



Monoacryloyl esters of carbohydrates: Synthesis, polymerization and application in ceramic technology



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ARTICLE INFO

Article history:

Received 7 February 2014

Received in revised form 17 April 2014

Accepted 3 May 2014

Available online 23 May 2014

Keywords:

Monoacryloyl esters

Fructose

In situ polymerization

Gelcasting

Ceramics

ABSTRACT

The article presents the interdisciplinary research among organic synthesis, chemistry of polymers and ceramic technology. It presents the synthesis of monoacryloyl esters of fructose and glucose that is 1-O-acryloyl-D-fructose and 3-O-acryloyl-D-glucose, conditions of their polymerization and application in shaping of advanced ceramic powders by the so called gelcasting method. The paper presents the influence of carbohydrate esters on the viscosity of Al₂O₃ suspensions and microstructure of final ceramic samples. The results showed that synthesized esters of saccharides can play the role of organic monomers able to polymerize in situ and self-cross-linking compounds in gelcasting. The paper presents the proposed structure of polymeric network which is formed from acryloyl ester of glucose during gelcasting process. The paper describes rheological behaviour of slurries composed of synthesized substances and Al₂O₃ powders, wetting angles of alumina substrate by synthesized compounds, differences in glass transition temperatures of polymers and the microstructure of obtained final ceramic samples.

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1. Introduction

Advanced ceramic materials currently represent a wide group of materials (for example: Al₂O₃, ZrO₂, Si₃N₄, BaTiO₃, Ni-Al₂O₃) which are becoming widely used as the materials for electronics, dental implants, cutting tools, abrasive elements of high quality, materials used in nuclear industry and medicine. In order to fabricate the above products, it is necessary to use ceramic powders of suitable properties; nevertheless the important stage of the production is shaping of the material. Colloidal processing plays nowadays the leading role in fabrication of advanced ceramics, mainly because it meets the demands of ceramic industry which is looking for cheap and environmentally friendly technologies. Colloidal suspensions are the basis for many shaping techniques of ceramics such as: slip casting (Suarez et al., 2009; Tallon Galdeano, Limacher, & Franks, 2010), gelcasting (Young, Omatete, Janey, & Menchhofer, 1991), electrophoretic deposition (Sakka, Suzuki, & Uchikoshi, 2008; Uchikoshi, Suzuki, Okuyama, Sakka, & Nicholson, 2004), direct coagulation casting (Graule, Gauckler, & Baader, 1996) or freeze casting (Dash, Li, & Ragauskas, 2012). The main challenge of colloidal methods lies in achieving time-stable, low viscosity suspensions having high solid loading of well dispersed particles

(De Hazan, Heinecke, Weber, & Graule, 2009; Lewis, 2000; Zhang & Binner, 2008). Only such suspensions can lead to achieve homogeneous final ceramic elements of good properties.

One of the willingly applied colloidal processes is gelcasting, which combines conventional shaping from ceramic slips with polymer chemistry (Omatete, Janney, & Nunn, 1997; Santacruz, Nieto, Binner, & Moreno, 2009). Gelcasting allows to obtain high-quality, complex-shaped ceramic elements by means of an in situ polymerization, through which a macromolecular network is created to hold ceramic particles together. There exist some commercially available monomers commonly applied in gelcasting process, such as acrylamide, 2-hydroxyethyl acrylate, acrylic acid, etc. (Ma, Huang, Yang, Le, & Sun, 2006; Ma, Xie, Miao, Huang, & Cheng, 2002) but they present excessive toxicity and must be used together with external cross-linking monomers. Gelcasting process can be performed also with the use of polysaccharides and proteins as gelling agents, which are non-toxic and environmentally friendly. The most often applied gelling agents are agar (Olhero, Tari, Coimbra, & Ferreira, 2000) agarose (Santacruz, Nieto, & Moreno, 2005), cellulose acetate (Mueller, Yu, & Willert-Porada, 2006), chitosan (Bengisu & Yilmaz, 2002), gelatin (Tulliani, Bartuli, Bemporad, Naglieri, & Sebastiani, 2009), etc. Significant disadvantages of applying polysaccharides and proteins in gelcasting are relatively long gelation time or necessity to dissolve the above compounds at the raised temperature (for example 60–70 °C for agaroids as reported by Millan, Nieto, and Moreno (2002). This

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affects considerably on deterioration of the rheological properties of suspensions through water evaporation. What is more, it complicates the process of shaping from a technological point of view.

The interesting alternative for commercial acrylic monomers and polysaccharides could be specially designed and synthesized compounds on the basis of carbohydrates which will be able to polymerize in situ. The obtained polymeric network would be able to hold ceramic particles together. Authors elaborated the synthesis of new compounds on the basis of glucose and fructose named 3-O-acryloyl-D-glucose and 1-O-acryloyl-D-fructose. These compounds should be able to maintain a stable ceramic suspension and polymerize in situ at room temperature. It is worth mentioning that the chemical structure of monosaccharides derivatives, i.e. the location of acryloyl group in a molecule, may have a big influence on the rheological properties of ceramic suspensions and polymerization rate. Mono-, disaccharides as well as carbohydrate polymers have been recently found to lie in area of researchers' interest as processing agents in ceramic technologies (Li & Akinc, 2005; Schilling, Sikora, Tomasik, Li, & Garcia, 2002; Srinivasan, Jayasree, Chennazhi, Nair, & Jayakumar, 2012; Tallon Galdeano & Franks, 2011; Yar, Acar, Yurtsever, & Akinc, 2010).

The paper shows the synthesis of 1-O-acryloyl-D-fructose and 3-O-acryloyl-D-glucose, then the polymerization conditions of above compounds and the proposed structure of nascent polymeric network. Authors discuss also the influence of the synthesized compounds on the properties of alumina slurries and sintered ceramic samples.

2. Experimental procedure

2.1. Materials

The reagents for the organic synthesis have been purchased from the following suppliers: D-fructose (POCh, Poland, >98%), acryloyl chloride (Sigma–Aldrich, 96%), methylene chloride (POCh, Poland, puriss), N,N-dimethylaniline (Merc. for synthesis) MgSO₄ (POCh, Poland, puriss), H₂SO₄ (POCh, Poland, puriss), PbCO₃ (POCh, Poland, puriss), anhydrous acetone (POCh, Poland, puriss), anhydrous ZnCl₂ (POCh, Poland, puriss), 85% phosphoric acid (POCh, Poland, puriss), P₄O₁₀ (POCh, Poland, puriss), 1,2:5,6-di-O-isopropylidene-D-glucofuranose (Biosynth, Switzerland, >95%).

The reagents for the in situ polymerization of synthesized compounds and shaping of alumina by gelcasting are described below. The first used ceramic was α-Al₂O₃ of symbol Nabalox 713-10 (Nabaltec, Germany) of mean particle size $D_{50} = 0.70 \mu\text{m}$, specific surface area 8.0 m²/g measured by BET on ASAP 2020 V3.01H (Micromeritics, USA) and density 3.92 g/cm³ measured by helium pycnometer on AccuPyc II 1340 Pycnometer (Micromeritics, USA). The second alumina powder used in the research was high purity α-Al₂O₃ of symbol TM-DAR (Tamei Chemicals, Japan) of an average particle size 0.21 μm (calculated from BET), density 3.80 g/cm³ and a specific surface area 14.1 m²/g.

Two synthesized esters of carbohydrates and a commercially available 2-hydroxyethyl acrylate, HEA (Fluka, >97%) were tested as monomers in the gelcasting process of alumina powders. Both esters named 3-O-acryloyl-D-glucose (3-acr-G) and 1-O-acryloyl-D-fructose (1-acr-F) were synthesized in a three step synthesis elaborated by authors described in the following paragraph. The chemical structures of synthesized compounds are shown in Fig. 1.

Diammonium hydrocitrate, DAC (POCh, Poland, puriss) and citric acid, CA (Sigma, puriss) were used as dispersing agents in the Al₂O₃ ceramic slurries. N,N,N',N'-tetramethylethylenediamine, TEMED (Fluka, >98%) played the role of activator and ammonium persulfate (Aldrich, ≥98%), used in the form of 1 wt.% aqueous

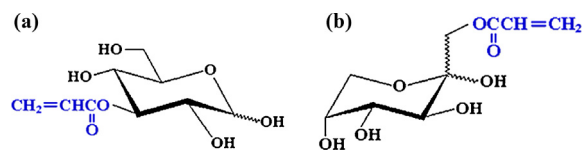


Fig. 1. Chemical structure of synthesized compounds: (a) 3-O-acryloyl-D-glucose, (b) 1-O-acryloyl-D-fructose.

solution, was the initiator of polymerization. Redistilled water was used as a solvent.

2.2. Characterization techniques

Reactions were followed by thin layer chromatography (TLC) on silica gel 60F₂₅₄ (Merck), as eluent heptane-acetone mixture 2:1 was used, for development 1%_{aq} solution of KMnO₄ and 1% alcoholic solution of 12MoO₃·H₃PO₄ × H₂O were used. The ¹HNMR and ¹³CNMR spectra were recorded on Gemini 200, Varian. The solvent residual peaks of D₂O and CDCl₃ were used as internal standards. Infrared spectra were recorded using a Biorad FTIR Spectrometer FTS165 on KBr pellet.

2.3. Synthesis of monoacryloyl esters of carbohydrates

The synthesis route is shown in the example of 1-O-acryloyl-D-fructose (Fig. 2). The aim of the synthesis was to obtain, from D-fructose, an organic monomer in which one of the hydroxyl groups is replaced by acryloyl group which enables free radical polymerization of the molecules. The synthesis of the new monomer was carried out in three stages. In the first stage 2,3:4,5-di-O-isopropylidene-D-fructopyranose (DIPF) was obtained in order to block four from the five free hydroxyl groups in a fructose molecule (Fig. 2a). This stage was performed on the basis of procedure described by Glen, Myers, and Grant (1951).

I stage. D-fructose (27.0 g, 0.150 mol), anhydrous acetone (142.5 g, 2.455 mol), anhydrous ZnCl₂ (36.0 g, 0.264 mol) and polyphosphoric acid (1.5 g, 0.005 mol P₄O₁₀ added to 3.0 g, 0.026 mol 85% phosphoric acid) were placed in the 500 cm³ flask and mixed for 26 h at 25 °C. Then 70 g, 0.875 mol of 50% NaOH_{aq} solution was added. The obtained precipitate was filtered off and the dark brown solution was discoloured by active carbon. Then acetone was evaporated, 50 ml of water was added and extraction by using 20 ml of heptane was carried out 5 times. The obtained extract was dried by MgSO₄. After filtering off MgSO₄, dichloromethane was distilled. Then 200 ml of 0.05 M H₂SO₄ was added and mixed for 8 h. The reaction mixture was extracted by 20 ml portions of dichloromethane, rinsed by saturated solution of NaHCO₃ and dried. After few hours the crystals of the product appeared. Melting point was 93–97 °C.

II stage. In the second stage esterification reaction was carried out to obtain 1-O-acryloyl-2,3:4,5-diisopropylidene-D-fructopyranose (1-Akr-DIPF) (Fig. 2b). DIPF (39.0 g, 0.15 mol), N,N-dimethylaniline (26.0 g, 0.165 mol) and methylene chloride (225 ml, 3.514 mol) were placed in the 500 cm³ two-necked flask equipped with condenser and dropping funnel. Acryloyl chloride (13.9 g, 0.154 mol) was added from dropping funnel during 7 min to the boiling reaction mixture. Then, the mixture was boiled for 20 h, stirred on a magnetic stirrer. The content of the flask was poured into water (750 ml) placed in separating funnel. Lower layer was separated and washed with 450 ml of 3% solution of sulfuric acid and with 750 ml of water. The solution was dried with magnesium sulfate and evaporated. Then 90 ml of hexane was added. After 24 h the precipitate was filtered off and dried on air.

III stage. In the third stage four hydroxyl groups were unlocked by hydrolysis (Fig. 2c). 1-Akr-DIPF (28.0 g, 0.089 mol) and H₂SO₄

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