

A novel casting forming for ceramics by gelatine and enzyme catalysis

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Abstract

A new kind of gelation process for forming a ceramic green body is discussed. The forming method is based on a process in which gelatine, enzyme (urease) and urea are used. Urea is employed to prevent attraction between gelatine molecules when the dissolved hot gelatine solution cools down for preparing a well-dispersed suspension by ball milling and degassing at ambient conditions. After urease is added into the suspension, gelatine molecules attract each other and form three-dimensional network through hydrogen bonding due to urea decomposition by urease. Slurry containing alumina and gelatin could be consolidated in situ by the above gelation process at room temperature. A green body with homogeneous microstructure and smooth surface was obtained. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years, some new colloidal forming techniques such as gel-casting and direct coagulation casting (DCC)^{1–4} have been developed to shape complicated ceramic parts which are homogeneous in the green as well as in the sintered state. Gelcasting, based on the in situ polymerization of organic monomer binder, shows the ability to fabricate complex-shaped green bodies with high green strength and <4 wt% binder. Unfortunately, acrylamide monomer widely used in the process is harmful to health. Therefore, the gel-casting process with low toxicity and without toxicity was paid more attention.⁵

As we know, many natural polymers without toxicity such as agarose, gelatine and agar show the gelation property^{6–8}. Some of them have been employed in the food industry.⁹ 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 Waals forces. We have reported that a ceramic suspension was gelled to a green body using agarose and gelatine in

previous work [10,11]. In these cases, a well-dispersed ceramic suspension containing agarose or gelatine was ball milled and heated at 80 or 40°C to dissolve them completely, and then cast in a non-porous mould. During cooling down to room temperature, the suspension gelled and formed a wet green body with the desired shape. Some ceramic parts with a complex shape, such as a turbine rotor, were produced by this method. However, the problem of the process is that the suspension has to be heated to a certain temperature before casting, which might increase the viscosity of the slurry due to water vaporization during the heating process.

To overcome this drawback of the forming process, a new kind of gelation process using gelatine for forming a ceramic green body is developed in this work. The forming method is based on the process in which gelatin, urea and urease are used. Urea can prohibit a hydrogen bond from forming between gelatin molecules when the hot gelatin solution cools down. As urease is added into the suspension, gelatin molecules attract each other and change to a three-dimensional network structure through hydrogen bonding due to urea decomposition by urease. Then the suspension containing ceramic powder and gelatin will be consolidated in situ by the gelation at ambient conditions. This process can avoid

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water vaporization and prevent viscosity increasing before casting. Also the process is more easily controlled for obtaining homogeneous microstructure in the green body.

2. Experimental procedures

2.1. Materials

The gelatine polymer with molecular weights ranging from 15,000 to 90,000 was provided by Shanghai Chemical Reagent Works. The analysis of the gelatine has been reported in previous work [11]. The gelatine powder can be dissolved in water in less than 20 min at $\sim 40^\circ\text{C}$, and shows a pH value of 5.5–7 for 1 wt% solution. Urea with a purity of 99% is a commercial grade (Beijing Chemical Company). The alumina powder used here was a commercial grade An-05, and the details about the powder were described in Ref. 11.

2.2. Procedure

The forming process is described in Fig. 1. First, the urea and gelatine were dissolved in deionized water at $\sim 40^\circ\text{C}$. As the solution cools down to room temperature, alumina powder and dispersant were added to the solution. Then mixture was ball milled for more than 12 h to obtain well-dispersed suspension with good fluidity. After degassing, urease solution was added and mixed at the lower temperature of $2\text{--}5^\circ\text{C}$. Then the slurry was cast in mould in ambient conditions and coagulated to a green body through gelation due to enzyme-catalyzed decomposition of urea.

2.3. Measurement and analysis

The rheological properties of the gelatine solution and mixed ceramic slurry were measured by a rotary rheometer (NXS-11, Chengdu, China). Zeta potential was calculated from the measured electrophoretic mobility using ELS (Electrophoretic Light Scattering) with a 5 mW laser source. The suspension of 0.05 vol% concentration was chosen. The pore size distribution in the green body was measured by mercury porosimeter (Autoscan Mercury Porosimeter, Quantachrome Company, USA). The microscopic morphology of the dried green body was observed by SEM (OPTON·CSM950).

3. Results and discussion

3.1. Prevention of urea on attraction of gelatine molecular

Gelatine, a kind of protein polymer, is mainly composed of various amino acids. Urea can act with amino

acids with hydroxide radical and restrain the formation of hydrogen bonds between polymer molecular or polymer and water. Fig. 2 shows that viscosity of 2 wt% gelatine solution change with urea content under the cooling stage from 40 to 20°C . The ratio of urea to gelatine is expressed as α . As $\alpha < 3$, the solution viscosity was high due to gelation of the gelatine. For the case

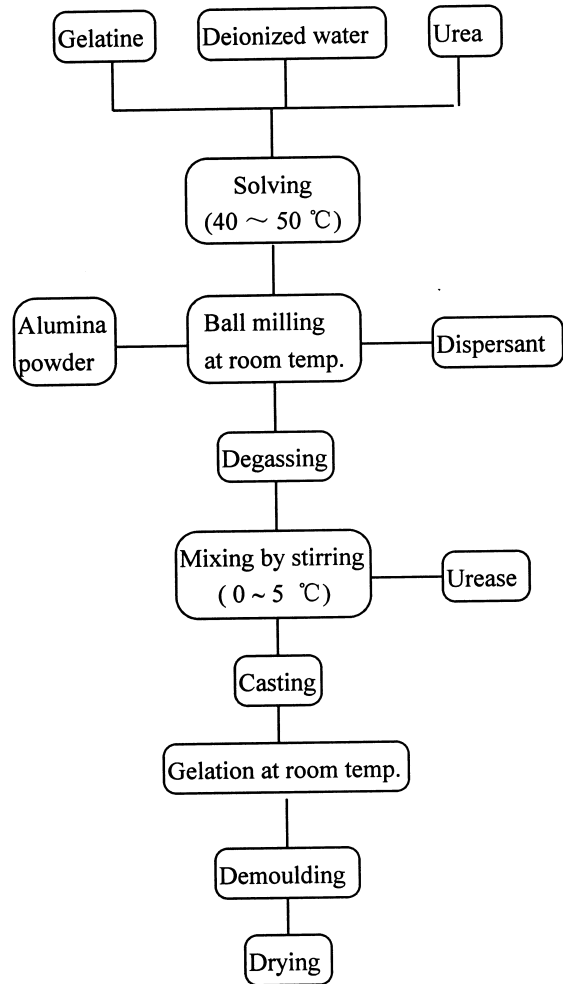


Fig. 1. Flow chart of the forming process.

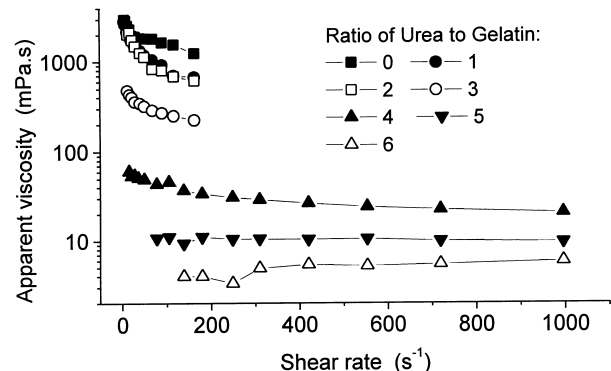
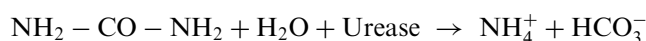


Fig. 2. Effect of urea content on viscosity of gelatin solution (2 wt%).

of $\alpha = 4$, the solution showed some fluidity and still appeared in a viscous state, in which flocculation was observed. However, the viscosity decreased to 10 mPa·s or lower when $\alpha < 5$. In this case, sufficient urea prevented gelatine to gel completely and a clear gelatine solution with perfect fluidity could be prepared. For the system of 3 wt% gelatine solution which also was investigated, almost similar to the above results was observed.

3.2. Gelling of gelatine solution under urease catalysis

When urease, as a kind of catalyst, was added into the gelatine solution, urea could be decomposed by urease catalysis. The reaction is as follows:



The reaction speed mainly depends on temperature and amount of urease addition. At a temperature lower than 5°C, decomposition of urea is very slow, but it would increase greatly with temperature. For example, one unit will liberate 1 μmol of NH_3 from urea per min at pH 7 and 25°C². During the decomposition of urea, the gelling of gelatine solution will occur through hydrogen bonding among gelatine molecules, and the gelation can take place at room temperature due to the gelling point ranging from 15 to 25°C. Fig. 3 shows the viscosity change with decomposition time after adding urease at 15°C for the solution containing 2 wt% gelatine and 10 wt% urea. The viscosity increased slowly at the initial stage due to less urea decomposition and less hydrogen bonding among molecules. However, the solution lost fluidity and gelled after about 3 h. This resulted from a formed three dimensional network by attraction among molecular chains.

The time to reach consolidation was clearly influenced by the amount of urease addition. From Fig. 4, it can be seen that about 10 h was needed for a urease concentration of less than 5 units, and only 3 h for a urease concentration of 10 units. There was almost no influence

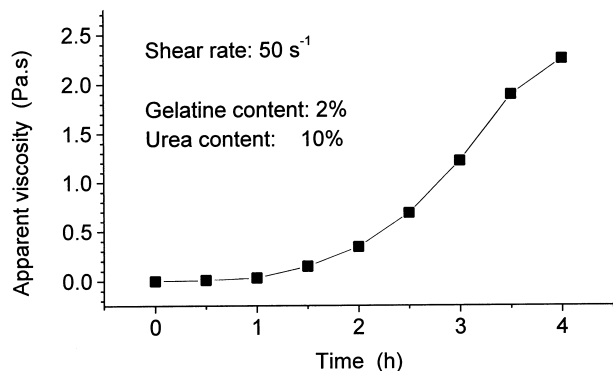


Fig. 3. Viscosity of gelatin solution vs time after adding urease.

of urease content on the time as the urease concentration reached 16 units.

3.3. Rheology and zeta potential of alumina suspension containing gelatine and urea

A suspension with 50 vol% alumina and 2 wt% gelatine (based on water) was prepared according to flow chart in Fig. 2, in which the suspension was ball milled for 24 h. The influence of the amount of urea on rheological properties was illustrated in Fig. 5. As the ratio of urea to gelatine (α) is equal to 4, the system showed a relative large viscosity (apparent viscosity reached 1500 mPa·s for the shear rate of 100 s^{-1}). Also a dilatant flow model was observed in which viscosity increased with shear rate. It was implied that there still was attraction joints among polymer molecules that resulted in a large viscous force during shearing. Under those conditions, agglomerates or flocculation may occur and the homogeneous microstructure of the ceramic body will be destroyed. When $\alpha \geq 5$, the viscosity sharply decreased to lower 100 mPa·s, which make degas and cast easily carry out. Moreover the suspension showed a Newtonian model. In this case, viscosity almost did not vary with shear rate, especially after the shear rate of 50 s^{-1} .

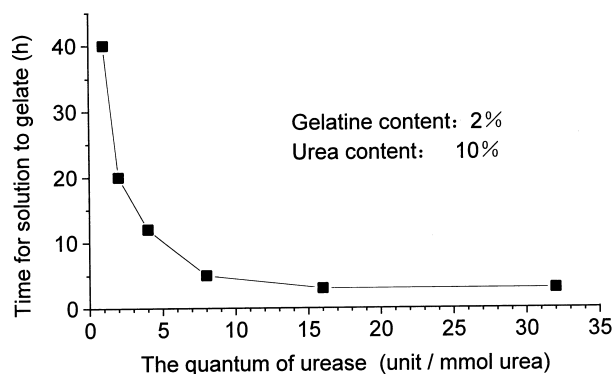


Fig. 4. Effect of urease concentration on gelation time.

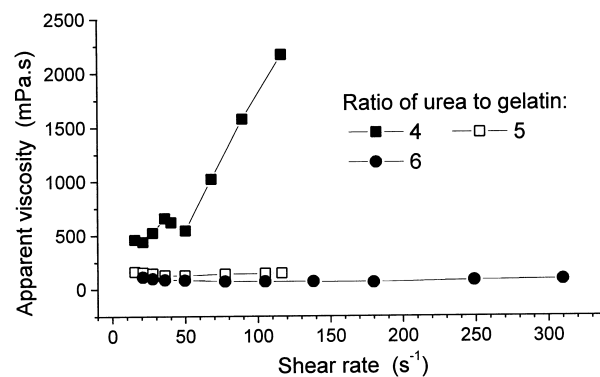


Fig. 5. Effect of urea content on fluidity of slurry with gelatin and alumina.

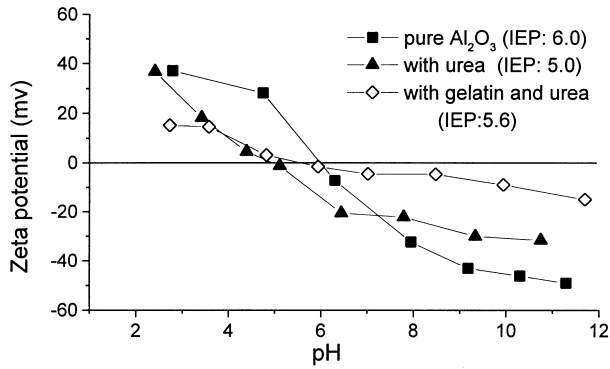


Fig. 6. Zeta potential vs pH value.

Similar results were also observed for the suspension with 50 vol% alumina and 3 wt% gelatine (based on water). This was helpful to the colloidal process. This rheological behavior was related to the structure of the system where the attraction between polymer molecules was limited by enough urea.

Zeta potential of alumina suspension was also influenced by gelatine and urea. As shown in Fig. 6, the pure alumina suspension had an isoelectric point (IEP) of 6 and relative high zeta potential (about 40 mV at pH 8–10). For the suspension containing gelatine and urea, zeta potential was clearly decreased. This may be resulted from the fact that the electrostatic double layer was compressed by ions with a high value in gelatine. It was noted that the suspension still showed a good fluidity when the ratio of urea to gelatine (α) was higher than 5.

3.4. Coagulation forming and microstructure of green body

The apparent viscosity vs time was measured at 15°C, when the urease (16 units per mmol urea) was added into 50 vol% alumina suspension with 2 wt% gelatine (based on water) and 10 wt% urea (based on water). From Fig. 7, the change in apparent viscosity of the slurry was similar to that of a gelatine solution (Fig. 3). The viscosity increased relatively slowly at the initial stage and rose greatly after 3 h. This is due to the fact that the coagulation of the slurry came from gel network forming of gelatine molecules which was strongly dependent on the speed the urease catalyzed decomposition of the urea. The viscosity reached more than 25 Pa·s after 7 h and then remained at that. At this point, a three-dimensional gel network was formed which resulted in complete coagulation of the slurry, and a rigid wet green body was obtained.

Microstructure and pore distribution of the dried green body were examined by scanning electronic microscopy and mercury porosimeter. As shown in Fig. 8, a homogenous structure could be observed, in which large agglomerates and babbles were removed. Also the pore distribution was characterized with a narrow single

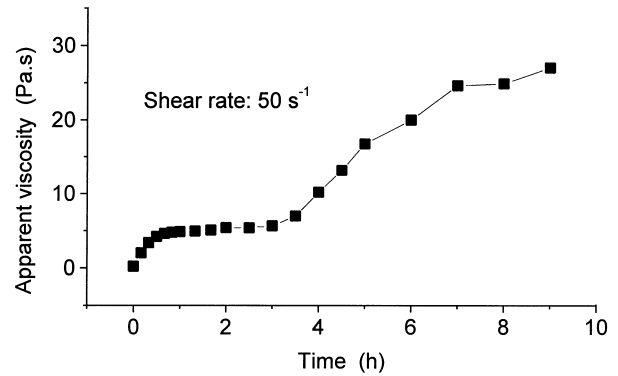


Fig. 7. Slurry viscosity change with time after adding urease.

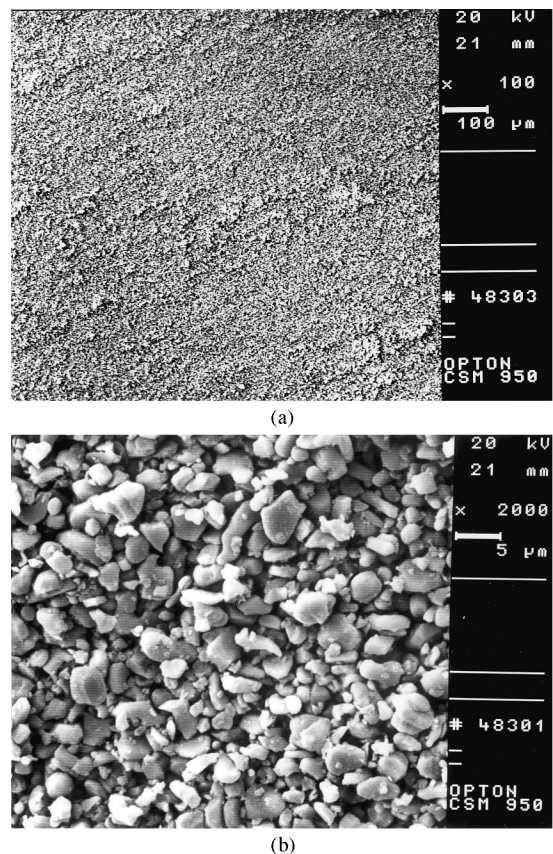


Fig. 8. SEM micrograph of dry green body.

pick while two picks were observed for dry pressed green body. These results suggested well-dispersed slurry, good degassing and casting could be performed by the colloidal forming process.

4. Conclusions

As the ratio of urea to gelatine (α) larger than 5, the gelling process was completely restrained when the

gelatine solution was cooled down from ~ 40 to 15°C (gel point). This was because hydrogen bonds and Van der Waals forces between molecules were limited as the urea existed, where the 2–3 wt% gelatine solution viscosity was less than 10 mPa·s. However, the gelling process of the solution was regained when urease was added, due to enzyme-catalyzed decomposition of urea. The time taken to form gel was strongly dependent on urease concentration. Coagulation speed of the solution increased greatly as urease concentration reached 10 units. There was almost no change in gelling time after 16 units of urease.

For the suspension with 50 vol% alumina and 2 wt% gelatine (based on water), apparent viscosity got down to 80 mPa·s and the suspension showed a Newtonian model when the ratio of urea to gelatine $\alpha \geq 5$, which makes the colloidal processes such as degassing and casting easily carried out. However, the slurry could be coagulated in a few hours by gelling of gelatine after the urease (16 unit per mmol urea) addition. The dry green body produced by this method showed homogenous microstructure.

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