A new gel casting of ceramics by reaction of sodium alginate and calcium iodate at increased temperatures

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Gel-casting has been widely studied for the last decade [1–5]. In this process, a slurry made from ceramic powder and a water-based monomer solution is poured into a mold, polymerized *in situ*. The gelled part is removed from the mold while still wet, and then is dried and fired. The dried green body is strong enough to be machined. However, the process is not perfect in that the polymerization of monomers is difficult to control in the ceramic suspension. Reductive agents usually restrain the free-radical polymerization of commonly used acrylamide. In addition, acrylamide is highly toxic. Therefore, new gelcasting process with a reduced toxicity have been investigated [6–8].

In fact, many polymer solutions can gelate under suitable conditions [9, 10], such as agarose, gelatin and sodium algaecide. Some of them have been employed in food industry [10]. When the polymer is dissolved in solvents, the molecular chains attract each other to form a three-dimensional network by hydrogen bonds or Van der Walls forces. The gelling property of agar has been used in the water-based injection molding [11]. Recently, we have reported that ceramic suspension was gelled to green body using gelatin and agarose [7, 12]. However, the suspension containing agarose has to be heated up to 80 °C before casting, which easily results in water vaporization. In addition, both agarose and gelatin are expensive when they are employed in industry.

Alginate is a type of gelling polysaccharide, which can be dissolved in water at room temperature and then gelled after casting by cross-linking with divalent metal ions at increased temperature. Like all cation-exchangers the selectivity and strength of binding depend on both the nature of the cation and the properties of the polymer. Divalent and polyvalent cations and bound strongly by all types of alginate and effectively cross-link the polysaccharide to form a gel matrix. However, regions of polysaccharide form particularly strong chelation complexes with divalent cations, especially the calcium ion [13].

The mechanism of crosslinking in alginate gels can be considered in terms of an "egg-box" model involving cooperative binding of calcium ions between aligned polyguluronate ribbons as shown in Fig. 1 [10, 14]. The buckled chains of polysaccharide form a structure akin to the cross-section of an egg-box in which the calcium ions are the "eggs". The binding of the calcium ion is strong because, in addition to the ionic binding to the carboxyl groups, various ring and hydroxyl oxygen atoms are able to chelate the cations.

Although there are many salts containing calcium ion, such as $CaCl_2 \cdot 4H_2O$, CaC_2O_4, $Ca(C_6H_{11}O_7)_2$, $Ca(IO_3)_2 \cdot 6H_2O$, which can react with alginate and crosses link together. However, it is generally very difficult to control the reaction rate for most of them. This makes it impossible to complete casting processing at certain period. Therefore, the divalent salts with a controlled reaction rate with alginate have to be considered. In other words, divalent cation concentration released from the salt can be adjusted with temperature or time. Examining the solubility of above salt substances at different temperatures, we found that $Ca(IO_3)_2 \cdot 6H_2O$ is good for gelcasting processing because they have a lower solubility (0.17 wt%) at room temperature and a high solubility (1.38 wt%) at increased temperature of 60 °C. So $Ca(IO_3)_2 \cdot 6H_2O$ was chosen in this study. In the present paper, the gelling properties of sodium alginate solution and resulting suspension with ceramic powder were investigated. The rheological behavior was examined. Near-net-shaped green bodies with different shapes were produced by the novel forming processing.

Sodium alginate used is a commercially available fine powder with white color. Sodium alginate solutions with different concentration were prepared by stirring in deionized water at room temperature. The apparent viscosity of the solution was examined by a rotary viscometer (Model NXS-11, Chendu Instrument Plant, China). Fig. 2 shows the results of rheological properties influenced by the alginate concentration. For lower concentrations of sodium alginate of 0.5 and 1.0 wt%, the flow properties are almost Newtonian mold, and shear-thinning characteristics of alginates are obvious at high concentrations. These results are in good agreement with other reports [10]. It should be noted that the viscosity of the solution with 3 wt% alginate had a maximum value at the shear rate of about 35 s^{-1}. This can be explained from the competition between promptly chain association and breaking down by shear.

To examine the controlled gelling process of calcium and alginate, 1 wt% calcium iodate was dispersed in the 3 wt% alginate solution by stirring, and then moved the bake containing alginate suspension to water bath at 60 °C. Fig. 3 illustrates that the viscosity varies with time for the system. As a comparison, viscosity curves without calcium iodate was included in same figure. At the initial period, viscosity increases very slowly from a
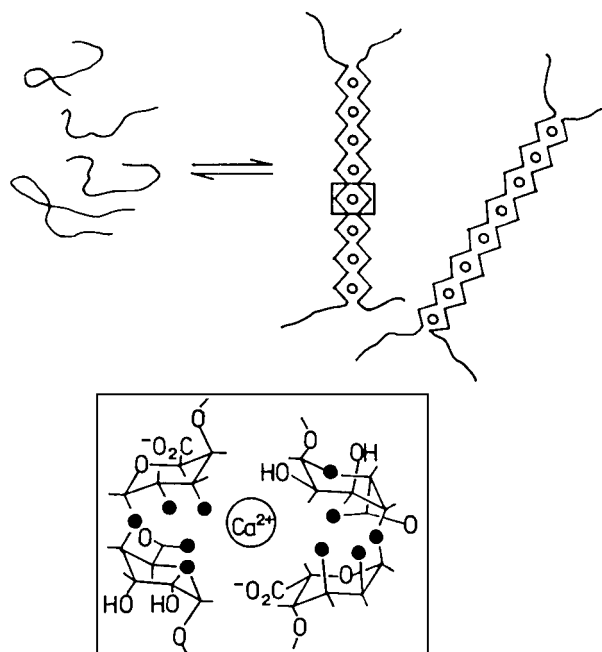
Figure 1 Schematic representation of association of polyguluronate within the alginate molecule by calcium.

Figure 3 Viscosity varies with time for 3 wt% sodium alginate solution with 1 wt% or without divalent salt at 60 °C.

Figure 4 Effect of sodium alginate and calcium iodate on alumina Zeta potential at 25 °C.

value below 1 Pa · s due to the fact that cross-linking does not occur instantly. After more than 40 min, with more calcium ions released and diffusion rate accelerated, apparent viscosity increased to 5 Pa · s until gel was formed. It is believed that the calcium ions bind the chains tightly to each other and a three-dimensional network of these interconnected regions is established.

The alumina powder used was a commercial grade An-05, and the details about the powder was described in a previous report [7]. Zeta potential and isoelectric point (IEP) of this alumina powder with and without alginate were measured by ZetaPlus (Brookhaven Instrument Corp., USA). The suspension of 0.05 vol% concentration was chosen. As shown in Fig. 4, the addition of sodium alginate produced a pronounced effect on alumina electrokinetic behaviors, in which IEP of the pure alumina suspension changed from pH 6 to pH 2.1. This is caused by the absorption of carboxyl negative charge on the alginate chain onto the surface of alumina particles. At the range of pH4–pH10, a negative Zeta potential below - 40 mV was also observed. Such a low Zeta potential was probably caused by the
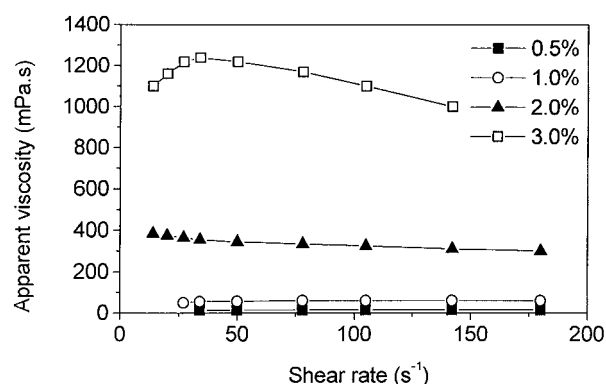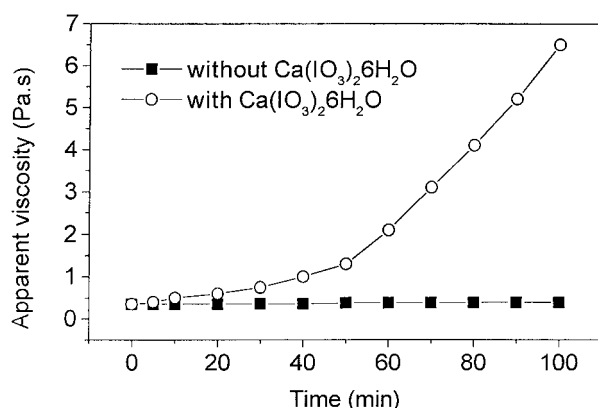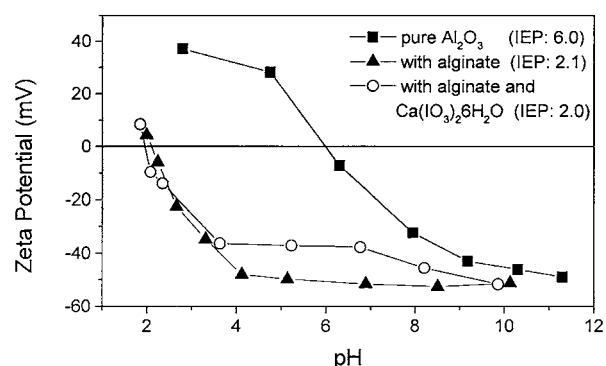
increased double-layer thickness of alumina particles due to absorption of alginate. The addition of calcium iodate to the alumina alginate suspension did not influence the IEP and Zeta potential. This implies that there is no character absorption or reaction between them at room temperature.

The gelling properties of the slurry with 50 vol% alumina and 1 wt% alginate solution were investigated. After mixing with 1 wt% calcium iodate, the slurry container was moved to water bath at 60 °C and viscosity was measured as a function of time. As shown in Fig. 5, there is little change in viscosity in the first 10 min. However, viscosity increased greatly from 2 Pa.s to more than 30 Pa.s, afterwards when the slurry temperature was the same as the water bath. Then a wet
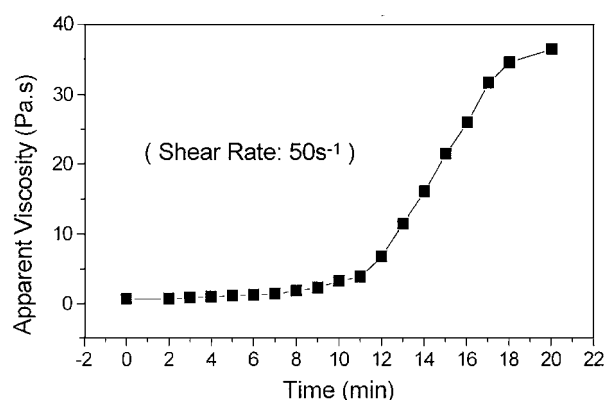

Figure 2 Influence of sodium alginate content on solution viscosity at 25 °C.

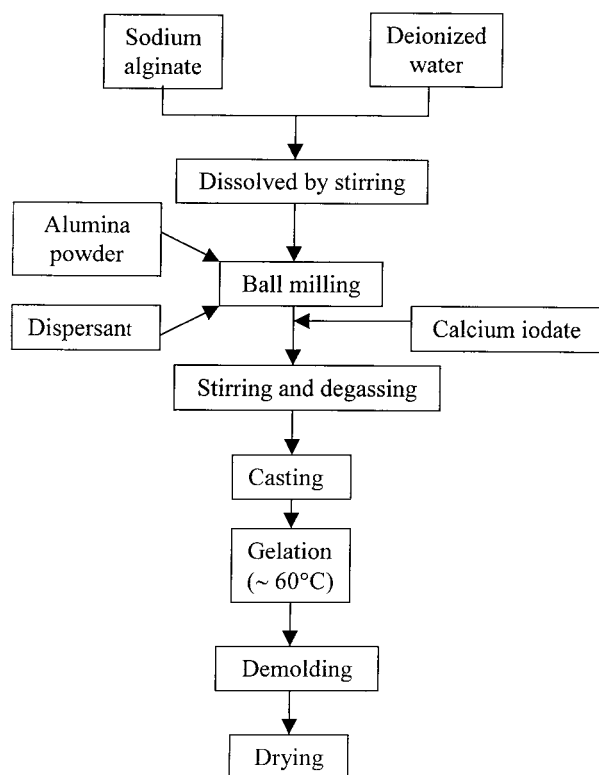Figure 5 Viscosity change with time at 60 °C.

Figure 6 Flow chart of the gel casting.

green body was gelled soon. The results suggested that the casting process could be controlled by heating rate and final temperature.

The forming process using the controlled reaction between alginate and calcium iodate is described in Fig. 6. First, alginate was dissolved in deionized water by stirring, and mixture of the solution and ceramic powder with dispersant was ball milled to break down agglomerate and reduce viscosity. After adding calcium iodate and degassing, the resulting slurry was cast into nonporous mold and heated to 60 °C. The gelled wet green body can be removed from the mold. In general, the demolded green parts show a good shape and a smooth surface.

After demolding, the wet green parts can be dried in ambient or directly in drying chamber without cracking and damage. A linear shrinkage of 2.4% was observed for drying period. Because the amount of organic binder of alginate is only 1 wt%, the green body can be sintered without special binder burnout. Microstructure and pore distribution of the dried green body were examined by scanning electronic microscopy and mercury porosimeter. A homogenous structure without large agglomerates was observed. Also the pore distribution was characterized with a narrow single peak. These results suggest that well-dispersed suspension, good degassing and casting could be performed by the colloidal forming process.

The casting forming process based on gelling of sodium alginate was presented. It is summarized as followings: (1) Sodium alginate is dissolved in water at room temperature, and the solution gels by cooperative binding with divalent cations at increased temperature. Gelling of the acidic polysaccharides polymer results from the replacement of Na^+ by divalent cations on the backbone of the polymer which bind the chains tightly together. (2) Calcium iodate was successfully used for the gel forming process of green body from ceramic suspension containing sodium alginate. The solubility of the divalent salt could be controlled by heating rate and final temperature. (3) Gelling process by reaction of alginate with calcium ion was completed fast and wet green body was formed at a shorter time, typically in the range of about 30 min to 2 h from casting to demolding. In addition, polymer sodium alginate is less expensive, which makes it possible to use in large scale production.

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