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Gelcasting of alumina using urea–formaldehyde
III. Machinable green bodies by copolymerisation with acrylic acid

K. Prabhakaran, C. Pavithran *, M. Brahmakumar, S. Ananthakumar

Regional Research Laboratory (CSIR), Thiruvananthapuram- 695 019, India

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Abstract

The present work is an attempt to improve the gel strength, green body strength and green machinability characteristics of gelcast alumina bodies by co-polymerisation of urea-formaldehyde (UF) with acrylic acid. Methylol urea and acrylic acid in the pre-mix solution undergo simultaneous polymerisation at 80°C. The polyacrylic acid stabilises the UF condensation products through hydrogen bonding and prevent precipitation, resulting in a transparent gel. The gel when heated at 110°C forms a tough polymer which gives a peak at 1738 cm^{-1} in the infrared spectrum indicative of crosslinking of the methylol urea condensation products and polyacrylic acid through ester linkage. The alumina slurries prepared in the premix solution, gels within 10–15 min at 80°C. The green strength of the gelcast bodies increases with acrylic content. A binder composition containing $>50\%$ acrylic acid shows diametrical compressive strength >7 MPa. The green bodies show excellent machinability and are subjected to lathing, milling and drilling using conventional tools and equipments. The green bodies during machining show chip resistance and machined body has good surface finish. A near steady state binder removal profile is achieved by heating the samples under both dynamic and isothermal conditions. The debinderised bodies on sintering gave up to 97% theoretical density. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Suspensions (aqueous); D. Al_2O_3; Gelcasting

1. Introduction

Gelcasting is a new near-net-shape ceramic forming process in which a highly concentrated slurry of ceramic powder is set in a mould by in situ polymerisation of monomers present in the system [1–4]. In our previous publications, development of a new gelcasting process for alumina in acidic aqueous medium using urea formaldehyde (UF) was presented [5,6]. The method is simple, inexpensive and provides advantages over conventional acrylic systems, in such a way that the binder removal is possible under isothermal conditions below 350°C. Also, the degradation products of UF are low molecular species such as H_2O, NH_3, CO_2 and CH_2O which would evolve through the narrow pores present in the green body without disrupting the powder compacts [6]. Nevertheless, the gelled body was not strong enough to be removed from the mould without partial drying and the green bodies showed poor mechanical strength and brittle fracture, which are deleterious to green machining, possibly due to low molecular weight and extensive cross-linking of UF polymer. It has been reported that the average molecular weight of a cross linked UF polymer was approximately 400 corresponding to 5–6 monomer (methylol urea) units [7]. The molecular weight of UF in the gelcast green bodies is expected to be lower than 400 since the alumina particulates may prevent the molecular weight build up.

Green machining of a ceramic is a cost effective technique since the method does not require special hard tools as for the machining of sintered ceramics. The machinability of a green body depends on various factors such as green strength and chip resistance. Although, high green strength is a desirable factor, extremely high green strength causes brittleness which makes the conventional drilling, milling and lathing very difficult. Conventionally, plasticisers are added to reduce the brittle nature and improve the machinability characteristics of green ceramics [8–10]. It has been reported that the machinability characteristics such as chip resistance of gelcast green bodies prepared using acrylamide

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* Corresponding author.

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monomers, were improved with increase in length of the cross-linking agent [11].

Acrylic acid undergoes free radical polymerisation in acidic aqueous alumina slurry medium and produces strong gels and green bodies by promoting both particle to polymer and polymer to polymer interaction through the carboxyl groups [12]. The co-polymerisation of UF with acrylic acid would decrease the brittle nature and increase the strength and machinability characteristics of green bodies without loss of thermal advantages of urea formaldehyde. The present work reports the gelcasting of alumina using urea formaldehyde-acrylic acid co-monomers. In this, the green strength of the gelcast bodies are studied with respect to binder composition and the results are presented along with the machinability characteristics, binder removal and sintering.

2. Experimental

Alumina powder used in this study was A16SG (ACC-Alcoa Ltd, India) with average particle size 0.34 μm and surface area (BET) 10.4 m^2/gm. Other chemicals used were reagent grade urea and formaldehyde solution (37%), aluminium nitrate (AR, CDH, India), hexamethylene tetramine (Fluka, Switzerland), Acrylic acid (Fluka, Switzerland) and ammonium persulphate (S.D fine chemicals, India).

The alumina powder was treated with hydrolysed aluminium (HA) using the procedure reported in our previous publication [5]. The HA treatment involved tumbling of 80 wt.% Al_2O_3 slurry in aqueous medium with 2.5 mg aluminium nitrate per m^2 alumina surface and stoichiometric amount of HMTA for a period of 12 h and centrifugal separation and washing of the particles with distilled water after 36 h. The powder was dried in an air oven below 80°C to a moisture content not less than 1%. The methylol urea solution was prepared as reported elsewhere [6]. Accordingly, urea (1 mol) was mixed with formaldehyde (4 mol) solution adjusted to pH 8.5 using NaOH solution and aged for 24 h before use.

The gelcasting pre-mix solution was prepared by mixing methylol urea solution, acrylic acid and ammonium persulphate with the required amount of water. The amount of acrylic acid used was such that the final binder composition contains 25–75% of acrylic acid and the ammonium persulphate used was ~0.3% by weight of acrylic acid. The HA treated alumina powder was dispersed mechanically in the pre-mix solution which is pre-cooled below 10°C in an ice bath [12]. The resulting slurry was supplemented with additional urea before casting to make the urea to formaldehyde mol ratio 1:2 and degassed in a round bottom flask having a stopcock with a nozzle at the bottom. The slurry after degassing was cast in a glass or aluminium mould through the bottom nozzle and allowed to gel by heating in an air oven at 80°C. The gelled body removed from the mould was dried at 70% relative humidity at room temperature to moisture content less than 5%, and subsequently in an air oven at 110°C.

The green strength of the gelcast body was measured by diametrical compression test using cylindrical specimens ($d=10$ mm, $h=4$ mm) in an Instron (model 1195) employing a loading rate of 0.5 mm/min [8]. The machinability studies of the gelcast body were performed using conventional tools and equipments. The body was lathed to form recessed steps, drilled to form a hole and milled to form slots. The swarf obtained from the machining process was analysed under an optical microscope.

Binder burn out profiles of the gelcast sample in air atmosphere, under dynamic and isothermal conditions were obtained by standard thermogravimetric analysis (Dupont Thermal Analyst 2000). Debinderisation of the gelcast green bodies were performed by employing a heating rate of 1°C /min with 1 h hold at 150, 170, 190, 300, 330 and 550°C. The debinderised body was sintered at 1550°C for 2 h. A typical sintering schedule involves heating the body up to 900°C at 5°C/min and then at 10°C/min up to the sintering temperature.

3. Results and discussion

It has been reported that the acrylic acid increases the viscosity of aqueous alumina slurry at ambient temperature due to its cationically initiated oligomerisation and the reaction could be retarded by keeping the slurry in an ice bath during mixing and degassing [12]. Fig. 1 shows the viscosity of a typical alumina slip (55 vol.%) containing 6 wt.% binder in which 50% acrylic–50% UF composition is present at a temperature of ~8°C. The slurry shows the initial viscosity value well below 1 Pa.s suitable for casting. The slurry viscosity increases after casting in a mould and becomes a gel within 15–30 min at ambient temperature (~30°C). However, the gel strength is low as in the pure UF system. When the slurry cast in a mould is heated in an oven from 60 to 80°C undergoes gelation within 15 min and the gelled body is strong enough to withstand the stresses developed during mould removal. The gelled body showed a linear shrinkage of ~1.5% during drying.

Previous studies have shown that the optimum properties of green bodies with respect to density are obtained at binder content 6% by weight of alumina. Therefore, in the present study gelcast green bodies containing 6 wt.% binder are prepared. It was already seen that, the gelcast green bodies containing 6 wt.% of pure UF and acrylic acid binders, showed the strength values of 0.35 and 11.5 MPa respectively [6,12]. The strength measurement data were carried out by changing the UF and acrylic composition and the results are presented in Fig. 2. The diametrical compressive strength increases from 0.35 to 2.5 MPa, when the acrylic content in the binder increases to 25%. When the acrylic content is further increased from 25 to 75%, the strength value rapidly increase to 10.6 MPa. The gelcast green bodies of binder composition containing > 50% acrylic acid shows a reasonable green strength, higher than 7 MPa, for green machining [8].

The chemistry of the pre-mix solution was investigated in order to understand the gelation process. When urea is added to a methylol urea–acrylic acid pre-mix solution with pH 3 and kept at room temperature, it forms a white gel within 30 min. But when the pre-mix solution is warmed at 80°C after the addition of urea, a transparent gel is formed which disintegrates when stirred with excess water due to the separation of white UF condensation products. The IR spectrum of the gel as well as the white precipitate did not show any peak indicative of covalent linkage between acrylic acid and UF. At ambient temperature, the acid catalysed polymerisation of the methylol urea and urea occurs at a faster rate than that of the acrylic monomers, resulting in a white gel with the UF polymer dispersed in a cold water soluble acrylic acid monomer–oligomer mixture. At elevated temperatures, at which the free-radical initiated polymerisation of acrylic acid become operative, the methylol ureas and acrylic acid polymerise simultaneously. As the polymerisation proceeds, the UF oligomers with free amino and hydroxyl groups are likely to be stabilised from precipitation through hydrogen bonding with carboxylic acid groups of the acrylic polymer, resulting in an intimate mix of the polymer chains (Fig. 3). The relatively high gel strength obtained for the co-monomer system with respect to a pure UF system is attributed to this cross-linking through hydrogen bonding. However, the polymeric gel after heating at 110°C in an air oven showed a peak at 1738 cm^{-1} in the IR spectrum (Fig. 4) indicating the presence of ester linkage. It was proposed that the methylol urea derivatives and their condensation products cross-link the polyacrylic acid chain through ester linkage (Fig. 5). The physical properties of the copolymers support this view that the 75% acrylic acid –25%

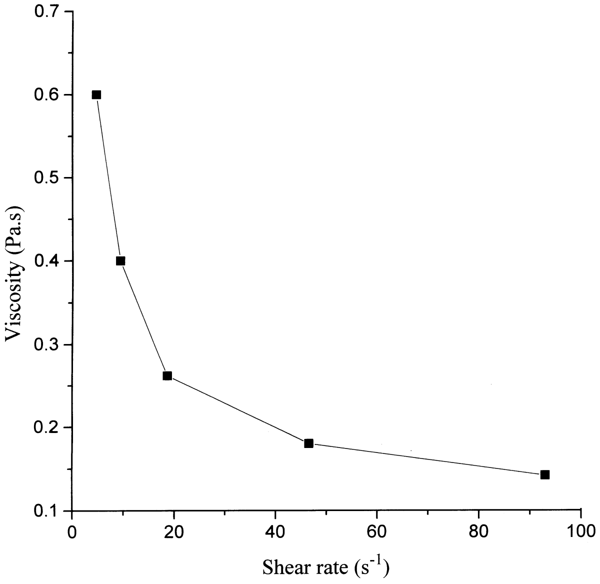


Fig. 1. Viscosity versus shear rate of a typical gelcasting slip. (55 vol.% alumina, monomers 6 wt.% of alumina, 50% UF–50% acrylic composition).

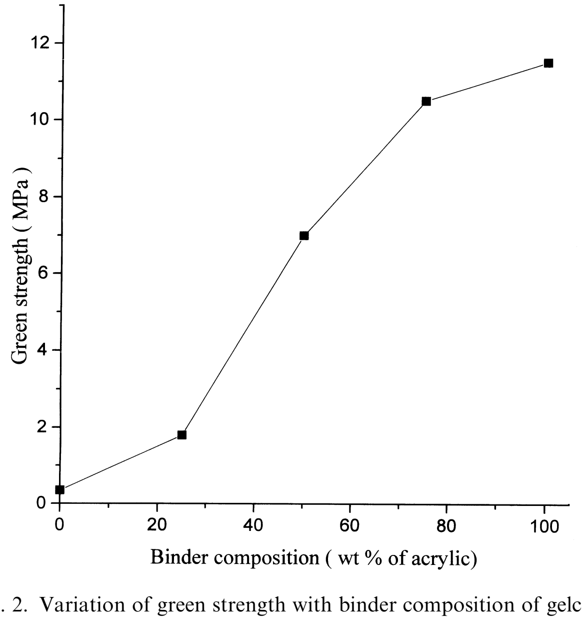


Fig. 2. Variation of green strength with binder composition of gelcast alumina bodies (total binder, UF + acrylic, 6 wt.% of alumina).

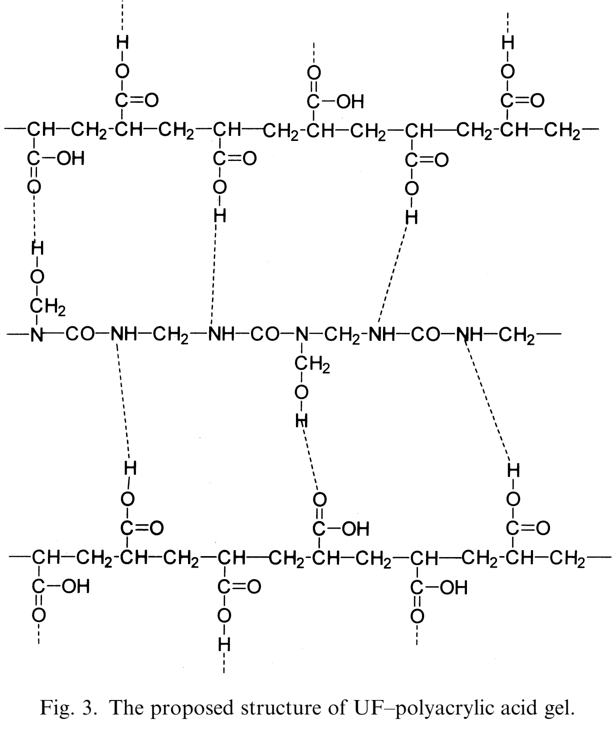


Fig. 3. The proposed structure of UF–polyacrylic acid gel.

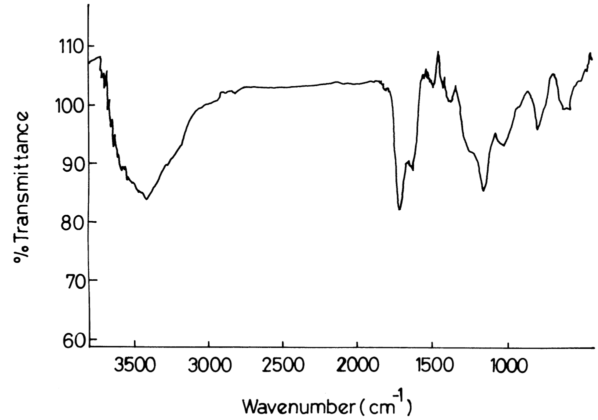


Fig. 4. IR spectrum of UF–acrylic acid copolymer obtained by heating the gel at 110°C.

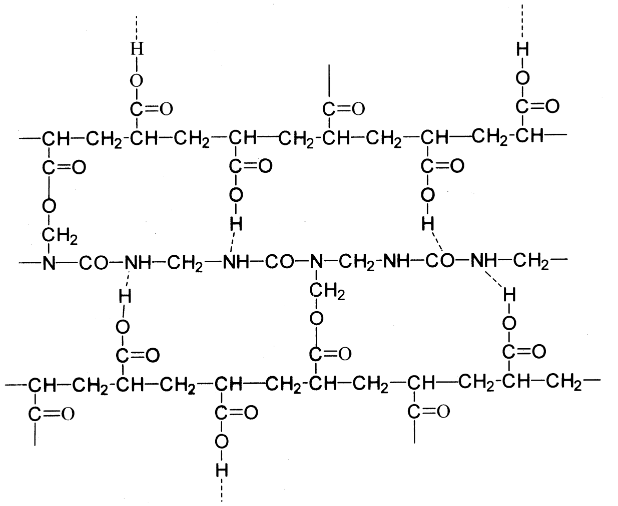


Fig. 5. The proposed structure of UF–acrylic acid copolymer obtained by heating the gel at 110°C.

UF copolymer is tough and no swelling was detected after aging in cold water for 24 h whereas polyacrylic acid was observed to be sticky and hygroscopic. However, 25% acrylic acid –75% UF and 50% acrylic acid –50% UF copolymers are glassy.

The use of low molecular weight species, which are removed at low temperature, is a common practice in binder formulations for injection moulding process. The degradation products of polymeric binder produced at elevated temperatures diffuse through the interconnected pores created by the removal of these low molecular weight species [13]. The UF in the gelcast green bodies serves this purpose since it decompose at ~200°C under isothermal condition into low molecular weight species such as NH_3, CO_2, H_2O and CH_2O [6]. The TGA patterns of gelcast samples are given in Fig. 6. In the case of 75% UF–25% acrylic and 50% UF–50% acrylic binder compositions ~50% of the binder is removed below 250°C.

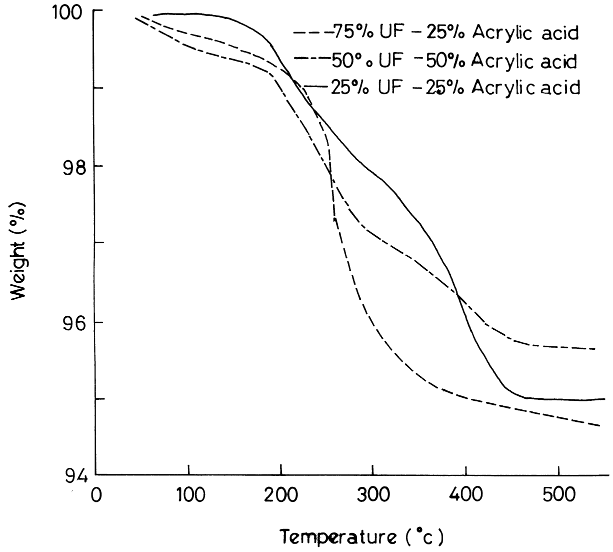
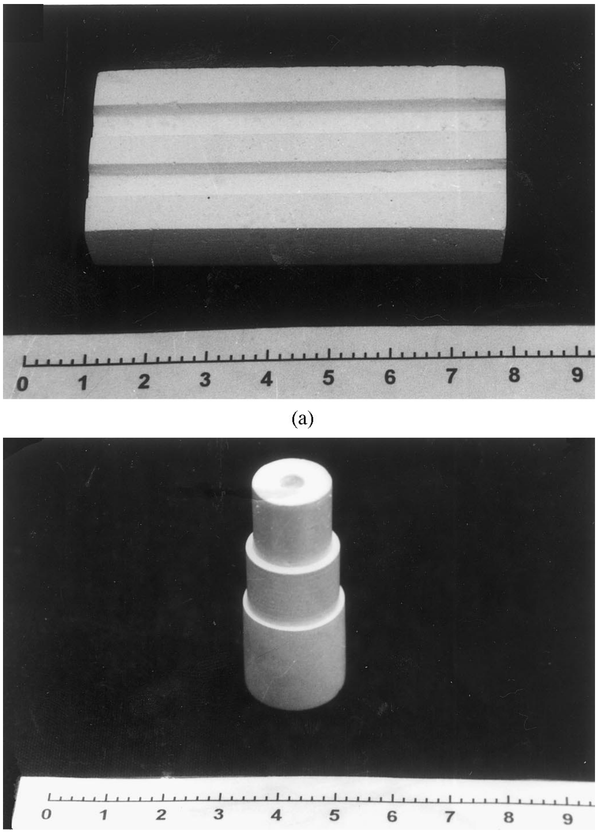


Fig. 6. TGA patterns of gelcast samples.



(a)

(b)

Fig. 7. Photograph of green machined gelcast bodies (50% UF–50% acrylic composition): (a) showing slots by milling, (b) showing recessed steps by lathing and a hole by drilling.

The machinability studies of green bodies were carried out with a view to arrive at binder formulation with a minimum amount of acrylic content for preparation of machinable green bodies since a higher amount of UF

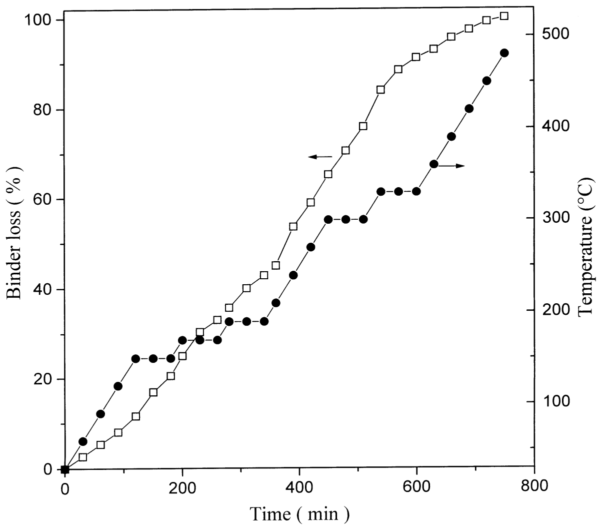


Fig. 8. The binder burnout profile of the gelcast sample (binder composition 50% acrylic–50% UF).

in the gelcast body provides thermal advantages. Binder formulation containing acrylic content 50% or above has mechanical strength sufficient for green machining. Fig. 7 a and b show the photographs of green machined bodies prepared from 50% UF–50% acrylic binder composition showing slots by milling, recessed steps by lathing and a centre cavity by drilling. The machining swarf has powder like morphology and the green machined bodies show good surface finish indicating better chip resistance [9]. This is attributed to the crosslinking of polyacrylic acid chains by long UF condensation products [11].

A near steady state binder removal rate was attained for samples gelcast using 50% acrylic–50% UF binder composition by employing both isothermal and dynamic conditions. Fig. 8 shows the binder burnout profile of gelcast samples obtained from conventional thermogravimetric analysis. The rate of binder removal is below 0.2% min up to the removal of 45% of the total binder and the maximum rate of binder removal observed was 0.28% min. The debinderised green bodies were sintered to ~ 97% of theoretical density at 1550°C as in UF system.

4. Conclusions

Strong and machinable alumina green bodies are prepared by gelcasting using methylol urea and acrylic acid co-monomers. The methylol urea condensation products crosslink the polyacrylic acid chain through ester linkage. The binder composition with 50% UF–50% acrylic acid shows good machinability characteristics without loss of thermal advantages of UF. The green bodies were lathed to form recessed steps, milled to form slots and drilled to form a hole. The green bodies showed chip resistance and the green machined body exhibited good surface finish. A near steady state binder removal profile from the gelcast sample with 50% UF–50% acrylic acid binder composition is obtained employing both dynamic and isothermal conditions. The debinderised bodies sinter to ~97% theoretical density.

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