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L-Ascorbic acid as a new activator in fabrication of ceramics by techniques using *in situ* polymerization

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Abstract

The paper reports the development of a new system applicable in shaping techniques using *in situ* polymerization. The system is based on saccharides derivatives and allows to eliminate harmful processing agents from ceramic slurry. Instead of commonly applied 2-hydroxyethyl acrylate or acrylamide (monomers) and N,N,N′,N′-tetramethylethylenediamine (activator) the compounds based on glucose were used. As a monomer 3-O-acryloyl-D-glucose was applied. As a new activator L-ascorbic acid (also known as vitamin C) was used. Research was carried out for YSZ. As initiators ammonium persulfate and hydrogen peroxide were used. The new system was studied in terms of zeta potential, pH and rheological measurements. Ceramic samples were prepared by gelcasting and gel-tape casting methods. The experiments showed that L-ascorbic acid used as the activator has positive influence on rheological properties of suspensions with YSZ and together with ammonium persulfate allows to form defect free ceramic bodies with a homogenous composition.

Keywords: Ascorbic acid; *In situ* polymerization; Saccharides; ZrO_2; Gel-tape casting

1. Introduction

Shaping of ceramics puts today's science and technology high requirements, above all the ability to produce ceramic components with complex geometries, short moulding time, minimized final machining with the use of expensive tools and the application of environmentally friendly processing agents. Nowadays, among a variety of the shaping techniques the leading role is played by methods based on colloidal processes, such as slip casting,[1] tape casting[2] or direct coagulation casting.[3,4] These methods can provide good mechanical properties, homogeneous microstructure and simplify the manufacturing process. The main challenge in colloidal shaping is to develop a homogeneous and time stable ceramic suspension with low viscosity and high concentration of solid phase.[5,6] For this purpose it is necessary to use a variety of organic and inorganic compounds, such as dispersing agents, binders, plasticizers, foaming agents.

There are various colloidal shaping methods which use the *in situ* polymerization through which a macromolecular network is created, to hold the ceramic particles together. As examples of these techniques gelcasting,[7,8] gel-tape casting,[9] gel-electrophoresis[10] and methods linking gelcasting with aeration for fabrication of porous ceramics[11] can be mentioned. Another interesting field of using the *in situ* polymerization are UV-shaping techniques.[12] They allow to form elements of complicated shapes by selective curing of suspensions of ceramic particles in a UV-curable medium of organic monomers and photoinitiators.[13,14] All these methods require effectively working processing agents like dispersants, organic monomers, activators and initiators of polymerization, which can ensure advantageous microstructure, good mechanical properties of green and sintered bodies. The processing agents used in ceramic technology and therefore in techniques using *in situ* polymerization should be low toxic and follow the recent 'green chemistry' trend. The less toxic and the less harmful for the environment they are, the more attractive they are to apply.

One of the first water-soluble monomer used in gelcasting was acrylamide. It ensures good mechanical properties

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of samples in a green state, nevertheless it is classified as strong neurotoxin and probably carcinogenic substance.[15] Secondly, it contains a nitrogen atom in a molecule, thus during binder decomposition nitrogen oxides are released into the atmosphere what makes it harmful for the environment. Later on researchers began to use substances which do not contain the nitrogen atom in the molecule such as 2-hydroxyethyl acrylate, acrylic acid, *etc.*[16] Nevertheless, organic monomers are not the only harmful substances used in gelcasting. Important role in the whole process is played also by initiator and activator of polymerization. The most important initiating system is N,N,N′,N′-tetramethylethylenediamine (TEMED)-ammonium persulfate (APS). N,N,N′,N′-tetramethylethylenediamine is harmful by inhalation and a highly flammable liquid. It causes severe skin burns, eye damage and has irritant smell. For that reason authors have began to examine compounds based on saccharides, which can substitute mentioned above toxic substances in shaping of ceramic powders.[17]

The use of mono- and polysaccharides in the ceramic technology, that is in the synthesis of ceramic powders and shaping techniques, seems to be a new trend but it has been already developed by researchers.[18–22] Mono- and disaccharides, as processing agents, have many advantages in comparison to commercially available acrylic monomers. They are non-toxic, water-soluble, inexpensive and renewable substances. Saccharides have many hydroxyl groups in a molecule; thereby the cross-linked polymeric network can be created by forming hydrogen bonds between polymeric chains. As a result the use of external cross-linking agent (*e.g.* N,N′-methylenebisacrylamide or poly(ethylene glycol) diacrylate) is not necessary as in the case of acrylamide or 2-hydroxyethyl acrylate, thus the amount of organic additives needed in the suspension is reduced and the whole process becomes less expensive.[23]

The application of L-ascorbic acid as a new activator in techniques using *in situ* polymerization opens a possibility to eliminate all harmful substances from the ceramic slurries. Ascorbic acid (one of its form is commonly known as vitamin C) is a naturally occurring compound, which can be found in single-cell organisms, plants and animals, where it is produced from glucose. It dissolves well in water and is not harmful for humans and environment. Moreover, due to its mild acidic properties, it can positively influence the stability of ceramic suspensions, while the addition of N,N,N′,N′-tetramethylethylenediamine, which is an alkaline amine, leads to the coagulation of some ceramic slurries.

Kitagawa and Tokiwa[24] described the application of ascorbic acid as an activator in polymerization of pure vinyl sugar esters. They used hydrogen peroxide as an initiator and analyzed the structures of synthesized polymers. The application of hydrogen peroxide as an initiator in radical polymerization derives from Fenton's reagent (H_2O_2–Fe^{2+}), but Fenton's system is hardly useful in ceramic technology due to the presence of iron. Ascorbic acid has been already used as an activator in the field of polymer chemistry[25] whereas the application of ascorbic acid in ceramic technology has not been studied before.

The paper reports the results of the application of the new system based on glucose derivatives in gelcasting and gel-tape casting of yttrium stabilized zirconia. The role of monomer is played by 3-O-acryoyl-D-glucose (described by authors elsewhere[17,26]), as activator L-ascorbic acid was used. Two types of initiator have been examined: ammonium persulfate and hydrogen peroxide. The main aims of the research was to elaborate the mechanism of the reaction between L-ascorbic acid and initiator of polymerization and investigate the influence of L-ascorbic acid on the properties of ceramic suspensions in comparison to N,N,N′,N′-tetramethylethylenediamine.

2. Materials and methods

The main powder used in the research was YSZ (Tosoh Corporation), α-alumina (Tamei Chemicals) was used only in experiments with hydrogen peroxide, as described below. Two organic monomers have been examined: commercially available 2-hydroxyethyl acrylate and synthesized by authors 3-O-acryloyl-D-glucose. As activators of polymerization L-ascorbic acid and commonly applied N,N,N′,N′-tetramethylethylenediamine were used. Ammonium persulfate in the form of 10% aq. solution was used as the initiator of polymerization and diammonium hydrocitrate as the dispersant. The characteristics of materials used in research are given in Table 1.

Ceramic suspensions were prepared in Milli-Q water. In the first step the dispersant diammonium hydrocitrate was added to water followed by monomer and activator. Zirconia powder was then added and the slurries were mixed in zirconia containers in a planetary ball mill PM100 (Retsch) for 90 min at a speed of 300 rpm. Six zirconia balls of diameter 10 mm were used. The viscosities of slurries as a function of shear rate were then measured using Physica rheometer. The shear rate was raised from 1 to 1000 s^{-1} and then back to 1 s^{-1}. The pH of ceramic slurries was measured on Methrom AG pH-metre with a special electrode for viscous liquids LL-Viscotrode. In the next step, the initiator was added and the slurry was ball-milled for additional 5 min. Then the viscosities as a function of time were measured using Brookfield DV+II- Pro rheometer. Measurements were carried out until a 95% torque. The ceramic slurries with the initiator were casted into identical PVC moulds (gelcasting) and on a carrier tape (Silicone Coated Mylar Film) with the use of square frame applicator BYK-Gardner (gel-tape casting). Gelation occurs at room temperature.

The zeta potential of pure powder and the powder mixed with other components of the ceramic slurry were measured using Zetasizer Nano ZS (Malvern Instruments). The concentration of zirconia powder in an electrolyte solution was *ca.* 100 ppm. The concentration of KCl electrolyte was 10^{-3} mol/dm^3. Before the measurements every sample was ultrasonificated for 5 min. The pH of the suspension was adjusted using 0.1 mol/dm^3 HCl or KOH solutions and varied from 3 to 11.

After thick gelled bodies were obtained, the specimens were removed from the moulds and dried for 24 h at 50 °C. Samples have been then sintered at 1500 °C/1 h. The densities of green and sintered specimens were measured by the Archimedes' method in kerosene and water, respectively. The microstructure of green bodies was observed on a scanning electron microscope (Zeiss, Germany).