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Gelcasting of alumina suspensions containing nanoparticles with glycerol monoacrylate

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Abstract

An acrylic monomer of low toxicity containing two hydroxyl groups has been synthesized and used for gelcasting in water. The results have been compared to those achieved with the use of a commercially available monomer (2-hydroxyethyl acrylate). Due to the chemical structure of the synthesized monomer, no addition of the crosslinking agent was necessary for gelation and similar results in terms of rheology of suspensions, density and microstructure of the bodies were obtained with respect to those obtained with the commercial monomer. However, higher time for gelation was observed.

Two alumina powders with very different particle sizes were used in this study: a commercial submicron-sized powder ($d_{50} = 0.35\ \mu m$) and a nanometer-sized alumina obtained by freeze-drying from aluminum sulphate solutions. The rheological behavior of concentrated suspensions was studied in order to establish their stability and to analyse the effect of the different monomers used in the process. Once the suspensions were optimized, the influence of the size of the powder on the gelation process was studied. The sintered density of submicrometer-sized alumina was higher (99%) than that measured when the bimodal suspension was used due to the difficulty to obtain highly concentrated suspensions from nanometric powder.

Keywords: Powders-chemical preparation; Precursors-organic; Shaping; Suspensions; Nanocomposites; Alumina

1. Introduction

The increasing effort recently devoted toward the development of nanostructured materials with improved behavioral properties has lead to the search of novel shaping methods allowing the preparation of ceramic parts for different industrial applications, which in most cases need complex shapes to be obtained.[1]

Although the most extensively practice is the green machining of pre-shaped parts, the best option seems to be the establishment of near-net-shaping techniques capable to reduce or remove the machining step, such as direct coagulation casting (DCC),[2] starch consolidation,[3] freezing (Quickset),[4] hydrolysis assisted solidification (HAS),[5] or gelcasting.[6–8]

The gelcasting process appeared as a way to overcome the limitations inherent to other shape forming methods like slip casting or injection moulding. The main drawback of the gelcasting method deals with the use of a toxic, expensive and hazard reactive, the acrylamide, which is a neurotoxic compound.[6,7] For this reason, other alternatives have been proposed, such as the use of non-toxic monomers[9] and thermal processes like the temperature induced gelation or the thermogelation of polysaccharides.[10–13]

The desired properties for a monomer to be used for gelcasting are that it must be water soluble, environment friendly and should have low toxicity and cost,[6,9] apart from allowing the consolidation in air without exfoliation. One such monomer is the 2-hydroxyethyl acrylate, which is commercially available.

A new monomer has been synthesized and successfully applied in the gelcasting of ceramic suspensions, namely glycerol monoacrylate.[14] The main advantage of this compound is to be a monomer containing two hydroxyl groups in a molecule. This allows using small amount of or even no crosslinking agent, thus reducing the amount of organic additives in the suspension, and achieving the same results without increasing the amount of the main monomer. In the previous work[14], the behaviour of this

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new monomer has been studied and compared with the commercially available 2-hydroxyethyl acrylate. In this work, the suitability of the new monomer in aqueous gelcasting has been tested with two different suspensions of alumina, a monomodal one with submicron-sized particles and a bimodal one containing submicron and nanoparticles.

2. Experimental

2.1. Ceramic suspensions preparation

Two different Al_2O_3 powders were used for preparing ceramic suspensions: commercially available α-Al_2O_3 (Condea HPA05, USA), with a mean particle size of 0.35 μm and a specific surface area of 9.5 m^2/g, and γ-Al_2O_3 synthesized by the freeze-drying method,[15] with a mean particle size of 15 nm and a specific surface area of 150 m^2/g, forming soft agglomerates.

Two different suspensions were prepared in deionized water: (1) suspension A, formed only by submicron-sized Al_2O_3, and (2) suspension A10a, as a mixture containing 90 vol.% submicronic Al_2O_3 and 10 vol.% of γ-Al_2O_3. Suspensions were always prepared to a total solids loading of 50 vol.% using a poly(acrylic acid) based polyelectrolyte (Duramax D3005, Rohm and Haas, USA). Zeta potential measurements of γ-Al_2O_3 were performed by laser Doppler velocimetry (Zetasizer Nano ZS, Malvern S, UK). This determination was carried out using diluted suspension of 100 mg/l in KCl 10^{-2} M as inert electrolyte. The concentrated suspensions were prepared by mechanical stirring and further ball-milling for 6 h. In the case of A10a, homogenization required the use of an ultrasounds probe for a few minutes (UP 400S, Hielscher, Germany).

2.2. Gelcasting components and process

Two monomers were selected for this study: a commercial monomer (monomer C) 2-hydroxyethyl acrylate (96%, Aldrich, Germany) and a monomer synthesized in the laboratory from acrylic acid and glycidol. In this reaction two isomers are formed: 2,3-dihydroxypropyl acrylate and 1,3-dihydroxypropyl acrylate, in a 70/30 ratio. The active compound in the gelcasting is the 2,3-dihydroxypropyl acrylate (glycerol monoacrylate), so from now on, although it is added as a mixture, it will be considered as a single monomer (monomer S). The crosslinking agent, the initiator and the activator agent were di(ethylene glycol) diacrylate (75%, Aldrich, Germany), ammonium persulfate (98% Aldrich, Germany) and *N*,*N*,*N*',*N*'-tetramethyl-ethylendiamine (98% Fluka, Belgium), respectively.

The mixing of the gelcasting components is performed gradually. First, the monomer and the crosslinking agent (only in the case of the commercial monomer) are added over the prepared suspension and ball-milled for 2 h to achieve a good homogenization. Then, initiator and activator are mixed by mechanical stirring. The mixture was cast into plastic and metallic molds.

In addition, the gelling behavior of the mixtures without ceramic powder was characterized by studying the rheological properties under different conditions and registering the temperature evolution during gelation.

2.3. Rheological measurements

The rheological behavior of suspensions with and without monomer and the gelation process were studied using a rheometer (RS50, Haake, Thermo Electron Co., Germany) with a double cone/plate sensor configuration (DC60/2°). Flow behavior was obtained with a three-stage measuring program with a linear increase of shear rate from 0 to 1000 s^{-1} in 300 s, a plateau at 1000 s^{-1} for 120 s, and a further decrease to zero shear rate in 300 s. In order to study the viscoelastic behaviour of the suspensions, considering the measuring conditions in the linear viscoelastic region for concentrated suspensions of alumina (even with high organic additives content)[16] and for concentrated suspensions with gelcasting additives similar to the ones used in this paper,[17] oscillatory tests were performed by applying a constant deformation of 1% at frequency of 1 Hz during 3000 s. Strain and frequency sweeps tests were not useful for characterizing the gelation process, since the applied shear stress destroys the incipient gel structure thus impeding gelation.

2.4. Sintering and bodies characterization

After gelcasting, the pieces were dried at room temperature. The bodies were sintered at 1500 °C for 2 h, at a heating rate of 5 °C/min. The cooling was carried out in two steps, with a cooling rate of 10 °C/min up to 1200 °C and 2 °C/min up to room temperature.

The green and sintered densities were measured by the Archimedes' method in mercury and water, respectively. The microstructure was observed by scanning electron microscopy, SEM, (DSM 950, Zeiss, Germany), on fracture surfaces of green bodies and on polished and thermally etched (1400 °C/1 h) sintered surfaces.

3. Results and discussion

3.1. Suspension characterization

The effect of gelcasting additives was analyzed for suspensions with submicron-sized and nanometer-sized alumina. The γ-Al_2O_3 nanoparticles obtained by freeze-drying from aluminum sulphate solution[15] form soft and porous agglomerates (Fig. 1), so it is necessary to break them to achieve a stable suspension.

This powder was mixed with α-Al_2O_3, whose better rheological behavior is reached using 0.8 wt.% PAA.[18] The zeta potential of γ-Al_2O_3 nanopowders as a function of the dispersant content was measured, the optimum amount being 1.5 wt.%, close to the other value due to the agglomerate state of the nanoparticles. However, to achieve the complete adsorption on particles surfaces the dispersant content was increased up to 2.1 wt.% for concentrated A10a suspension, due to the breaking of these agglomerates and the apparition of new surfaces.

Fig. 2a shows the viscosity curves of both suspensions after ball-milling. Although the shape of both curves is similar, a higher viscosity is observed for A10a suspension, as expected when nanopowders are to be dispersed. The results

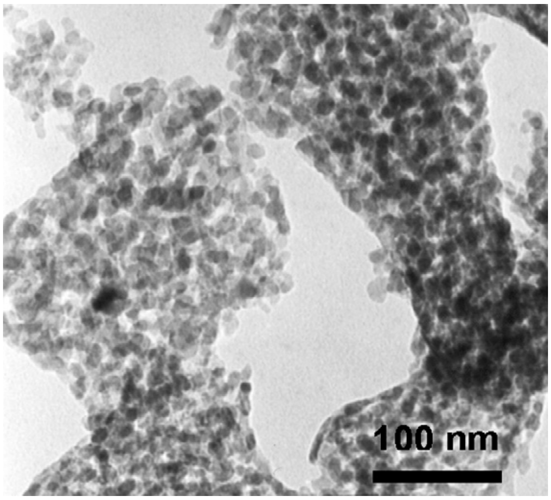

Fig. 1. TEM micrograph of γ-Al_2O_3 synthesized by freeze-drying.

of dynamic measurements of both suspensions are shown in Fig. 2b. If a constant deformation of 1% is applied to suspension A, the complex viscosity value, [η*], keeps constant all over the measuring test. However, in the case of the A10a suspension, this value slightly decreases, suggesting that some kind of structure or agglomeration is forming during the oscillatory test.

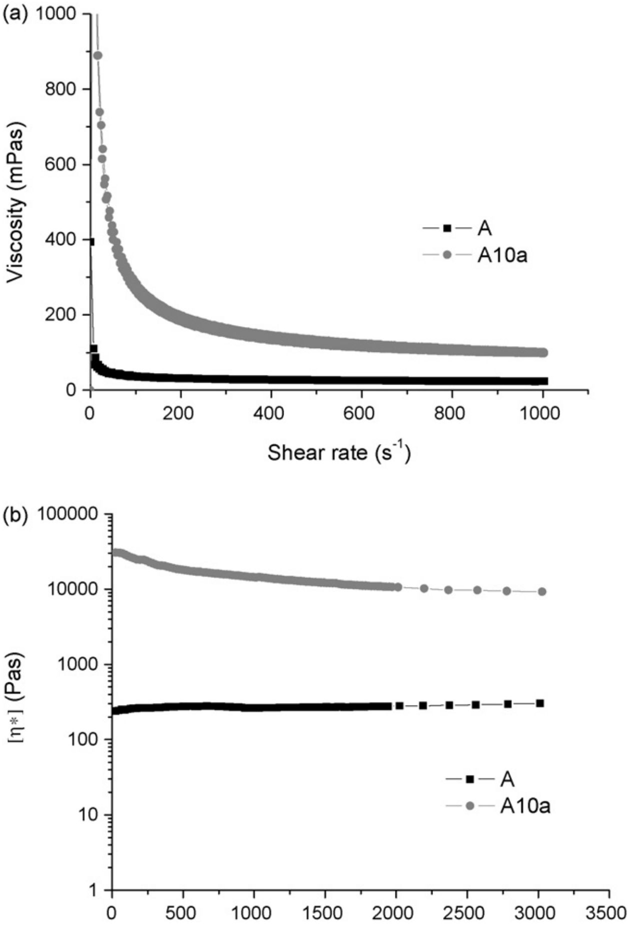

Fig. 2. Viscosity curves for A and A10a suspensions measured by linear (a) and oscillatory (b) tests.

3.2. Monomers and gel characterization

The synthesized monomer containing two OH groups is capable to formed stiff gel without external agents. In contrast, the commercial monomer 2-hydroxyethyl acrylate (monomer C) needs the crosslinking agent to form the network. The concentration of main monomer in both cases has been fixed in 3 wt.% on a dry solids basis, to minimize the amount of organic compounds in the mixture. The amounts of initiator and catalyst were 0.5 wt.% and 2 wt.% with respect to the monomer, respectively, as it was previously optimized[14]. For the commercial monomer the crosslinking agent concentration was 5 wt.% with respect to monomer.

Gelation behavior was first studied without ceramic powder. Fig. 3a plots the results of the oscillatory measurement for these batches. The increase of the complex viscosity values corresponds to the gel formation, being faster and more drastic in the case of the C monomer, whereas S monomer shows a more sequential gelation. Besides, the gel obtained using the C

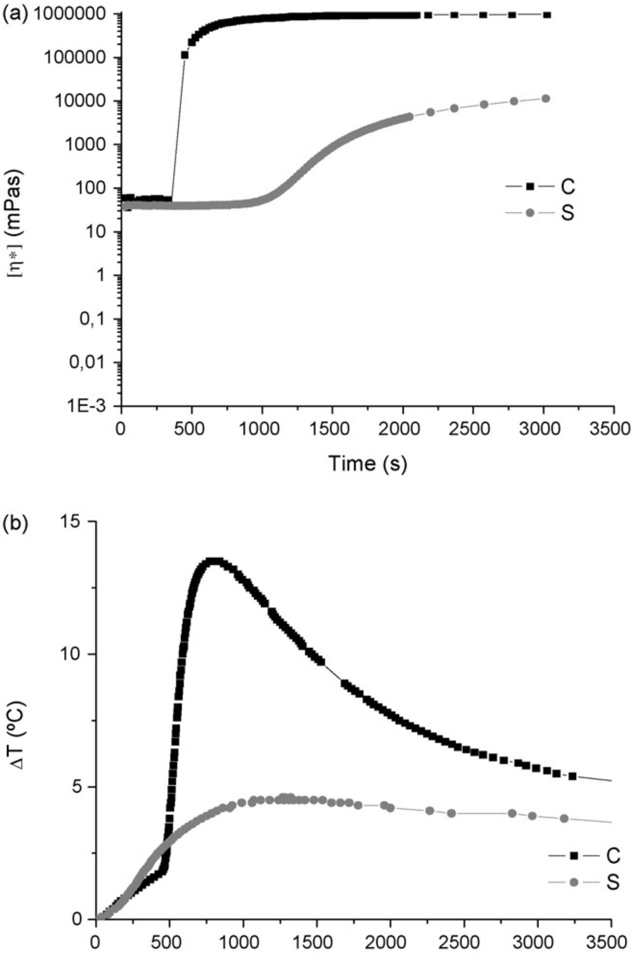

Fig. 3. Variation of complex viscosity (a) and temperature (b) with time for both the commercial and the synthesized monomers.

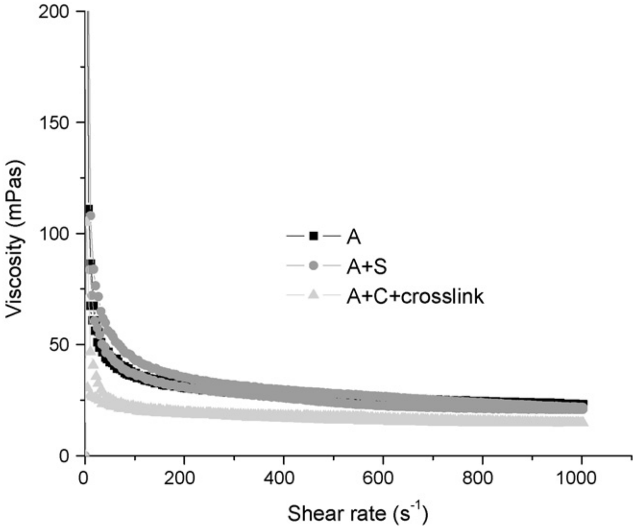

Fig. 4. Viscosity curves of the suspension A itself and after mixing with both monomers.

monomer seem to be stronger (almost a solid) than in the case of S monomer, due to the differences observed between the viscosity values. In the presence of crosslinking agent, the gel is obtained faster due to the formation of the crosslinked structure with covalent bonds. The increase of complex viscosity value is a consequence of the polymerization rate due to the Tromsdorff effect (the increase of the viscosity hinders the diffusion of polymer radicals in the medium, decreasing the possibility of a termination reaction but encouraging the propagation reaction by means of diffusion of smaller monomer molecules)[19]. In contrast, in the case of monomer S the gel is formed due to the presence of relatively strong hydrogen bonds between hydroxyl groups of the resultant polymer molecules.

The polymerization process involves an exothermic reaction whose temperature change can be registered simultaneously to the rheological measurements, as can be seen in the Fig. 3b. The increase of temperature roughly occurs during the gap of the [η*] values, confirming the correspondence between both parameters. The maximum increase of temperature registered for the synthesized monomer is 4 °C versus the 14 °C observed for the commercial one. In the absence of suspension the curve is sharper for the commercial monomer, which shows a gelation time of 345 s, while this time increases above 1100 s for the synthesized one.

3.3. Gelcasting process

Once the rheological behavior of the suspensions and the polymerizable additives was studied, the gelcasting process was then evaluated. First, suspension A was mixed up with each monomer, and in the case of the C monomer, with the crosslinking agent too.

Fig. 4 shows the viscosity curves of the suspension A without and with the monomers S and C. The differences observed between them suggest that either the commercial monomer or the crosslinking agent helps in the stabilization.

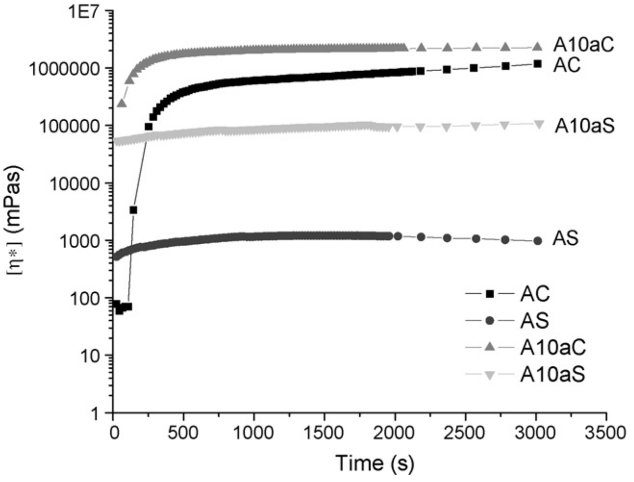

Fig. 5. Variation of complex viscosity with time for A and A10a suspensions mixed with each monomer.

When the initiator and activator were added to the slurry, the rheological behavior was determined by oscillatory measurements performed at constant deformation, as plotted in Fig. 5. The C monomer produces a stronger increase of the complex viscosity than the S monomer, as it was previously observed for the gels without suspension. Moreover, the A10a suspension enhances the formation of the gel structure and accelerates the consolidation stage.

The value of complex viscosity reached for suspensions containing nanoparticles is clearly higher than that measured for the submicron-sized suspension regardless the type of monomer used.

When no particles are present in the system the gelation time is very different depending on the selected monomer, the commercial one being much faster. Nevertheless, when acting into the powdered suspension the differences of gelling time are rather small, although it remains slightly faster for the commercial monomer.

3.4. Microstructure

The characterization of the pieces obtained by gelcasting using both monomers and both suspensions are summarized in Table 1.

No significant shrinkage was appreciated during the drying or consolidation steps. The measured green densities are about 60% of the theoretical value. The weight loss after sintering corresponds to the total weight of gelcasting additives. It has

Table 1
Characteristics of the gelcasting process and bodies obtained from both monomers

Sample	Gelling time (s)	Green density (% TD)	Sintered density (% TD)
AS	135	61	99
AC	155	57	96
A10aS	<100	56	94
A10aC	120	57	93

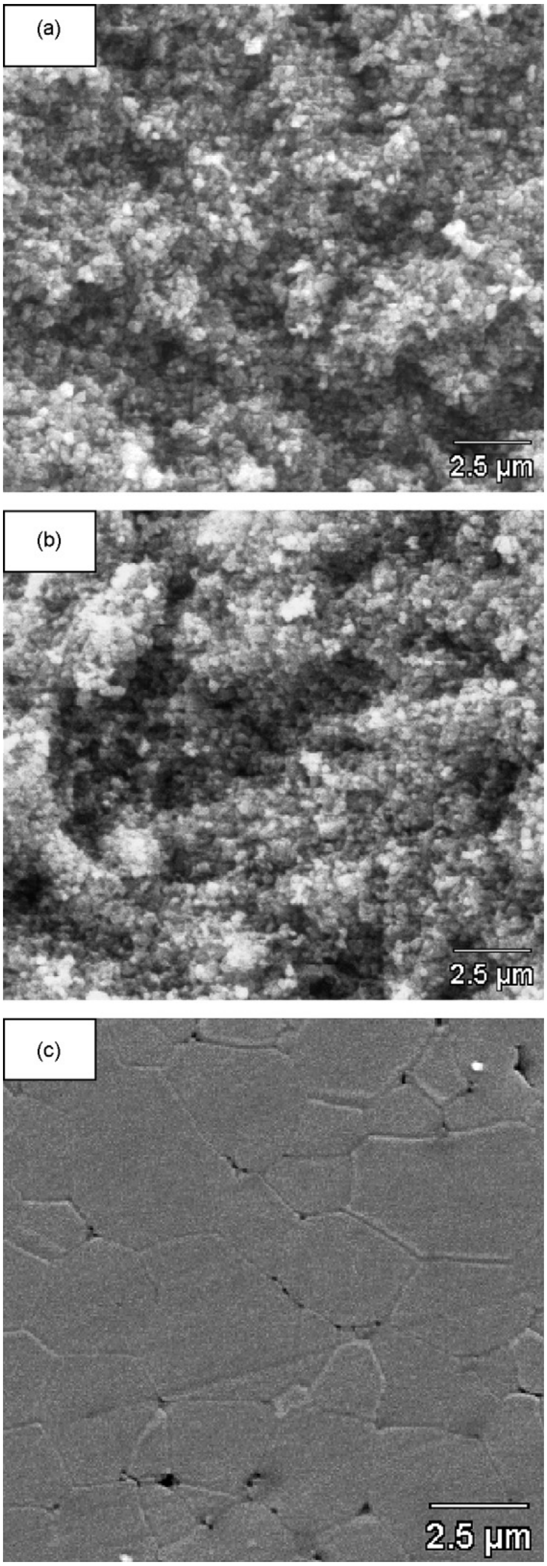

Fig. 6. SEM micrographs corresponding to the fracture surface of green bodies A10aS (a) and AS (b), and to the polished and etched surface of sintered piece AS (c).

to be noted that the sintered AS bodies present relative density values of 99% of theoretical, higher than that reached with the commercial monomer. It is also worthy to note that the density values measured for the A10a suspensions are reasonably high for suspensions of nanoparticles.

Fig. 6a and b show SEM micrographs of fresh fracture surfaces of green AS and A10aS bodies. In agreement with the green density values, AS specimen has high microstructural uniformity with small pores; however, A10aS has more number and larger size of pores although the nanoparticles are well-dispersed and no agglomeration is detected. Fig. 6c corresponds to a SEM picture of a sintered AS sample. The sample has a homogeneous grain size and presents some small intra and intergranular pores, formed during burn out of gelcasting additives.

4. Conclusion

Concentrated suspensions of submicron-sized and bimodal submicron-nanometer-sized alumina have been obtained and characterized for studying the effect of additives. A low-toxic monomer, glycerol monoacrylate, has been synthesized and compared with a commercial 2-hydroxyethyl acrylate for the gelcasting of concentrated ceramic suspensions. The commercial monomer leads to shorter gelation times although the densities reached in the green and sintered bodies are lower than those obtained for the synthesized one. For the same gelcasting conditions, bimodal suspensions seem to accelerate the gelcasting process.

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