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Control of the inner stresses in ceramic green bodies formed by gelcasting

L.G. Ma[a], Y. Huang[a], J.L. Yang[a], H.R. Le[b,*], Y. Sun[c]

[a] *State Key Laboratory of New Ceramic and Fine Processing, Department of Materials Science and Engineering, Tsing Hua University, Beijing 100084, Peoples' Republic of China*

[b] *Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB21PZ, UK*

[c] *Teaching Centre of Basic Physics Experimentation, School of Physics, Peking University, Beijing 100871, Peoples' Republic of China*

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Abstract

The negative effect of inner stresses on the ceramic green body formed by gelcasting is discussed. It is found that a proper amount of hydroxyethyl acrylate (HEA) added into the concentrated suspension can adjust polymer network structure and thus reduce the inner stresses and cracking in the ceramic green body. The debindering time of large ceramic parts can be significantly shortened by reducing the harmful inner stresses in the green body.

Keywords: Gelcasting; Green body; Inner stresses; Debindering process

1. Introduction

Property reliability and product cost are two major considerations in the applications of advanced ceramics and ceramic composites. Both are directly or indirectly related to the micro-structural defects occurring in manufacturing process [1]. The random nature of these defects is often responsible for the poor reliability and performance of ceramic products. It is well known that defects like delamination, micro-cracks or large pores are often present in the green bodies formed by traditional forming processes such as dry-pressing, isostatic pressing and injection moulding. These defects can hardly be removed in the subsequent processes and become fracture origins reducing the properties of the product or leading to higher rejection rate. Since 1990s more attention has been paid to colloidal forming processes such as gelcasting, direct coagulation casting and colloidal vibration forming due to their potential to improve the homogeneity of ceramic body and reduce harmful micro-structural defects.

Among these colloidal forming processes, gelcasting, by which complex ceramic parts can be prepared [2], has been widely studied and applied to various ceramic materials [3–5]. Homogeneous green bodies with good strength required for machining can be made through this process. The mechanical properties of the materials after sintering are greatly improved [6–8]. The main steps of gelcasting are as follows [3–5,9]: First, the ceramic powder (e.g., alumina or silicon nitride, etc.) is thoroughly mixed with small quantities of gel initiators, catalysts, monomers, crosslinkers and sintering additives to form a homogeneous suspension with high solid loading and low viscosity. Second, gelation is initiated by casting the suspension into a non-pore mould at elevated temperature. A green body is then formed by in situ polymerisation with a three-dimension gel network holding all the ceramic particles together. The green bodies are then demoulded, dried, debindered and finally sintered at a high temperature.

In this process, the mould temperature is utilized as a method to induce polymerisation in the suspension. However, a temperature gradient exists in the suspension due to the heat transfer from the mould surface to the concentrated suspension. Due to the temperature gradient,

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* Corresponding author. Tel.: +44 1223 332609; fax: +44 1223 332662.
E-mail address: hl220@eng.cam.ac.uk (H.R. Le).

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the solidification of the suspension is not uniform, resulting in inner stresses in the green bodies. The inner stresses are often responsible for the cracking of the green bodies in subsequent drying or debindering process. The larger the parts are, the more harmful the inner stresses are. Therefore, it is of great importance to control the inner stresses in the green bodies in order to prepare large-size ceramic parts by gelcasting.

The inner stresses in the green body originate from differential contraction so that the magnitude of the inner stresses increases with the shrinkage rate and the elastic modulus. There are two sources of shrinkage in gelcasting process: one being the forming shrinkage due to slight contraction in the polymerisation of monomers and the other being the drying shrinkage due to the removing of the moisture. A high solid loading in the suspension is preferred in gelcasting in order to reduce the shrinkage of the green body. However, there is a limit of solid loading in the suspension for desirable viscosity and uniformity [7–8]. In order to control the shrinkage rate, the wet green body is usually dried slowly under controlled temperature and humidity and then debindered at a very low heating rate. This is not favourable in practice because it leads to a prolonged operation time and high production cost. Recently, the authors developed a pressure-assisted gelcasting process using injection moulding of colloidal suspension [10]. The mould temperature and hence the temperature gradient can be reduced owing to the pressure-induced solidification mechanism. The reliability of the products is improved due to more homogeneous solidification but with an extra cost. The authors found that the cracking of the green bodies could be reduced by the addition of a plasticizer or a moderator in the suspension [11–12]. It is thought that the inner stresses are correlated with the elastic modulus of the green body that can be controlled by the modification of the gel network by moderators. This mechanism has been explored in this paper using lab simulations. The strategies to minimize the inner stresses will be reported and the implications on the cracking of green body and the efficiency of debindering process will be discussed.

2. Experimental procedure

2.1. Materials

A commercial Al_2O_3 powder with mean particle size of 3.84 μm, produced by Xin-yuan Al_2O_3 Plant of He-nan in China, was used. Other chemical reagents used were: deionized water with conductivity of 1.02 $\mu S\ cm^{-1}$, acrylamide (AM) as monomer, hydroxyethyl acrylate (HEA) as moderator, methylenebisacrylamide (MBAM) as crosslinker, $(NH_4)_2S_2O_8$ as initiator, ammonium citrate as dispersant and *N*,*N*,*N*′,*N*′-tetraethylmethylenediamine (TEMED) as catalyst.

Table 1
The weight percent of HEA in the monomers in different premix solutions

Pemix solution	HEA/(HEA + AM)
M_1	1
a	1/3
b	1/5
c	1/9
d	1/11
e	0

2.2. Procedure

Premix solutions were prepared by dissolving MBAM, AM and HEA in deionized water. Since the moderator (HEA) was in fact a kind of monomer, the total concentration of HEA and AM was kept constant at 14 wt.% while the ratio of HEA to AM varied. The concentration of the crosslinker, MBAM was kept at 0.6 wt.%. The concentrations of initiator and catalyst are referred to reference [10]. Six premix solutions with decreasing HEA concentration, M_1, a, b, c, d, e, were prepared, as summarized in Table 1. Al_2O_3 powder was dispersed into the premix solutions at a solid loading of 50 vol.%. In order to obtain a low viscosity, 1 wt.% of ammonium citrate of the ceramic powder was added into the suspensions as dispersant. The suspensions were subjected to ball milling for 24 h and then poured into a mould to form ceramic green bodies. The moulds are listed in Table 2. The green bodies were dried for 48 h at the room temperature and then put into an oven at 80 °C until constant weight was obtained. The dried green bodies were debindered for 40–50 h by heating slowly from the room temperature to 600 °C and then sintered in a furnace at 1560 °C for 2 h.

2.3. Testing methods

Viscosity of suspensions was measured using a viscometer (MCR-300 mode, Physica Corporation, Germany). The images of the cracks in the ceramic green bodies were taken at a short focal distance ratio with a digit camera. Test bars with dimensions of 6.5 mm × 5.5 mm × 42 mm were prepared for evaluation of the flexural strength and elastic modulus of the dry green bodies using three-point bending tests on a testing machine (Dujin 2000A, Japan).

In order to simulate the asynchronous solidification of ceramic suspensions, an organic glass mould was made.

Table 2
The moulds used to form green bodies

Number	Name	Dimensions
1	Simulation mould	Shown in Fig. 1
2	A glass beaker of 150 ml	Φ5.6 cm
3	A plastics beaker of 1000 ml	Φ11.3 cm
4	An annular stainless steel mould	External: Φ12.0 cm Inner: Φ5.3 cm
5	A spherical nylon mould	Φ7.0 cm