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Gelcasting of alumina suspension using gellan gum as gelling agent

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Abstract

As one of the excellent colloidal ceramic forming methods for fabricating complex shaped ceramic components, gelcasting has been extensively investigated in the past two decades. In this article, a novel nontoxic system for gelcasting of ceramics was investigated using gellan gum as gelling agent. The rheological and gelling properties of gellan gum solutions with different types of cations and different concentrations of divalent magnesium ions were studied. Influences of concentration of gellan gum and solid loading of alumina suspension on the rheological properties and gelling properties of alumina suspension were investigated. The rheological properties of concentrated alumina suspension mixing with gellan gum and magnesium chloride were evaluated. Dense ceramics prepared by gellan gum gelation showed homogeneous microstructure and good mechanical properties.

Keywords: Gelcasting; Alumina; Gellan gum; Cations; Rheological properties

1. Introduction

Gelcasting is a well-established colloidal processing method which has been used to prepare high-quality and complex-shaped ceramic parts by means of in situ gelation through which a macromolecular network is created to hold the ceramic particles together [1,2]. The gelcasting process was first developed by Omatete and Janney during the 1990s [3–6]. Gelcasting is suitable for fabricating complex shape ceramics by offering short forming times, high green strength, and low-cost machining compared with other forming methods [7,8]. In aqueous gelcasting, acrylic acid and acrylamide (AM) are commonly used. However, acrylic acid and water cannot completely dissolve in each other, a cosolvent needs to be added, the premixed solution may be partly gelated, and a high solid loading with acrylic acid is difficult to be achieved. The main component of the monomer acrylamide system is a neurotoxin, which makes it prohibitive for industrial applications [9]. Due to these reasons, many researchers focus on developing low-toxicity or the nontoxic gelcasting system to replace acrylamide to reduce environmental pollution.

Thermal gelation of polymeric binders such as methylcellulose polymers were used as gelling agent for injecting ceramics [10]. Methylcellulose derivatives show a thermal gelation behavior, and concentration as low as 0.08 wt% of methylcellulose had been found to be sufficient enough to convert an alumina slurry of 74–75 wt% solid loading, to consolidated shapes by thermal gelation at 70–80 °C [11]. The use of agarose for gel-forming ceramic parts was reported firstly by Fanelly et al. [12]. Slip containing the gelling agent was prepared by mixing the well dispersed alumina suspensions and the agarose after heating to 60 °C and then was cooled below T_g [13]. Complex shaped green part with high gel strength can be obtained via gelation of very low concentration of agarose, such as 1 wt% referred to as ceramic powders [14,15]. However, the cost of agarose is so high that limits the industrial application. Also it must be added to the ceramic slurry at a temperature above 80–90 °C in order to dissolve it completely. However, the viscosity of the slurry will increase greatly at this temperature because of the rapid evaporating of the suspension which promotes agglomeration and flocculation [16]. For these reasons the search for new additives with

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excellent gelling properties and lower costs has been concerned. Some other additives have been researched, including starches and pectins, gelatin, and so on [17,18]. But much high concentrations are required to provide a sufficient green strength, or the gel strength is too poor.

Gellan gum, commonly used in the food industry, is a polysaccharide manufactured by microbial fermentation of the *Sphingomonas paucimobilis* microorganism. It can be dissolved in water when heated at 90 °C, then mixed with cations and cooling to form a gel at the temperature under mild conditions [19]. There are existing two forms of gellan gum, acetylated and deacetylated, the latter is the most common and has been commercially available. Gellan gum is in the coil form at high temperature, upon temperature decrease, a thermally reversible coil to double-helix transition occurs, which is a prerequisite for gel formation. Thus, the structure of anti-parallel double helices self-assembled to form oriented bundles, called junction zones, is formed. Untwined regions of polysaccharide chains, in the form of extended helical chains, link the junction zones, leading to the formation of a three dimensional network, that creates the gel. Both the chemical nature and quantity of cations present strongly influence the gelation of gellan gum solutions. So the presence of cations is critical to prepare a structurally stable gel. Divalent cations promote the gelation much more strongly than monovalent cations [20–22].

The aim of this work is to investigate a new gelcasting system using gellan gum as gelling agent. The influences of concentration, temperature and cations on the rheological and gelling properties of gellan gum were studied. The rheological properties of alumina suspension with different concentrations of gellan gum were investigated. The properties of green and sintered bodies were characterized.

2. Experimental procedure

2.1. Materials

A CT3000SG alumina powder (Almatis, Ludwigshafen, Germany) with an average particle size of 330 nm and specific surface area of 8.08 m^2/g was used to prepare the concentrated alumina suspension evaluated in this study. For the suspension with negatively charged ions on the surface of the alumina particles, 0.3 wt% triammonium citrate (TAC) based on alumina powder was used as the dispersant. Suspension with positively charged ions on the surface of the alumina particles was prepared by adding 3 wt% hydrochloric acid (2 mol/L) based on alumina powder. Gellan gum (Beijing TIANZHUNIAO Food Additives Co., Beijing, China) was used as gelling agent. Analytical reagent grade magnesium chloride ($MgCl_2$) and sodium chloride (NaCl) (Guoyao, China) were used as source of cations. Deionized water was used in all the preparation process.

2.2. Suspension preparation and gelcasting

Alumina suspensions with solid loading of 55 vol% and 50 vol% were prepared by tumbling the alumina powder, water, and the dispersant in polyethylene containers for 12 h. Zirconia balls with a diameter of 5–10 mm were used as grinding media. The mass ratio between grinding media and alumina powder is 1:2. The pH of prepared suspensions is 9.2 and 4.5 for negatively charged and positively charged suspensions, respectively. Gellan gum aqueous solutions were prepared with concentrations of 1–3 wt% by mechanical stirring in water and further heating up to 90 °C in order to allow the complete dissolution of gellan gum. The solution was kept at 70 °C before mixing with alumina suspensions. Magnesium chloride and sodium chloride solutions with the concentration of 1 mol/L were prepared.

Before casting, the suspension was degassed in vacuum condition for 30 min and then was heated to 70 °C. Different concentrations of $MgCl_2$ and gellan gum solutions were added into the suspensions by constant stirring for 2 min. Then the suspension was cast into a plastic mold and cooled down at room temperature. The samples were demolded without any deformation after resting at room temperature for 12 h.

2.3. Characterizations

The rheological properties and the elastic modulus of the suspension and the gellan gum solution were measured using a KINEXUS rheometer (Malvern Instruments, UK). In viscosity measurement, the shear rate was set at 100 s^{-1} and the oscillatory measurement was conducted at a frequency of 1 Hz and a stress strain of 1%. The measurements were taken at temperature ranging from 70 °C to 10 °C, and the cooling and heating rate is 5 °C/min, the scanning time was 10 s per point. At these conditions a probe of temperature allowed the continuous determination of viscosity both on cooling and subsequent heating. The mixture of alumina suspensions and gellan gum was heated to 70 °C before measurement. Then, magnesium chloride solution was added to the suspension. The rheological properties of the mixture were evaluated by cooling down to 10 °C.

For wet compressive strength measurements, cylindrical bodies with 25.5 mm in diameter and a height between 25 and 30 mm were cast. After gelling at room temperature, the samples were de-molded, and their wet green strength was measured immediately in an AG-IC20KN (Shimadzu, Japan) testing machine with a crosshead speed of 0.5 mm/min. The wet green strength was determined as the yield point, extrapolated from the tangents to the curve. The pictured data represent mean values from 3 to 10 samples. The dried samples were sintered at 1550 °C for 2 h at a heating rate of 5 °C/min. The samples were cut into 3 mm × 4 mm × 36 mm and then grinded. The bending strength was measured with a mechanical machine (AG-IC20KN, Shimadzu, Japan) using three-point bending test with a span length of 30 mm and a crosshead speed of 0.5 mm/min. The microstructure of sintered samples was observed by a SSX–550 (Shimadzu, Japan) scanning electron microscope (SEM).

3. Results and discussion

3.1. Rheological properties of gellan gum

Fig. 1 plots the rheological properties of gellan gum at different temperatures. The measurement was taken by cooling