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Gelcasting of alumina and zirconia using chitosan gels

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Abstract

A new gelcasting system has been analysed. The gel forming system is based on a solution of 1% chitosan in diluted acetic acid and reaction with glutaraldehyde. An Al_2O_3 powder-loading rate of 50 vol.% was achieved under optimised conditions. Advantages of this new system include the use of a biopolymer (chitosan), possibility of air drying of green parts, possibility of gelcasting at ambient temperature, and versatility of the process by changing process parameters leading to well specified reaction times. The effect of process parameters on reaction time, slurry properties, and green part properties are presented. Slurries prepared from ZrO_2 powders were not fluid. However, dense green parts could still be obtained by transferring these slurries to a mould and drying. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: D. Al_2O_3; D. ZrO_2; Gelcasting; Chitosan; Gel; Ceramic; Preconsolidation

1. Introduction

Gelcasting is a preconsolidation process with promising features and significant advantages over other processes such as slip casting and dry pressing. Some of these advantages are near-net shape capability, complex shape capability, simplicity, and versatility in the controlling the process output by various parameters. The challenge in this process lies in achieving a high solids loading (> 50 vol.%) in the gelcasting slip and not using toxic ingredients in the slip formulation. Various approaches have been used to obtain a stable slurry and a homogeneous green product, while keeping the solids content high. The original study in this domain involves polymerisation of acrylamide monomers [1]. The neurotoxic effect of acrylamide is a major disadvantage for industrial applications. Many alternative systems have been developed since then. These processes can be categorized as cross-linking of polymers by metal ion complexation [2,3], thermoreversible gelation of slips containing biopolymers such as agarose [4] and carrageenans [5], and temperature activated cross-linking of polymers [6]. Both oxide [2,3] and non-oxide [5,7] systems were studied for gelcasting. The present work attempts to optimise process parameters in a new chitosan based gelcasting system with ceramic oxide powders (Al_2O_3 and ZrO_2). Results of detailed investigation of the process parameters including polymer concentration, cross-linking agent concentration, ceramic powder content, pH, and temperature on gelation time are presented. A discussion of optimisation of these parameters and resulting green part properties are also given.

2. Experimental

2.1. Slurry preparation and gelation

Baikowsky-Baikalox CR1 α-Al_2O_3 powders were used as the ceramic ingredient. Powder properties stated by the supplier are as follows: surface area < 4 m^2/g and sedigraph median particle diameter $d_{50} = 1.1$ μm. ZrO_2 powders had a particle diameter of $d_{50} = 1.0$ μm (Magnesium Elektron, Sc 15 m-ZrO_2). Low molecular weight chitosan flake (Fluka, $M_r \sim 150{,}000$) was used to prepare chitosan solutions in acetic acid. Although it is harder to dissolve chitosan flakes in acetic acid compared to chitosan in the powder form, stirring the flakes in 0.5–1% (v/v) acetic acid solutions overnight provided

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full dissolution. Glutaraldehyde used for gelation of chitosan solutions was a 25% (w/w) aqueous solution (Aldrich). In order to find the lower limits of both glutaraldehyde and chitosan concentration, a series of gelation studies were performed. The gelation time was measured by flipping 12 mm diameter and 100 mm long glass tubes with 5 ml solution until gelation occurred. Gelation is completed when the product within the tube does not move at all when upside down [8]. The effect of pH, temperature, and solid particles content on gelation was also studied by similar experiments.

The ceramic powder content in the slurry was increased by trying various approaches while maintaining the flow behaviour at a level allowing pouring and easy filling of the mould. A measure of the flow properties was the possibility to wet ceramic powders by the liquid and the maximum solids content that could be added to the slurry until no mixing is possible. The best approach involved adding the ceramic powders initially to acetic acid solution only. This was followed by adding the chitosan solution, which has a higher viscosity than the acetic acid solution, and more ceramic powders. A mixing tip of glass was used that was periodically cleaned to prevent adherence of powders onto it. A maximum solids content of 50 vol.% was achieved with this approach.

2.2. Casting, drying, and evaluation of dried parts

Before adding glutaraldehyde, the stabilised slurry was de-aired in vacuum for 2 min. After mixing the required amount of glutaraldehyde, the slurry was poured into polyethylene moulds. Air-drying for 3–12 h without the use of a controlled humidity chamber was applied. Dimensions of the preconsolidated parts were measured with a Mitutoyo LSM 9506 laser scan meter. Percentage of theoretical densities of these parts were then found by comparing the calculated density (= mass/volume) to the theoretical density of the ceramic (taken as 3.98 g/cc for Al_2O_3 and 5.31 g/cc for ZrO_2).

2.3. Evaluation of the slurry

Viscosities of chitosan solution and well-dispersed slurries were measured by a rotary viscometer (Viscometers UK). A spindle with 3.5 mm diameter was fully immersed in the solution contained within a 12 mm diameter glass tube and readings were taken at a rotational speed of 3–60 rpm. The shear rates were calculated from the shear rate-rotational speed equation for a concentric cylinder viscometer [9]. pH measurement was performed with a Phillips pH meter using standard procedures.

2.4. FTIR analysis

FTIR analysis was used for an optimised gel and gelled ceramic slurry. The optimised gel was prepared by crosslinking 1.0 ml chitosan solution (1% w/v) in 1% v/v acetic acid with 2 vol.% glutaraldehyde (25% w/w). The gelled slurry consisted of 1% (w/v) chitosan solution in 1% (v/v) acetic acid containing small amounts of alumina such as 0.1 or 1.0% by volume and 2% by volume glutaraldehyde. A Mattson Satellite 5000 FTIR spectrophotometer was used. The samples were analysed in KBr pellets.

3. Results and discussion

3.1. Gelcasting with Al_2O_3 powders

Cross-linking of chitosan with glutaraldehyde takes place through a reaction between the amine groups (–NH_2) on the chitosan chain and the carbonyl groups (–C=O) of glutaraldehyde. The imine (–C=N–) bonds formed link chitosan chains to each other leading to gelation at sufficiently high chitosan and glutaraldehyde concentrations at a given temperature. The parameters that influence the rate of gelation in the chitosan-acetic acid-glutaraldehyde system are concentration of chitosan, concentration of glutaraldehyde, concentration of acetic acid, and temperature. The ceramic powder content of the gelcasting system also affects the rate of gelation. The relationship of gelation time with temperature, concentration of acetic acid, concentration of chitosan and concentration of glutaraldehyde is shown in Figs. 1–4, respectively. In accordance with previous publications about the chitosan-glutaraldehyde system, the rate of gelation increases with chitosan or glutaraldehyde concentration and with increasing temperature [10,11]. The temperature increases the rate of gelation considerably. For a solution of 1% (w/v) chitosan-1% (v/v) acetic acid-2% (v/v) glutaraldehyde (note that the glutaraldehyde solution is a 25% w/w aqueous solution in all of the experiments), time to gelation is 120 min at a temperature of 17 °C while it decreases to about 3 min at 55 °C [Fig. 1(a)]. A similar trend is observed for a solution of 1% (w/v) chitosan-1% (v/v) acetic acid-4% (v/v) glutaraldehyde [Fig. 1(b)]. Even if the solution is not heated intentionally, changes of a few degrees in ambient temperature can have a significant effect on the gelation time. Increasing acetic acid concentration decreases the rate of gelation resulting in longer gelation times. 0.5 and 1% acetic acid concentrations in a 1% (w/v) chitosan-2% (v/v) glutaraldehyde solution at 17 °C yield gelation times ranging from 1 to 120 min, respectively (Fig. 2). Increasing acetic acid concentration causes a decrease in the fraction of unprotonated, free amine groups needed for gelation, leading to longer gelation times. Another set of experiments indicated that the time to gelation increases from 3 to 133 min when the concentration of chitosan in 1% (v/v) acetic acid solution is reduced from 1 to 0.4% (w/v) at a constant

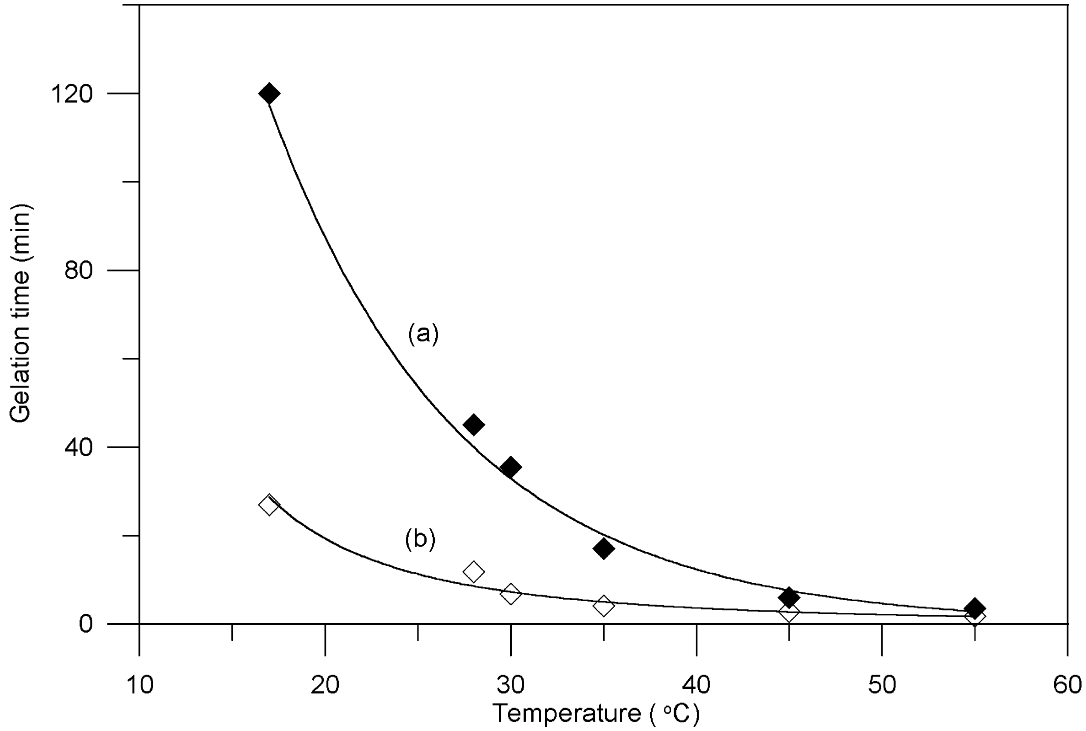

Fig. 1. Effect of temperature on time to gelation in a solution of (a) 1% (w/v) chitosan-1% (v/v) acetic acid-2% (v/v) glutaraldehyde and (b) 1% (w/v) chitosan-1% (v/v) acetic acid-4% (v/v) glutaraldehyde.

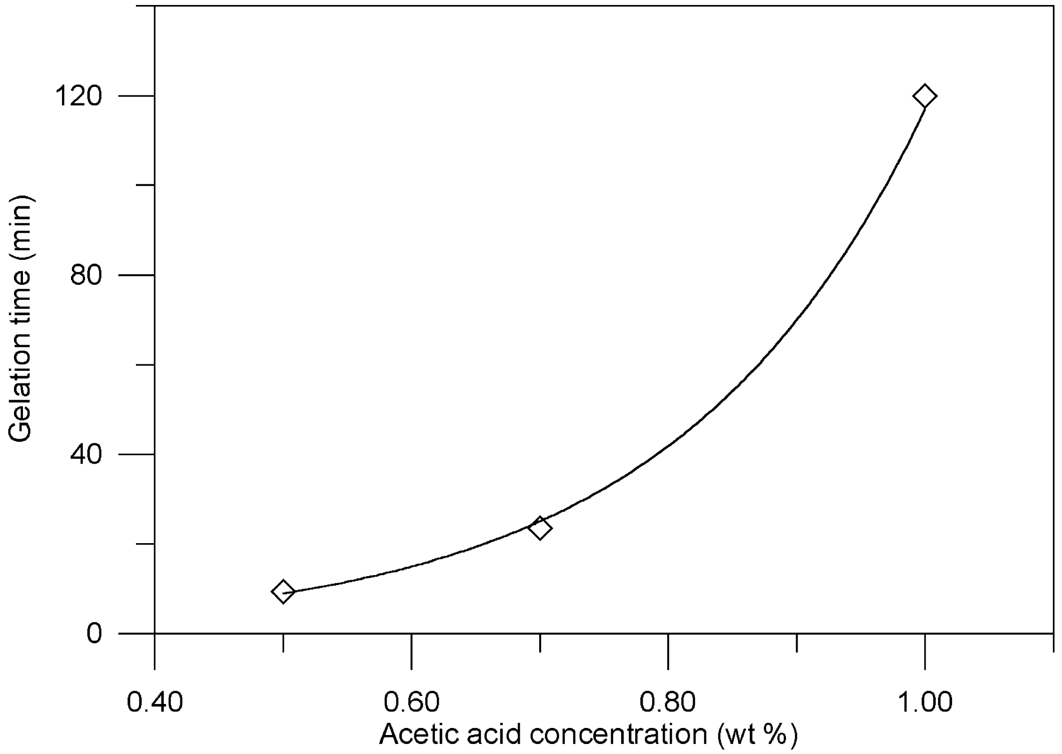

Fig. 2. Effect of acetic acid concentration on time to gelation in a solution of 1% (w/v) chitosan-2% (v/v) glutaraldehyde at 17 °C.

glutaraldehyde concentration of 10% by volume (Fig. 3). Time to gelation decreases with increasing glutaraldehyde concentration. For the system of 1% chitosan in 1% (v/v) acetic acid at 17 °C, time to gelation decreased from 120 to 7 min when glutaraldehyde concentration was increased from 2 to 9% by volume (Fig. 4). The time to gelation in the presence of 20 vol.% alumina powder was observed to be 98 min for

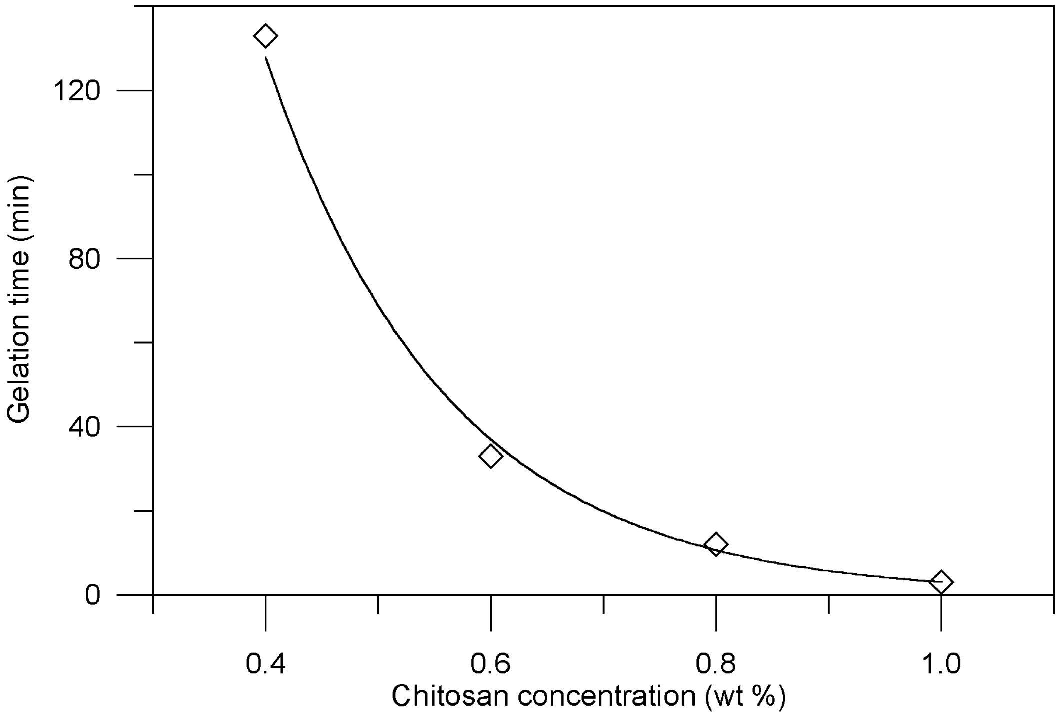

Fig. 3. Effect of chitosan concentration on time to gelation in a solution of 1% (v/v) acetic acid-10% (v/v) glutaraldehyde at 19 °C.

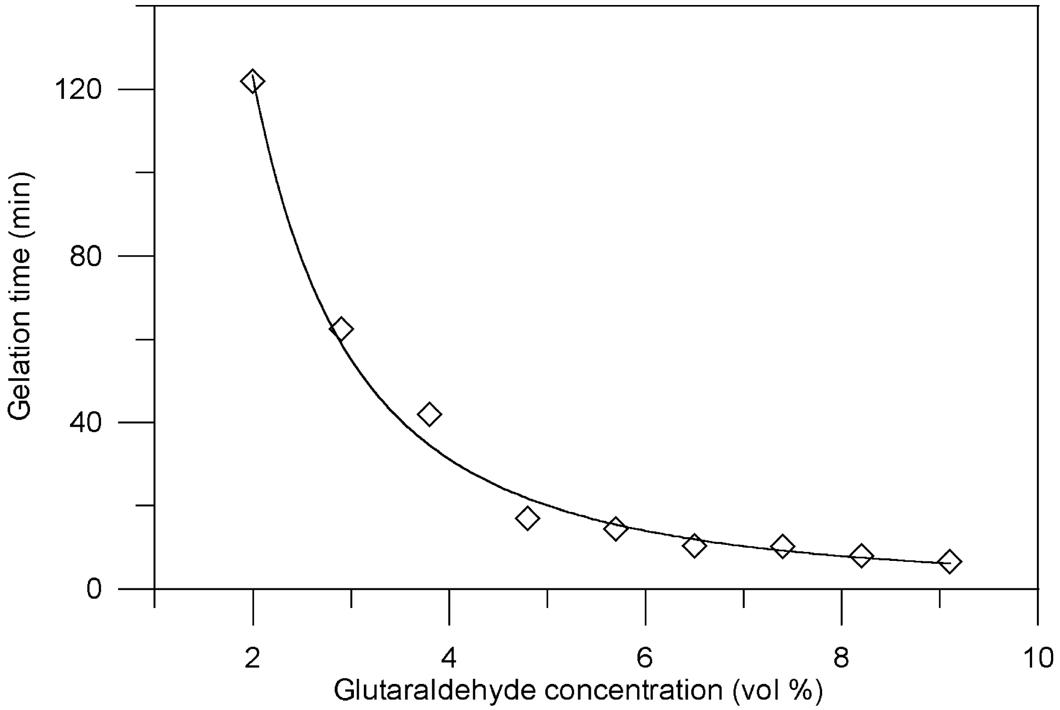

Fig. 4. Effect of glutaraldehyde concentration on time to gelation in a solution of 1% (v/v) acetic acid-1% (w/v) chitosan at 17 °C.

0.5% (w/v) chitosan and 2% (v/v) glutaraldehyde in 1% (v/v) acetic acid solution at 25 °C. It was found that the presence of 50 vol.% alumina decreases the time to gelation from 98 min to approximately 2 min as shown in Fig. 5. Gelation could not be observed for a ceramic powder content less than 20 vol.% with the same chitosan/acetic acid/glutaraldehyde system at the same temperature. A similar trend to the one seen in Fig. 5

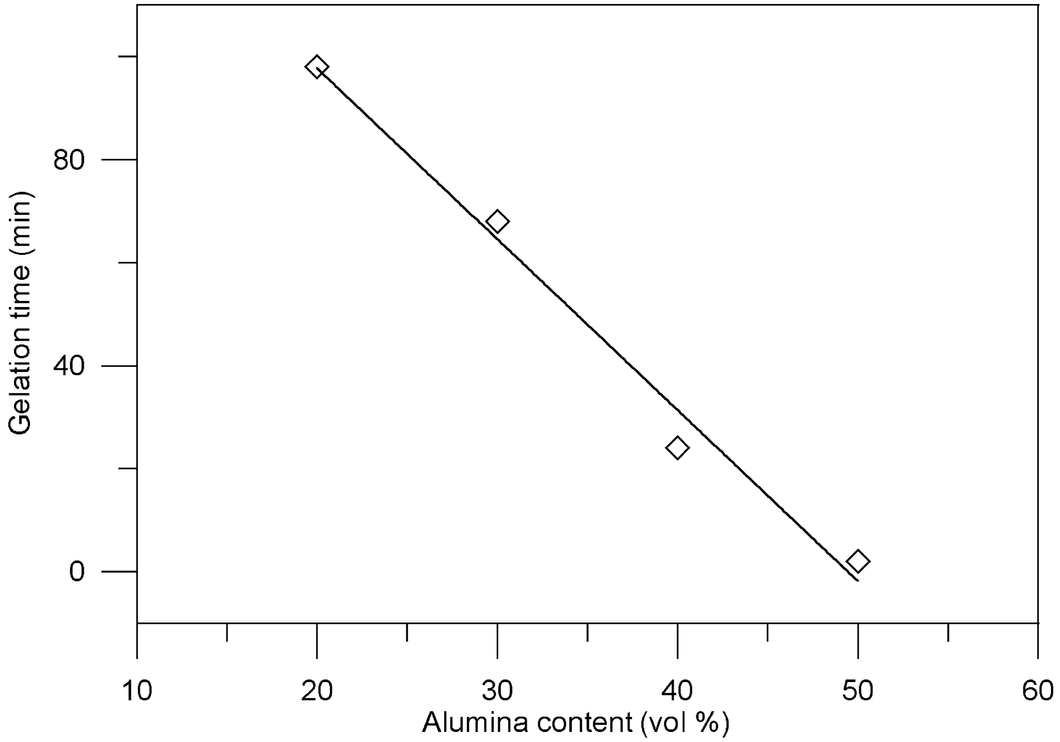

Fig. 5. Effect of Al_2O_3 powder content on time to gelation in a solution of 1% (v/v) acetic acid-1% (w/v) chitosan-2% (v/v) glutaraldehyde at 25 °C.

was observed in a colloidal organic system [12] suggesting that this phenomenon is common for solid particles dispersed in a solution that forms a gel.

3.1.1. FTIR analysis

The addition of ceramic powders to chitosan solutions decreased the gelation time immensely. FTIR analysis was used to understand if there is a change in the bond structure of the gel. A comparison of the gel with and without ceramic powders yields no identifiable difference. Fig. 6(a) belongs to chitosan used in this study. Fig. 6(b) is the spectrum of the gel obtained by crosslinking 1% chitosan solution with 2% glutaraldehyde at 25 °C. The two spectra are similar to each other exhibiting characteristic chitosan peaks such as amide I stretching at 1658 cm^{-1} and etheric stretchings of the pyranose ring at 1155, 1111, 1065 and 1030 cm^{-1}. The amine absorption band that appears around 1600 cm^{-1} in highly deacetylated chitosan is not observed in the spectrum of the gel. Instead, two new bands appear at 1569 and 1507 cm^{-1} that are clear evidences for crosslinked structure through the formation of imine linkages. In the spectra of samples with 0.1 and 1% alumina content, spectral features similar to those of chitosan gel are observed [Fig. 6(c) and (d)]. Thus, the acceleration of gelation can be attributed to a physical cause such as decreased polymer chain mobility as a result of increased viscosity of the solution on addition of ceramic powder. The fact that systems with chitosan concentration of 0.5% w/v, glutaraldehyde content of 2 vol.% and with alumina content less than 20 vol.% did not form gels indicates that there is a critical composition below which gelation does not occur. Increased number of nucleation sites upon addition of ceramic powders to the gelling system could be an additional factor leading to faster gelation.

3.1.2. Optimisation of the gelcasting process

An industrially feasible slip for gelcasting should have the following features:

1. zero or very low content of toxic substances,
2. a high solids content (preferably > 50 vol%),
3. a low polymer content,
4. a slip viscosity allowing easy transfer to the mold, and
5. a homogeneous slip.

The amount of glutaraldehyde used in this system should be minimised since glutaraldehyde is designated as a very toxic and corrosive substance [13]. It is also desirable to minimise the concentration of chitosan since it would be less costly to use a lower concentration of chitosan for the same ceramic body formulation and also because large polymer concentrations can cause internal defects during pyrolysis due to evolution of gaseous species [14]. Based on the information gathered for gelation (Figs. 1–5) the chitosan concentration was selected as 0.5% (w/v). A low pH value is desired for stabilisation of the ceramic slurry [15]. However, lowering the pH by increasing the acetic acid concentration

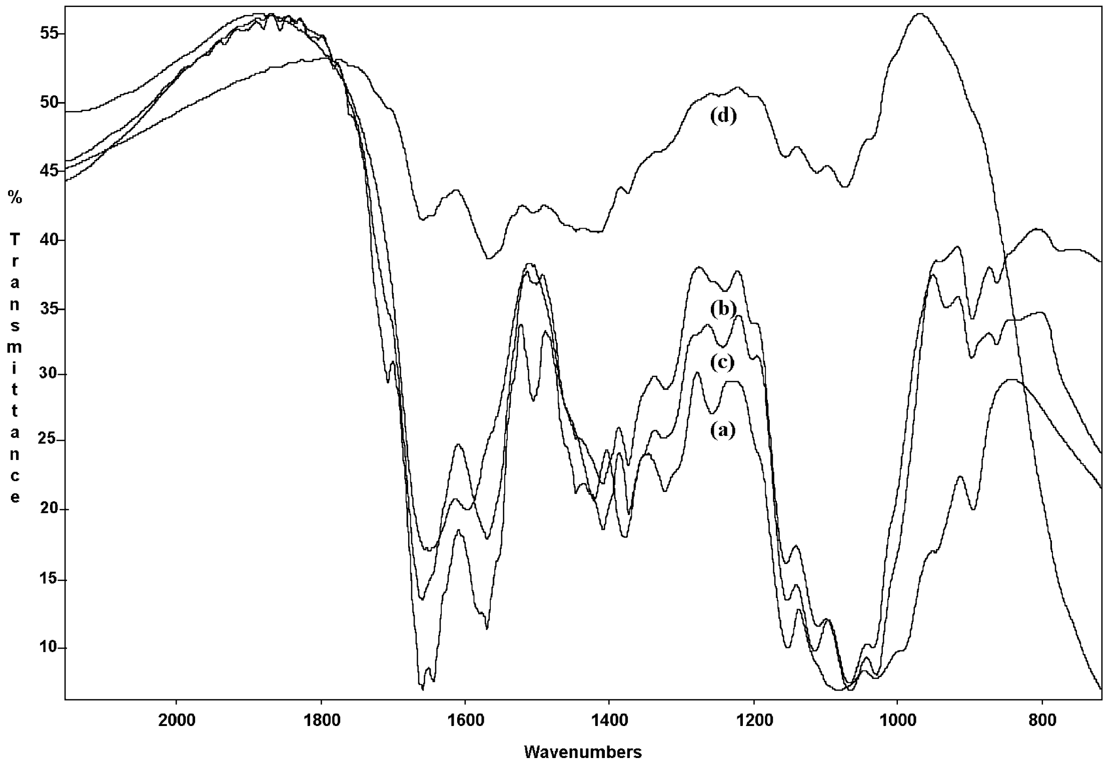

Fig. 6. FTIR spectra of (a) chitosan (b) chitosan gel obtained from 1% w/v chitosan-1% acetic acid-2% (v/v) glutaraldehyde (c) gel from the slurry composed of 1% (v/v) acetic acid-1% (w/v) chitosan-0.1% (v/v) Al_2O_3 powder and (d) gel from the slurry composed of 1% (v/v) acetic acid-1% (w/v) chitosan-1% (v/v) Al_2O_3 powder.

increases the time to gelation (Fig. 2). Hence, 1% acetic acid was chosen as the most suitable solvent. The pH values were 2.8 for 1% acetic acid, 4.2 for 1% chitosan in 1% acetic acid, and 3.8 for 0.5% chitosan in 1% acetic acid (optimised solution). The low pH value of 1% acetic acid solution alone makes it a better dispersing medium for the powders.

After stabilisation of the maximum amount of ceramic powders possible in this medium, 1% (w/v) chitosan solution of equal amount was added to yield 0.5 wt.% chitosan on average. For small-scale applications, it is possible to add about a quarter of the final solids content initially at once and mix the slurry by hand. The rest of the powders should be added gradually while mixed initially by hand and subsequently by a mechanical mixer, in order to prevent agglomeration and obtain a homogenous slip. The green densities were calculated as 47–49% of theoretical density.

The slurry containing 50 vol ceramic powders acts as a thixotropic (shear-thinning) solution, where the viscosity decreases with increasing shear rate (Fig. 7). The shear-thinning effect is reversible for stabilised slurries, i.e. when the shearing action stops, the viscosity increases to its original value. Furthermore, the slurry viscosity increases significantly in a few hours when stored without any interference. Therefore, casting should be done immediately after obtaining the fully dispersed slip.

Various mould geometries were used to demonstrate the versatility of the process. The resulting pre-consolidated parts are shown in Fig. 8. Note that the lines on the part surfaces are not cracks but marks from mating borders between the mould halves. Intricate surface detail was copied from some poly(ethylene terephthalate) moulds but some cracking occurred in these experiments due to internal stresses developing during rapid drying in air. The dimensions of the air-dried parts ranged from 12 to 27 mm in diameter and 4 to 10 mm in thickness. It was observed that after 1 h following gelcasting, it is possible to remove the part from the mould without damaging it and machine it to the desired shape. Fig. 9 demonstrates the ease in machining by cutting the partly dried green part with a sharp knife. Machining becomes harder and the probability of damaging the part is higher due to the lower plasticity once the part is fully dried. A significant advantage of the present gelcasting system over previously studied ones is the ease with drying. Controlled humidity chambers and long drying times are required with other systems [1,16]. In gelcasting with chitosan solutions, air drying can be used without damaging the parts and drying is achieved within a few hours; the time being dependent on the part dimensions. For example, a 4 mm thick and 12 mm diameter cylindrical (pill-sized) part was fully dried in air within 3 h. For a larger sample (6 mm thick and 20

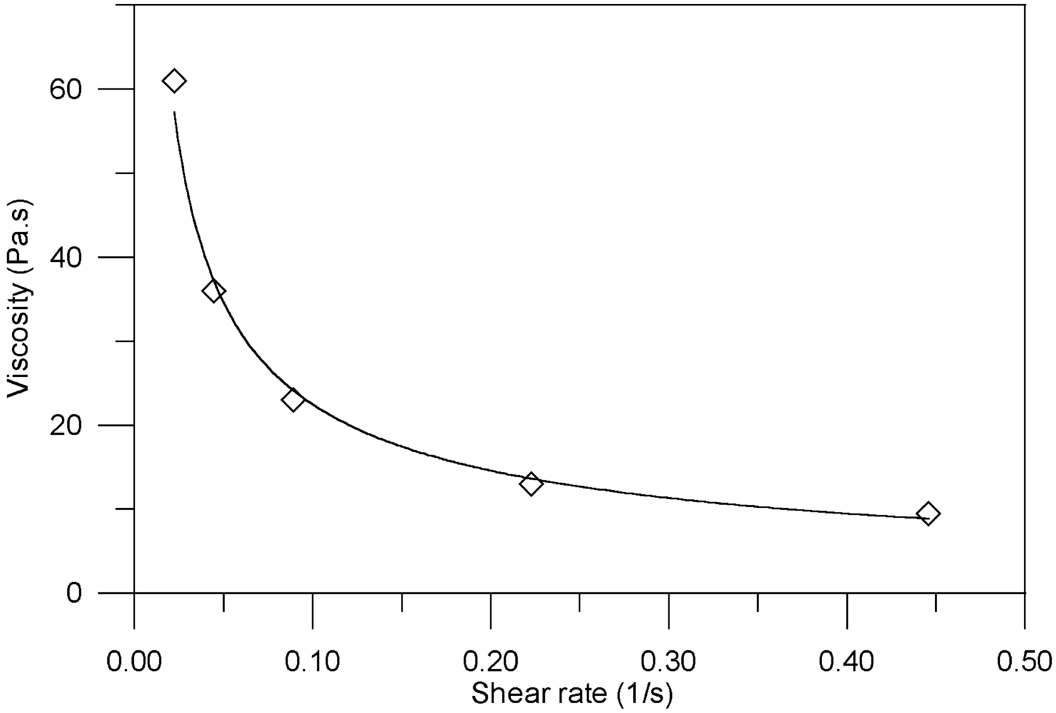

Fig. 7. Flow behaviour of optimised slurry composed of 1% (v/v) acetic acid-1% (w/v) chitosan-50 vol.% Al_2O_3 powder.

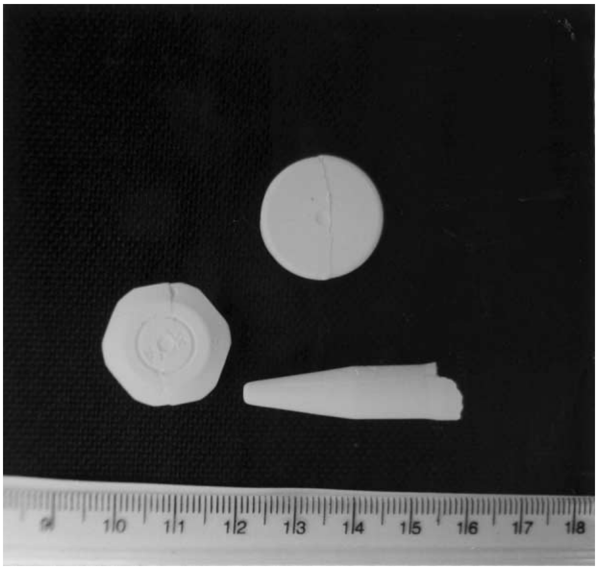

Fig. 8. Gelcast and air-dried preconsolidated Al_2O_3 part geometries.

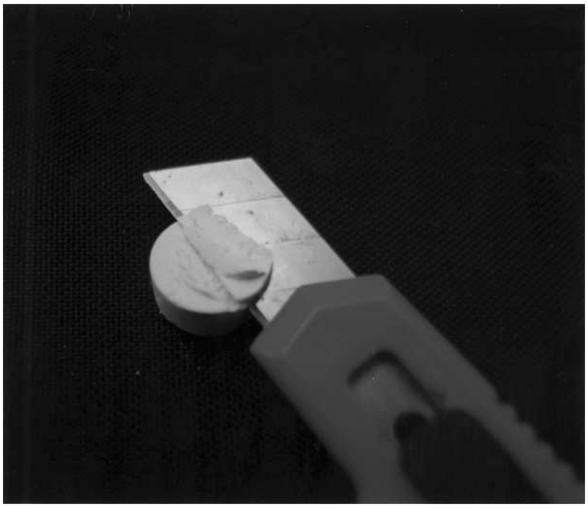

Fig. 9. Easy cutting after partial drying of gelcast ZrO_2 body demonstrating ease in machining operations on green parts.

mm in diameter), the drying time was approximately 8 h. While systems employing other biopolymers such as agar, alginate, gelatine, or carrageenans require heating for gelation [5,6], gelation is obtained at ambient temperature in the present system. Another advantage is the higher Al_2O_3 powder content achieved in the aqueous slip compared to similar gelcasting systems (50 vol.% compared to 40–45 vol.%) [2,5,17]. The powder content in the slurry is important because it corresponds approximately to the green density of the dried part, which in turn affects the ease in sintering.

Although glutaraldehyde may lead to restrictions in industrial practices due to its toxicity and corrosiveness, it is not a neurotoxin and potential human carcinogen, which is the case for acrylamide [18]. A more significant difference between the acrylamide polymerisation process [1] and the current study is that the amount of toxic substances involved is much less for chitosan gels (14 wt.% acrylamide compared to 0.7 wt.% glutaraldehyde in the slurry).

3.2. Gelcasting with ZrO_2 powders

The optimised gelcasting procedures developed for Al_2O_3 powders were also applied to ZrO_2 powders. Although the particle sizes were similar, processing with ZrO_2 powders was more difficult. The resulting slurry had an appearance and consistency similar to shaving foam. Thus, transfer to moulds required manual feeding in our experiments. Alternatively, injection or extrusion can be used for industrial scale applications.

Surface pores were observed on the dried parts unlike the smooth surface of Al_2O_3 parts. While cylindrical parts were crack-free, cracking occurred during drying of irregular shaped (conical) parts. However, the resulting green density (62% of theoretical density) obtained in simple shapes is encouraging. Further study such as use surfactants in the slip system and deairing before casting and/or controlled drying may be worthwhile in order to improve the slip and part properties, respectively.

4. Conclusions

A simple gelcasting process was developed for Al_2O_3 and ZrO_2 using chitosan-acetic acid solutions containing 48–50 vol.% ceramic powders, de-airing, addition of glutaraldehyde, casting into suitable moulds, and cross-linking at ambient temperature. Intricate surface detail and a smooth finish can be achieved with Al_2O_3 parts. Irregular shapes with high green densities could be obtained with Al_2O_3 parts without observable cracking, whereas only simple shaped ZrO_2 parts could be obtained without cracks induced during drying. The differences can be attributed to the better flow properties of Al_2O_3 slips, resulting in a homogeneous casting and better filling of the mould.

The following advantages of gelcasting with Al_2O_3-chitosan-acetic acid-glutaraldehyde systems compared to other gelcasting systems are noted:

- air drying in short times instead of long drying procedures requiring controlled humidity chambers,
- versatility of the gelation process by controlling parameters such as time; temperature; acetic acid, chitosan concentration, and glutaraldehyde concentration,
- gelation at ambient temperature instead of heat-induced gelation,
- a higher solids content compared to similar gelcasting systems,
- use of a biopolymer (chitosan) which is environmentally benign, instead of synthetic mono/polymers.

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