxide, to generate stronger nucleophiles to attack the etheri-
fying agent (Fig. 1).

Ten grams of lignin was suspended in 270 mL of ethanol (72%)
under magnetic stirring, and 27 mL of aqueous solution of NaOH
30% (w/v) was added dropwise (30 min), at room temperature
(25 °C). After stirring for 1 h 30 min, 12.0 g of monochloroacetic acid
were added within a period of 30 min. The mixture was stirred for
3 h and 30 min at 55 °C. The solution was filtered and the filtered
suspended in 670 mL of aqueous ethanol (95%, v/v), and neutralized
with acetic acid. After filtration, the product was washed several
times with ethanol (95%), thus yielding the anionic sodium
carboxymethyl lignin (CML), whose solubility in water depends on the
degree of substitution (DS). The CML was dried in an oven at 60 °C
to constant weight, and its DS was determined through complex-
ometric titration (Klemm et al., 1998). The procedure, described
below, was repeated three times.

Fig. 3. Schematic representation: possible interactions between alumina surface and CML: (a) pH = pH pcz; (b) pH < pH pcz; (c) pH > pH pcz; (d) CML.
A sample of 30 mg of purified CML (as sodium salt) was dissolved in 30 mL of distilled water under continuous stirring (pH 7.0, 25 °C). An aqueous solution of 0.1 mol dm$^{-3}$ (based on monomer unit) polydimethyl diallylammonium chloride (Sigma–Aldrich) was added under continuous stirring (flow rate of 0.2 mL min$^{-1}$), until a sudden flocculation was observed. The volume of the titrant used up to this equivalence point was used to determine the concentration of carboxymethyl groups (c, given in mmol g$^{-1}$ of the CML sodium salt), which in turn was used to determine the DS value (0.46 ± 0.01 by C9 unit of lignin).

Alumina was supplied by Treibacher Schleifmittel (Brazil), with surface area of 2.4 m$^2$ g$^{-1}$ (BET) and average particle size 1.0 μm, as informed by the producer. Aqueous alumina suspensions (60 wt%) were prepared with 220 mL distilled water and 402 g alumina powder, stirred for 1 hr, in a 500 mL glass beaker (25 °C). The viscosity measurements were performed with a rotational Brookfield Viscometer-model DVII, cylindric geometry, using spindle 3 and 3 rpm, at room temperature (25 °C), with accuracy of ±1%. The rotating spindle was immersed in the beaker containing the suspension. Under this condition the applied shear rates are not constant within the measurement chamber, but the stirring is sufficient for reaching 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 to observe the effective action of the stabilizer, within a pH range where the electrostatic stabilization occurs, as will be discussed later. The CML with a substitution degree 0.46 ± 0.01 by C9 unit of lignin, was added into the alumina suspensions directly as powder, varying the amount of CML added, to evaluate the effect on the viscosity of the suspension (Fig. 2a).

For the zeta potential and particle size measurements, 2.0 wt% alumina suspensions were used. The average particle size and zeta potential were measured by Photon Correlation Spectroscopy (PCS) using a Brookhaven Instrument apparatus (50 mW, λ = 532 nm neodymium laser) and ZETA PALS system from Brookhaven Instruments Corporation, respectively, with accuracy of ±10%.

The scanning electron microscopy (SEM) analysis was carried out with a Zeiss–Leica apparatus, model 440, with an electron acceleration of 20 kV.

**3. Results and discussion**

The study of a possible use of macromolecules for stabilizing alumina suspensions requires the optimization of the experimental conditions. The data indicate that adding 0.1 wt% of CML was sufficient to reach a low viscosity, while adding 0.2 wt% allowed us to obtain a small particle size and have a minimum in the zeta potential (Fig. 2). For a low viscosity and small particle size to be achieved, the alumina particles should be dispersed with no agglomerates, as the latter yield sedimentation and de-stabilization of the system. Therefore, 0.1–0.2 wt% of CML is the maximum quantity for interacting with the alumina particle surface under the experimental conditions in this study. Higher amounts of CML induce an increase in viscosity owing to the presence of free CML in the

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**Fig. 4.** (a) Viscosity as a function of pH, 0.1 wt% CML, (b) particle size, (c) zeta potential: as a function of pH, 0.2 wt% CML, 25 °C.
suspension. From the zeta potential data, evidence of a stable system comes from the larger concentration of positive (or negative) charges on the particle surface. CML adsorbed on the particles shifts the zeta potential to more negative values.

Using the optimized concentrations of CML, the viscosity, particle size and zeta potential were measured as a function of the pH. The point of zero charge (pzc) represents the point at which the alumina shows natural trend to aggregate. The addition of other species such polyelectrolytes as CML can interact with alumina particles surfaces, hindering the approach of other particles and increasing stability (Bimal et al., 2005; Zhou and Wang, 2008). Some of the possible interactions between alumina and CML are depicted schematically in Fig. 3.

Fig. 4a shows that in the pH range from 3.0 to 6.0, the viscosity was low due to repulsive interactions among alumina particles themselves, mostly charged positively in this pH range. Within this range some carboxyl groups will be dissociated, increasing the proportion of carboxylate groups as the pH shifts to the alkaline region. The carboxylic group can act as a proton donor or acceptor in hydrogen bonds, while the carboxylate group can act as a proton acceptor. Electrostatic interaction between the positively charged alumina and carboxylate anions may also occur. The stabilization is probably electrostatic due to repulsion between positive sites on the alumina surface, in addition to steric repulsion caused by adsorption of the macromolecule on the alumina surface (electrosteric stabilization).

As also shown in Fig. 4a, above pH 6.0 the viscosity increased due to electrostatic attraction between positive and negative sites on the particles. However, the presence of carboxymethyl lignin hinder the approximation of particles which can interact in an attractive way, as for instance ALOH/ALO−, contributing to the dispersion and stability of the suspension. As expected the viscosity increased at higher pHs, reaching maximum values for suspensions without CML between 7 and 8.5, which include the pzc (Fig. 4a). With the particles possessing positive as well as negative charges, agglomeration owing to electrostatic attraction is inevitable. With addition of CML, additional interactions may take place, since carboxylate groups may find positive sites for adsorption. The presence of CML in this pH range is essential to afford the stability that the system without stabilizer has in an acidic media.

Fig. 4b and c show particle size and zeta potential of the alumina suspension as a function of pH, respectively. When 0.2% of CML was added to the suspension, the zeta potential shifted to negative values, when compared to the suspension containing only alumina. In the alkaline region, CML can adsorb on alumina surface through interactions similar to those shown in Fig. 3c. The carboxylate ions (COO−) groups contribute to the high negative values of zeta potential and cause increased electrostatic repulsion leading to stable suspensions. With addition of CML the point of zero charge (pzc) was shifted from 7.0 to 4.5, thus indicating that CML adsorbed on the particles surface. The average size of the particles in suspension in Fig. 4b was strongly affected by addition of CML, especially in the pH range from 5.5 to 10.0, which also points to dispersion stability, consistent with viscosity measurements.

The stability of the alumina suspensions was investigated by measuring the average particle size as a function of the time. At low pH, the electrostatic repulsion among alumina particles is sufficient to maintain a small average size, as shown in Fig. 5a,
and the addition of CML actually decreases the stability, but the particles keep still in small values (ca. 400 nm). In contrast, the adsorption of CML on the alumina particles has a marked effect at pH 7, not only leading to a smaller average particle size, but also stable in time, as illustrated in Fig. 5b. The average size for the particles with no stabilizing agent was ca. 1000 nm, with sedimentation being visually observed. The addition of CML however, decreases the particle size (Fig. 5b), and no sediment was observed.

For pH 9, Fig. 5c shows that again CML is beneficial with a decreased particle size. The improvement is nevertheless modest because the adsorption of CML is precluded as the alumina particles are negatively charged at high pH.

The stability of the suspensions containing CML was also confirmed with the zeta potential measurements shown in Fig. 6. At pH 4, where the alumina suspension is stabilized by the electrostatic repulsion of the positively charged particles, the zeta potential is stable regardless of the presence of CML. As expected, it is more positive without CML, and approaches zero as the negative charges of CML compensate for the positive charges at the alumina particles surface. Analogously to what was concluded from the particle size and viscosity measurements, the usefulness of CML becomes apparent at pH 7, with Fig. 6b showing that the adsorption of CML improved stability by inducing a negative zeta potential. As discussed before, the advantage of using CML at pH 9 is not as clear, confirmed by the time dependence of the zeta potential in Fig. 6c.

Fig. 7 shows the average particle size distribution in the suspensions and scanning electron microscopy images for the various samples studied. The micrographs shown 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.

The addition of CML at pH 3 increases the average size of the particles, as illustrated in Fig. 7a, even though the sizes are not typical of agglomerates. A stable suspension with a rather homogeneous distribution of particle sizes is also supported by the SEM image in Fig. 7b. For pH 7, the distribution curve is broader in the presence of CML (Fig. 7d), with a larger variety of sizes. The average size is smaller than for alumina particles in the absence of CML, as in the latter case there is agglomeration. For pH 9, Fig. 7g shows a broader distribution, with a larger average size, for the suspension without CML. In the SEM images of Fig. 7e and f for samples obtained at pH 7.0 and 9.0, one notes that the addition of CML decreases the porosity of the agglomerates of alumina particles observed in Fig. 7i and j in the absence of CML. Fig. 7f and i shows an irregular morphology with agglomerates and spaces between particles sedimented from suspensions with no stabilizing agent.
A previous study had shown that other anionic derivative of lignin, namely lignosulfonates (LS), may be used to coat alumina particles in aqueous suspensions, thus reducing their aggregation (Cerrutti et al., 2004). The chemical structure of CML is different from that of lignosulfonates, because the anionic sulfonic groups are fixed at the C9 of the lignin C9 unit, whereas the anionic carboxymethyl groups are linked at the phenolic oxygen (Figure 1). There are interactions between LS and alumina surface involve different sites, when compared to those involved in the interactions CML/alumina surface. Moreover, the carboxymethyl substitution degree, e.g. the amount of carboxylates based on C9 units of lignin, can be adjusted by the chemical reaction conditions, which is not the case for industrial lignosulfonates, byproducts of pulping industry.

4. Conclusion

The incorporation of a modified lignin, referred to as CML, altered the properties of alumina suspensions, with an increase in stability over time. The most important effects occurred at pH close to 7.0, in which alumina suspensions become unstable owing to aggregation of particles. In this pH range, the addition of 0.1–0.2 wt% of CML induced a considerable decrease in viscosity and in the particle size for the alumina suspensions. Furthermore, the zeta potential became increasingly negative with an increasing concentration of CML, with the point of zero charge (pzc) shifting from 7 for an alumina suspension with no additives to 4.5 upon addition of CML. At low pHs, CML did not enhance the alumina suspension stability, but this was not an issue as the alumina suspensions are already stable at pH < 4 owing to the electrostatic repulsion of the positively charged particles. At pH 9 and above, the addition of CML has a small stabilizing effect, which was expected because the electrostatic effect is minimized. Scanning electron microscopy images of the alumina suspensions confirmed the stability-enhancing effect of adding CML, with a decrease in porosity.

The positive results in terms of enhanced stability for alumina suspensions induced by a modified lignin reported here were obtained under optimized conditions. However, because the chemistry of lignins allows major alterations in physicochemical and electrical properties be obtained in a controlled fashion, one may envisage further uses of modified lignins, not only as stabilizing agent demonstrated in this paper but also for the production of advanced materials with tailored properties.

Fig. 7. Distribution of the particle size of the alumina suspension and SEM images: (a) (pH 3.0); (b) alumina suspension with 0.2% of CML; (c) alumina suspension without CML; (d) (pH 7.0); (e) alumina suspension with 0.2% of CML; (f) alumina suspension without CML; (g) (pH 9.0); (h) alumina suspension with 0.2% of CML; (i) alumina suspension without CML.
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References