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Eco-friendly alumina suspensions for tape-casting process

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ABSTRACT

The aim of this study is focused on the elaboration of new bio-based alumina concentrated suspensions with rheological properties adapted to the tape casting process and with low environmental impact. Natural polymers extracted from plants were identified as promising candidates in order to substitute the classical organic additives. The aqueous suspensions were prepared from bio-polymer additives. The interactions between different organic additives with alumina were characterized by zeta-potential and quartz crystal microbalance measurements. The influence of the incorporation order of the different organic additives on the viscosity of the suspension was evaluated. Then, mechanical properties of the green and sintered tapes were determined in relation with the nature of bio-polymer additives.

1. Introduction

Tape casting process is widely used in the ceramic industry in order to produce thin and flat ceramic tapes for microelectronics [1,2] or membranes for gas separation [3,4]. The suspensions used in the tape casting process are basically composed of a ceramic powder, a solvent, a dispersant, a binder and a plasticizer. The binder and plasticizer are usually polymers coming from the petrochemical sector and they may present risks for the operator health or the environment (in particular with organic solvents).

Due to the REACH regulation in Europe (Registration, Evaluation, Authorisation & restriction of Chemicals), the use of some of these products could be forbidden in the near future. In this respect, the preparation of aqueous suspensions formulated with a binder based on a methylcellulose compound was previously described by A. Kristoffersson et al. [5], T. Chartier and A. Bruneau [6] or D. Hotza and P. Greil [7].

The aim of this work is to go further in the sustainable approach in order to substitute all the additives coming from petrochemicals by biosourced additives which do not present risks for the operator's health. However, the rheological properties of the ceramic suspension must be adapted to the tape casting process. The green tapes must be easily handled without cracks or bubbles, and the sintered tapes must be dense.

This work focuses on the preparation of alumina suspensions with some biosourced additives for the tape casting process. First, the selection of dispersants has been performed by a sedimentation test of alumina suspensions. Pectin, which is widely used in the food-processing industry [8] has been used as binder. Pectin presents interesting gelation properties and has not yet been used in the ceramic processes. Finally the glycerol has been used as a plasticizer [7]. The influence of each organic additive on the rheological behavior of ceramic suspension has already been studied by Moreno [9,10] or Hotza and Greil [7]. In a similar way, a particular attention is given in the first part of this paper on the role of the introduction order of the different organic additives on the physicochemical properties of the suspensions. Curiously, the influence of the introduction order of the different organic additives are scarcely studied in the literature. The second part of the paper presents the rheological behavior of the suspensions elaborated from the bio-polymer additives and the characterization of the green and sintered tapes obtained with these suspensions.

2. Physicochemical study of aqueous ceramic suspensions

This first part focuses on the role of binder and dispersant on the physicochemical characteristics of the aqueous alumina suspensions.

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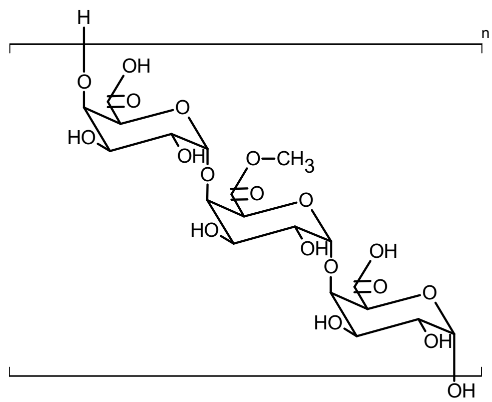

Fig. 1. Partial molecular structure of Pectin.

2.1. Experimental procedure

2.1.1. Starting materials

The powder used was the alumina P172SB (Alteo, Pechiney, France). The mean particle size is 0.1 μm and the specific area is 7.5 $m^2\,g^{-1}$.

The biosourced polymeric binder was a powder of Pectin Citrus (280 000 g/mol) provided by Alfa Aesar. This binder leads to the formation of a viscous gel with water which ensures a satisfactory cohesion of the green tapes after the drying stage. The pectin citrus powder is extracted from the peel of citrus, it is composed of a minimum 74.0% of galacturonic acid and a minimum 6.7% of methoxy groups (data of suppliers). The gelation of pectin is due to a combination of hydrogen bonds and hydrophobic interactions. The resulting tridimensional network is able to fix the solvent or the water molecules and is constituted of an assembly of esterified homogalacturonic zone with a helical shape [11]. The partial molecular structure of pectin is reported on Fig. 1.

Two dispersants have been selected to stabilize the alumina suspensions: an ammonium polymethacrylate dispersant (Darvan C-N, Vanderbilt Minerals, LLC, 15 000 $g\,mol^{-1}$) which is well known to disperse alumina in water[12] and an ammonium lignosulfonate dispersant (Arbo T11 N5, Tembec Avebene, 6 600 g/mol) extracted from maritime pines of the Landes region (France). Magiatto Jr. et al. [13] have already highlighted the stabilizing properties of the ammonium lignosulfonate for aqueous alumina suspensions. The partial molecular structure of dispersants is reported on Fig. 2.

2.1.2. Incorporation of the additives in ceramic suspension

The Figs. 3 and 4 show the different tested protocols. In particular, three different protocols have been tested in this work in order to evaluate the impact of the incorporation order of the additives on different parameters (rheological behavior, zeta potential, pH, conductivity) of the alumina suspensions.

In the protocol 1 as reported on Fig. 3, the pectin is firstly solubilized in the deionized water at 60 °C by mechanical stirring. After the total dissolution of the binder, the solution is cooled in a refrigerator at 5 °C during 24 h. This first step leads to the formation of a gel due to natural gelation mechanism of pectin chain in water. The gelation depends mainly on the methoxylation rate and the degree of esterification of the pectin chain [14]. Then, the alumina and the dispersant (ammonium lignosulfonate or ammonium polymethacrylate) are added to the gel, and mixed by ball milling during 20 h at 120 rpm. Finally, the suspension is de-aired on rollers during 24 h.

In the protocol 2 as reported on Fig. 3, the gel formation step is identical to the protocol 1. The main difference with protocol 1 is the addition of the alumina powder without dispersant.

In the protocol 3 as reported on Fig. 4, the dispersant is added in the alumina suspension and mixed during 4 h at 120 rpm. The water is removed at 80 °C during 24 h, and the resulting powder is ground and sieved at 200 μm. Then, this alumina powder is ball milled with the gel during 20 h at 120 rpm. This protocol corresponds to the addition of the dispersant in the alumina suspension before the binder, as usually recommended in the literature [15].

In this study, the selected dispersants for the preparation of the alumina suspensions are ammonium lignosulfonate or ammonium polymethacrylate.

2.1.3. Characterisations

2.1.3.1. Zeta-potential and conductivity experiments. Zeta-potential measurements were performed with an AcoustoSizer II equipment from Colloidal Dynamics which enables to obtain the surface charge and the point of zero charge (PZC). Electrical conductivity measurements were carried out on the solution in contact with the alumina powder. These two techniques are complementary since the zeta-potential method measures the charge at the surface particle and in Stern's plane [16] whereas the conductivity gives information about the diffuse layer. The pH of the suspensions was adjusted with solutions of NaOH and HCl at 0.1 mol/L. Suspensions at 1%wt. solid loadings were tested for both methods.

2.1.3.2. Quartz cristal microbalance with dissipation monitoring (QCM-D). Adsorption of Pectin with or without dispersant was studied by Quartz Crystal Microbalance with dissipation monitoring (QCM-D) on a quartz sensor covered with alpha alumina. QCM-D experiments were performed using a Q-Sense analyzer (QCM-D E4) from Biolin Scientific (Gothenburg, Sweden). The temperature was set constant to 23 °C and a constant flow of 0.2 mL/min was applied. The pH of the solution was adjusted to 8.5 with an ammonia solution.

According to Dunér et al. [17], and thanks to the frequency and dissipation shifts, the thickness of the adsorbed layer can be calculated.

2.1.3.3. Viscosity experiments. Viscosity experiments were performed using an AR 1500 equipment, a controlled stress rheometer from TA Instrument. A cone/plate geometry with a 60 mm diameter and a 2° angle was used. The cycle of measure at 23 °C was the following: the shear rate was raised from 0 to 200 s^{-1} in 100 s, then a dwell was realized at 200 s^{-1} during 180 s, and finally a descent from 200 to 0 s^{-1} was performed in 100 s. The evolution of the shear stress as function of the shear rate was modeled with Herschel and Bulkley's model [18]:

$$\tau = \tau_0 + k\dot{\gamma}^n \quad (1)$$

where τ is the shear stress, τ_0 is the yield stress, k is the consistency factor, $\dot{\gamma}$

Viscosity experiments were done to study whether the different suspensions would have an adapted rheological behavior to the tape casting process and display any thixotropic behavior or not. They were also used to optimize the incorporation order of the additives during the formulation step in order to get the viscosity as low as possible.

2.2. Results and discussion

2.2.1. Dispersion efficiency of Ammonium Lignosulfonate

Zeta potential experiments as function of pH were carried out in order to evaluate the intensity of repulsive electrostatic forces between alumina particles in suspension and the stability of suspension in the time. Fig. 5 shows the zeta potential of three alumina suspensions in relation with pH: a suspension of alumina without

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