CrossMark

Rheological behavior of aqueous mullite-albumin-methylcellulose systems

M.L. Sandoval*, M.A. Camerucci

División Cerámicos, INTEMA (UNMdP–CONICET),, Av. J. B. Justo 4302, 7600 Mar del Plata, Argentina

A R T I C L E   I N F O

A B S T R A C T

In this work, the thermogelling behavior of aqueous mullite-bovine serum albumin (BSA) suspensions was studied by dynamic rheology in order to determine the experimental conditions that must be used to form mullite green bodies by thermal consolidation. Viscoelastic properties (G' and G'') as a function of temperature (30–95 ℃) and time were determined by temperature sweep tests and time sweep tests, respectively. On the other hand, the influence of methylcellulose (MC) (2 wt%) as a binder on the viscoelastic properties of the aqueous mullite-protein system as a function of both experimental parameters (temperature and time) was also studied. In addition, shear flow properties of aqueous mullite (40 vol%; 0.45 wt% of polyacrylic polyelectrolyte as a dispersant)−BSA (10 and 15 vol%)-MC (2 wt%) suspensions were analyzed to obtain information on the rheological behavior of the suspensions at room temperature. The results obtained showed that the presence of mullite particles and MC changed the onset temperature of gelation of the protein and increased the gelation time. Thus, both the mullite particles and methylcellulose intervened in the formation of the developed protein gel.

1. Introduction

Mullite ($2SiO_2 \cdot 3Al_2O_3$) is a powerful candidate material as much for conventional ceramics as for advanced structural and functional ceramics due to not only to its good mechanical properties at high temperature but also its low thermal conductivity, low thermal expansion coefficient and good chemical stability under severe chemical environments [1,2]. These properties make the development of mullite materials useful in several applications, such as dense bodies (e.g. structural components and microelectronic industry devices, among others) or highly porous bodies (e.g. thermal insulators, catalyst supports, combustion burners) [3,4]. The importance of this material, particularly as a porous ceramic, in both the scientific and technological fields has been demonstrated by the large amount of studies that have been published over the last several decades and its continued performance today. In recent years, however, the increased demand for porous ceramics with controlled specific microstructures and properties adequate for new applications in diverse technological fields has been notable [1]. For this reason, the development of novel processing methods and the design of different modifications to the processing routes conventionally used are critical aspects currently being discussed at length [5].

Among the several processing methods employed to prepare porous ceramics, the direct consolidation methods combined with the sacrificial template method are considered highly promising. This is due to

the fact that a ceramic suspension consolidates inside non-porous molds through the formation of a physical or chemical gel on cooling or on heating, without compaction or removal of solvent, and the porosity is generated after a burning process at temperature. In this context, an innovative non-contaminant colloidal processing of porous ceramics with a cellular microstructure, denoted as "protein casting", combines the direct-foaming technique with on-site forming by thermogelling a ceramic-protein suspension [6–8]. This method is based on thermal consolidation at temperatures lower than 90 ℃ by gelling an aqueous ceramic suspension foamed with globular proteins and the formation of a macro-cellular ceramic structure after burn-out (removing organic additives) and sintering treatments at high temperature. The globular proteins have the ability to reduce the surface tension of gas-liquid interfaces and, in consequence, stabilize the gas bubbles formed within the suspension and form a gel in water after heating at 70–80 ℃. It is worth noting that this method, in general, requires the design of strategies to allow the consolidation of the ceramic suspension by protein gelation to occur before the foam destabilization processes begin, which will culminate in rupturing the bubbles . Thus, increasing the suspension viscosity is a possible solution to reduce the drainage rate of the liquid phase (drainage is one of destabilization mechanisms of wet protein foams), although the viscosity should not be so high as to reduce the foaming capacity of the ceramic suspension. In addition, the presence of both the ceramic particles and processing additives, particularly thickener agents, which can be included in order to

---

* Corresponding author.
  E-mail address: laura.sandoval@fi.mdp.edu.ar (M.L. Sandoval).

improve the foamed suspension's stability, also influences the protein gelation process and its microstructural features. The protein gelation process, which is associated with its denaturation, formation of aggregates and cross-linking to generate a three-dimensional polymeric network, implies the occurrence of changes in the global rheological behavior and viscoelastic properties of the aqueous ceramic-protein suspensions, which also are affected by the ceramic particles [7].

Based on the above-mentioned, it can be deduced that a rigorous study of both the viscoelastic properties and shear flow of aqueous ceramic-protein suspensions will provide useful information with which to establish the experimental conditions that allow cellular ceramic bodies with controlled and homogeneous microstructures to be obtained.

Therefore, in this work, the rheological behavior of aqueous mullite–bovine serum albumin (BSA) suspensions was studied by dynamic rheology as a function of temperature and time. From these tests, the influence of mullite particles on the gelation process of the protein was also analyzed. In addition, the impact caused by adding methylcellulose (MC) as a binder on viscoelastic behavior of the aqueous mullite–BSA suspensions was also studied. Furthermore, shear flow properties of aqueous mullite–BSA–MC suspensions were analyzed to obtain information on the rheological behavior of the suspensions at room temperature.

2. Experimental data

2.1. Starting materials

A high-purity commercial mullite powder (MULS, Baikowski, Annecy, France) was used as ceramic raw material. A complete characterization of the mullite powder has been published in a previous work by the authors [9]. The main characteristics of this powder are shown in Table 1.

A commercially available high-purity (> 98%) bovine serum albumin (BSA; A7906, Sigma-Aldrich, USA) and methylcellulose powder (MC; M6385-Sigma-Aldrich, USA) were also employed. The globular protein exhibited a density of 1.27 g/cm^3 measured by He-pycnometry (Multipycnometer, Quantachrome Co., USA), 583 amino-acids, a molecular weight of 66.5 kDa [10] and an isoelectric point (IEP) of approximately 4.8–5.2 [11,12]; as for the polysaccharide, it exhibited a density of 1.28 g/cm^3 measured also by He-pycnometry (Multipycnometer, Quantachrome Co., USA), 1.7 of DS (average number of substituted hydroxyl groups per glucose) and a molecular weight of 17 kDa.

2.2. Rheological behavior of aqueous mullite-BSA suspensions and aqueous mullite-BSA-MC suspensions

The thermogelling behavior of aqueous mullite-BSA suspensions was studied by dynamic rheology with the aim of determining the

Table 1
Characteristics of commercial mullite powder.

Commercial mullite powder	
Purity level	> 99.8 wt%
Phases	Mullite 3/2[a], α-alumina[+], θ-alumina[+], cristobalite[+] and non-crystalline silicate phases[+]
Pycnometric density	3.07 g/cm^3
Mean particle diameter (D_{50})	1.46 µm
Specific surface area	13.5 m^2/g
Particle morphology	Equiaxial three-dimensional and faceted particles

[+]Secondary phases.
[a] Main phase.

experimental conditions that should be used for forming mullite green bodies by thermal consolidation. Thus, viscoelastic properties (storage and loss moduli, G' and G'', respectively, and the phase shift, δ=arc tan G''/G') of aqueous mullite–BSA (10 and 15 vol%) suspensions as a function of temperature (30–95 ºC) and time were determined by temperature sweep tests at a heating rate of 2 ºC/min and time sweep tests at different temperatures (64–70 ºC), respectively. From these tests, the onset temperature of gelation ($T_G \cdot ^O$: temperature from which G' abruptly increased) and the gelation time ($tG \cdot ^O$: time corresponding to the abrupt increase of G') were determined. Temperature values slightly lower than the $T_G \cdot ^O$ values obtained for each system were selected in order to carry out the tests under isothermal conditions. In addition, a time period of 3000 s was considered as the maximum time of duration of these tests. The influence of the mullite particles on these parameters was studied, and thereby, the gelation process of the ceramic-protein system was analyzed.

In addition, the variation of viscoelastic properties of mullite–BSA systems with 2 wt% of methylcellulose (MC) as a function of temperature was also studied. Moreover, , the dynamic rheological behavior of BSA (10 and 15 vol%) solutions and BSA (10 and 15 vol%)–MC (2 wt %) solutions as a function of the temperature and time was also investigated for comparative purposes. The preliminary results indicated that for the selected MC concentration, the complete development of the methylcellulose gel should not occur.

The results obtained from these studies were taken into account for analyzing the impact of the polysaccharide on the gelation of aqueous ceramic-protein systems. It should be noted that the free water loss due to evaporation during the oscillatory isothermal tests (a typical experimental problem for rheological tests at temperature associated with heating using dry air), which are performed using small suspension volumes, and the additional formation of hydrogen bonds among water molecules and hydroxyl groups of MC, contributed to the instability of the mullite concentrated suspension and inhibited the development of the gel into the aqueous mullite–BSA–MC suspensions. For these reasons, the study of the rheological behavior of the mullite–BSA–MC systems as a function of time could not be carried out.

All the dynamic measurements were carried out using a rotational rheometer (Physica MCR 301, Anton Paar GmbH, Ostfildern, Germany) in the oscillatory mode and operated with a 25 mm-diameter parallel-plate geometry, a gap of 1 mm and a frequency of 1 Hz (6.28 rad/s). Preliminary measurements were conducted in order to obtain the linear viscoelastic range. A strain of 0.4% was used to ensure that all the temperature and time sweep tests were within the linear region. In all the measurements, a thin layer of low viscosity silicone oil was spread on the surface of the sample exposed to the atmosphere to minimize the evaporation of water from the suspension.

Additionally, shear flow properties at room temperature of aqueous mullite–BSA (10 and 15 vol%)-MC (2 wt%) suspensions were also studied in order to analyze the rheological behavior at room temperature in steady state. The obtained apparent viscosity vs. shear rate curves were compared with those recorded for aqueous mullite [13] and mullite-BSA suspensions as reported in previous work [9]. Tests were done using the afore mentioned rheometer for the oscillatory measurements along with the experimental conditions reported in previous work for the aqueous mullite suspension [13]. In this case, the rotational rheometer was operated under controlled-rate operating modes with a coaxial cylinder sensor (DIN 53019, Anton Paar GmbH) and a gap of 1 mm. Flow curves were obtained with a three-stage measuring program with a linear increase of shear rate from 0 to 1000 s^{-1} in 300 s, 60 s at 1000 s^{-1}, and a final decrease to zero shear rate in 300 s.

The optimum colloidal stability conditions for preparing the aqueous mullite suspension and mullite–BSA suspensions were previously determined by measuring zeta potential and shear flow properties [9,13]. Thus, stable and homogeneous aqueous mullite suspensions