

Synthesis of carboxymethylcelluloses with different degrees of substitution and their performance as renewable stabilizing agents for aqueous ceramic suspensions



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ABSTRACT

Low average molar mass cellulose has been submitted to carboxymethylation reactions to yield carboxymethylcellulose (CMC) materials with different degrees of substitution (DS) that have been investigated as alternative renewable stabilizing agents for aqueous alumina suspensions to usual synthetic polyelectrolyte additives. The CMC materials were characterized by infrared, X-ray diffraction and ¹H nuclear magnetic resonance (NMR) spectroscopies, as well as by size exclusion chromatography (SEC), thermogravimetry (TG) and differential scanning calorimetry (DSC). All CMC materials reported (DS of 0.7, 1.3 and 1.8 as estimated by ¹H NMR) proved to be good additives to stabilize aqueous alumina suspensions with high solid concentrations (60%, w/w). Addition of low amounts of CMC (from 0.10% to 0.20%, w/w) produced suspensions with small and uniformly distributed particle sizes, thereby yielding colloids with lower viscosity, negative zeta potential values and longer sedimentation times. The present work demonstrates the viability of substituting synthetic fossil-based polyelectrolytes in traditional industrial activities with renewable cellulosic biomass-based ones.

1. Introduction

The rich and complex macromolecular structure of cellulose, hemicelluloses and lignin allows a large number of chemical modifications to be carried out in order to change their properties. However, it is imperative that chemical manipulations do not significantly alter the molecular structure of the biomacromolecules so that microorganisms can still recognize and degrade the chemically modified materials once they are discharged in the environment (Fischer and Mackwitz, 2016).

In this context, an alkali-O₂ oxidized lignin derivative has been investigated as a renewable cement dispersant (Kalliola et al., 2015), whereas lignopolyurethanes, which have been prepared from oxypropylated lignosulfonates and diphenylmethane, have been studied as renewable polymeric matrices in sisal reinforced composites (Oliveira et al., 2012). Bendahou and co-workers reported hybrid aerogels prepared from zeolites and cellulose nanofibers that presented superior insulating properties (Bendahou et al., 2015). The microcrystalline cellulose investigated in the present study has been modified via imidazole-catalyzed acylation reactions with carboxylic acid anhydrides (Pires et al., 2015) to yield bio-based ionic liquids as well as to prepare nanocrystalline cellulose via ultrasonic-assisted enzymatic

hydrolysis (Cui et al., 2016).

Our group has been involved in a continuous effort aiming at replacing non-renewable fossil-based derivatives in material design and processing with renewable biomacromolecules. For example, we have shown that lignins can partially replace phenol in the preparation of phenol-formaldehyde thermoset composites reinforced with several lignocellulosic fibers (Botaro et al., 2010; Megiatto et al., 2007a,b, 2008, 2009, 2010; Ramires et al., 2010a,b,c; Trindade et al., 2005).

Another industrial activity that might benefit from the use of biomacromolecules as renewable alternatives to petrochemicals is the colloidal ceramic processing industry. In the colloidal ceramic processing, suspensions with high solid concentration and with uniform particle size distribution are necessary to yield ceramic objects with higher density, lower defects and excellent mechanical and thermal properties. However, thermal collisions among the fine particles in suspensions cause formation of larger particle aggregates with random size distributions that ultimately lead to ceramic objects with poor mechanical and thermal performances. To avoid such problems, synthetic polyelectrolytes (charged macromolecules) able to interact with the surface of the particles are added to the suspensions to create electrostatic and/or steric barriers at the solid/liquid interface that

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prevent particle aggregation upon thermal collision (Ohtsuka et al., 2011; Wisniewska et al., 2014).

Aqueous alumina suspensions are extensively used in ceramic processing. When dispersed in water, alumina particles acquire surface charges that are pH dependent. In acidic medium, the alumina surface hydroxyl groups are protonated and the overall particle surface charge is positive. On the other hand, the alumina surface hydroxyl groups are deprotonated in alkaline pH regime, thereby the net surface charge of the particles in suspension is negative. At those two extreme pH regimes, alumina suspensions are stabilized by the electrostatic mechanism as the mutual electrostatic repulsion among the surface like-charged particles minimize formation of aggregates. However, in intermediate pH regimes, some surface hydroxyl groups are protonated, while others are deprotonated. This uneven surface charge distribution creates attractive electrostatic forces among the particles in suspension that drive aggregation. There is a specific pH value in which the number of protonated and deprotonated surface hydroxyl groups is roughly the same. At this pH value, namely isoelectric point (IEP), particle aggregation is most favored due to the mutual attractive electrostatic interactions among the particles in suspension (Cerrutti et al., 2010, 2012, 2013; Megiatto et al., 2016; Ohtsuka et al., 2011; Wisniewska et al., 2014)

To circumvent aggregation in intermediate pH regimes, synthetic polyelectrolytes such as sodium polyacrylates are used as stabilizing agents for aqueous alumina suspensions in ceramic processing. Polyelectrolytes interact with the alumina particle surface by van-der-Waals forces, formation of hydrogen bonds and electrostatic interactions. Lignosulfonates and chemically modified lignins have proved to be excellent polyelectrolytes to stabilize aqueous alumina suspensions in a wide pH range (Megiatto et al., 2016).

Continuing our efforts to expand the scope of biomacromolecules in material processing, herein is described the investigation of carboxymethylcelluloses (CMC) (Fig. 1) with three distinct degrees of substitution (DS) as polyelectrolytes for the stabilization of aqueous alumina suspensions. CMCs are versatile platforms that have been used as the carbon precursor to prepare carbon microspheres with ordered, mesoporous structures (Wu et al., 2015), or blended with carboxymethyl-carrageenan to be used as host to prepare green polymer electrolytes (Rudhzhiah et al., 2015).

In the present work, microcrystalline cellulose (MC) was submitted to carboxymethylation reactions in heterogeneous medium to afford CMCs with relatively high DS values. The use of MC as starting material is based on its low average molecular mass compared to other celluloses. The low average molecular mass enables easier access of reactants to the hydroxyl functionalities on the MC chemical structure, thereby facilitating the heterogeneous carboxymethylation reactions to yield materials with high DS. Furthermore, the low average molecular mass of the resulting CMCs might provide a benefit in the stabilization process of aqueous alumina colloids. CMCs with high average molecular masses are composed of long cellulose chains that might interact with several alumina particles in suspension at the same time (“bridging effects”) to promote aggregation instead of dispersion. Congruently, CMCs with shorter cellulose chains should cover single alumina particles in suspension to create an electrosteric barrier that might prevent aggregation and collapse of the colloid (Cerrutti et al., 2012; Cerrutti et al., 2013; Wisniewska et al., 2014).

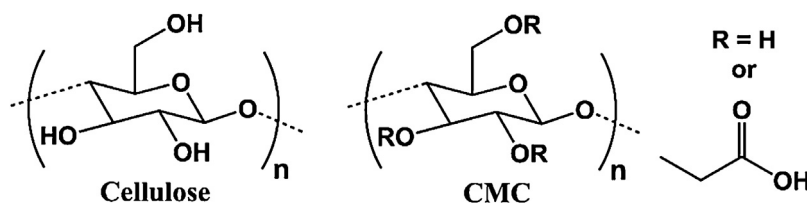


Fig. 1. Cellulose and carboxymethylcellulose (CMC) chemical structures.

2. Experimental

2.1. Materials

Alumina was kindly provided by Treibacher Schleifmittel Brasil Ltda, São Paulo, Brazil. This material is an α -alumina, mesh325 (particle size < 440 μ m), with superficial area of 2.4 m²/g (BET). Microcrystalline cellulose Avicel(MC) was kindly provided by Valdequímica – Comércio e Importação, São Paulo, Brazil. MC had average molecular mass of 20,500 g mol⁻¹ as measured by the Ubbelohde capillary (Φ = 0.53 mm) AVS-350 viscometer from Schott-Geräte, which was equipped with Visco Doser AVS 20 Piston Burette also from Schott-Geräte. Isopropanol, ethanol, sodium hydroxide, sodium chloride, acetic acid and hydrochloric acid were purchased from Synth, whereas sodium monochloroacetate was purchased from Acros Organics and deuterated sulfuric acid and deuterated water were purchased from Merck. All purchased chemicals were analytical grade and used as received. Unless otherwise noted, deionized water was used throughout the investigation.

2.2. Synthesis (Barba et al., 2002; Heinze et al., 1999; Heinze and Koschella, 2005; Kutsenko et al., 2002; Ramos et al., 2005; Vashney et al., 2006)

2.2.1. Procedure for the synthesis of carboxymethylcellulose with 0.7 degree of substitution (CMC07)

Five grams of MC were dispersed in 130 mL of isopropanol under mechanical stirring for 20 min at room temperature. To the resulting suspension, it was added NaOH (34.00 g, 0.85 mol) and sodium monochloroacetate (12.00 g, 0.1 mol) and the reaction mixture was heated at 55 °C for 3.5 h. After cooling, the crude product was neutralized with acetic acid and precipitated with 500 mL of methanol. The afforded solid was copiously washed with an ethanol/water mixture (9:1, v/v) and re-dissolved in 1000 mL of water. The solution was mechanically stirred for 12 h at room temperature. Addition of 1000 mL of aqueous NaCl 0.2 mol/L promoted precipitation of impurities, which were separated by filtration and discarded. The product in solution was precipitated with ethanol and filtered off. The solid was washed with several portions of ethanol to yield the final product CMC07, which was dried at room temperature until constant mass.

2.2.2. Procedure for the synthesis of carboxymethylcellulose with 1.3 degree of substitution (CMC13)

Five grams of CMC07 were submitted to recarboxylation under the same reaction conditions and purification processes as described in 2.2.1 to yield CMC13. This recarboxylation procedure was necessary to yield materials with degree of substitution higher than 0.7.

2.2.3. Procedure for the synthesis of carboxymethylcellulose with 1.8 degree of substitution (CMC18)

Five grams of CMC13 were submitted to recarboxylation under the same reaction conditions and purification processes as described in 2.2.1 to yield CMC18. This re-recarboxylation procedure was necessary to yield materials with degree of substitution higher than 1.3.

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