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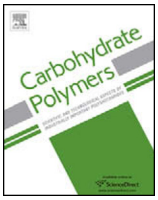

Monoacryloyl esters of carbohydrates: Synthesis, polymerization and application in ceramic technology

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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 Al_2O_3 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 A_2O_3 powders, wetting angles of alumina substrate by synthesized compounds, differences in glass transition temperatures of polymers and the microstructure of obtained final ceramic samples.

1. Introduction

Advanced ceramic materials currently represent a wide group of materials (for example: Al_2O_3, ZrO_2, Si_3N_4, $BaTiO_3$, Ni-Al_2O_3) 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 homogenous 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) $MgSO_4$ (POCh, Poland, puriss), H_2SO_4 (POCh, Poland, puriss), $PbCO_3$ (POCh, Poland, puriss), anhydrous acetone (POCh, Poland, puriss), anhydrous $ZnCl_2$ (POCh, Poland, puriss), 85% phosphoric acid (POCh, Poland, puriss), P_4O_{10} (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-Al_2O_3 of symbol Nabalox 713-10 (Nabaltec, Germany) of mean particle size $D_{50} = 0.70\ \mu m$, specific surface area 8.0 m^2/g measured by BET on ASAP 2020 V3.01H (Micromeritics, USA) and density 3.92 g/cm^3 measured by helium pycnometer on AccuPyc II 1340 Pycnometer (Micromeritics, USA). The second alumina powder used in the research was high purity α-Al_2O_3 of symbol TM-DAR (Tamei Chemicals, Japan) of an average particle size 0.21 μm (calculated from BET), density 3.80 g/cm^3 and a specific surface area 14.1 m^2/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 Al_2O_3 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 solution, was the initiator of polymerization. Redistilled water was used as a solvent.

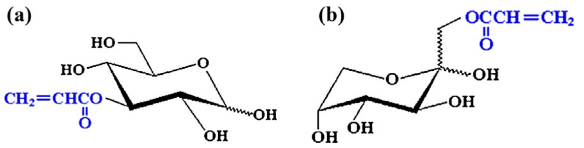

Fig. 1. Chemical structure of synthesized compounds: (a) 3-O-acryloyl-D-glucose, (b) 1-O-acryloyl-D-fructose.

2.2. Characterization techniques

Reactions were followed by thin layer chromatography (TLC) on silica gel $60F_{254}$ (Merck), as eluent heptane-acetone mixture 2:1 was used, for development $1\%_{aq}$ solution of $KMnO_4$ and 1% alcoholic solution of $12MoO_3 \cdot H_3PO_4 \times H_2O$ were used. The ^{1}HNMR and ^{13}CNMR spectra were recorded on Gemini 200, Varian. The solvent residual peaks of D_2O and $CDCl_3$ 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 $ZnCl_2$ (36.0 g, 0.264 mol) and polyphosphoric acid (1.5 g, 0.005 mol P_4O_{10} added to 3.0 g, 0.026 mol 85% phosphoric acid) were placed in the 500 cm^3 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 $MgSO_4$. After filtering off $MgSO_4$, dichloromethane was distilled. Then 200 ml of 0.05 M H_2SO_4 was added and mixed for 8 h. The reaction mixture was extracted by 20 ml portions of dichloromethane, rinsed by saturated solution of $NaHCO_3$ 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 cm^3 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 H_2SO_4

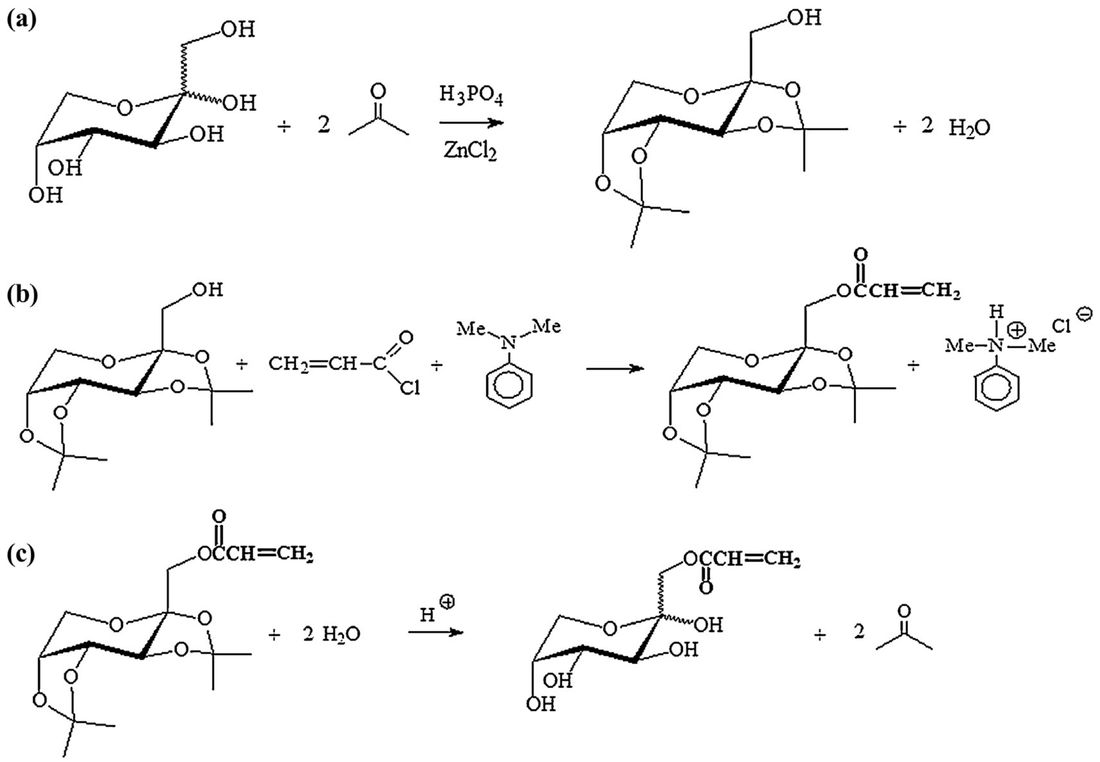

Fig. 2. Synthesis of 1-O-acryloyl-D-fructose: (a) stage I: synthesis of 2,3:4,5-di-O-isopropylidene-D-fructopyranose, (b) stage II: synthesis of 1-O-acryloyl-2,3:4,5-diisopropylidene-D-fructopyranose, (c) stage III: synthesis of 1-O-acryloyl-D-fructose.

(224 ml, 0.02 M) were placed in the flask (equipped with condenser and mechanic stirrer) and heated from room temperature up to 110 °C on the oil bath. Additionally, 0.05 g of phenothiazine was added to prevent polymerization during heating. After 25 min the reaction mixture got clear and colourless. The reaction progress was monitored by thin layer chromatography (TLC). The TLC-plates were developed by the mixture heptane–acetone (2:1). The difference between R_f values for the substrate and the products is relatively large (the disappearance of substrate is easy to observe) and the difference of R_f values for partially hydrolysed product (monoisopropylidene derivative) and the final compound is small, but it is sufficient to determine the moment when the reaction completes. Therefore, on the basis of TLC measurements, after ca. 3 h 30 min the reaction was completed. The mixture was cooled and 2.5 g of lead carbonate was added in one portion in order to neutralize the acidic solution. The mixture was stirred during 5 min, then filtered and concentrated on air.

In case of the synthesis of 3-O-acryloyl-D-glucose, the first stage of the synthesis could be omitted, because 1,2:5,6-di-O-isopropylidene-D-glucofuranose was commercially available. The procedure in the second and the third stage was analogous to the synthesis of fructose ester. 3-O-acryloyl-D-glucose has been obtained in a crystalline form and used in further research as received. 1-O-acryloyl-D-fructose is a resin like substance, therefore was used in the form of a 50% aqueous solution in order to facilitate its dosage. The ^{1}HNMR, ^{13}CNMR and FTIR spectra of 1-O-acryloyl-D-fructose are presented in Figs. 3 and 4.

2.4. Measurements of wetting angle and glass transition temperature

In order to examine the new compounds as monomers (binders) in fabrication of alumina ceramic by using the in situ polymerization, the wetting angle of alumina substrate and the glass transition temperature of polymers obtained from synthesized monoacryloyl derivatives of carbohydrates were measured. For comparison the measurements were also done for 2-hydroxyethyl acrylate, commonly used in ceramic technology. Wetting angle of compounds was measured by applying a drop of monomer on polished alumina substrate and then taking a picture. On the resulting photographs the tangent to the droplet surface at the point of contact between the phases was drawn and the angle was measured. The glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC) on Perkin-Elmer Pyris 1. First, polymeric tapes were obtained from monomers by free radical polymerization. The polymerization was carried out with the use of TEMED and ammonium persulfate as redox initiator. The T_g was marked by reading the temperature at the point of inflection in the curve of heat capacity changes as a function of temperature. The measurements were made in the temperature range from −100 °C to 100 °C at heating rate 20 °C/min. The results of wetting angle and glass transition temperature measurements are presented in Table 1.

Table 1
Values of wetting angle and glass transition temperature of examined compounds.

Monomer	Wetting angle of alumina surface (°)	Glass transition temperature of polymer [°C]
3-O-acryloyl-D-glucose	11	5.5
1-O-acryloyl-D-fructose	20	−19.0
2-Hydroxyethyl acrylate	29	−27.4
Water	46	–

2.5. Preparation of ceramic suspensions and shaping

Alumina aqueous suspensions with investigated monoacryloyl esters of carbohydrates (which played the role of organic monomer able to polymerize in situ) were prepared in redistilled water at room temperature. First, the dispersant used as a mixture of diammonium hydrocitrate and citric acid was dissolved in water

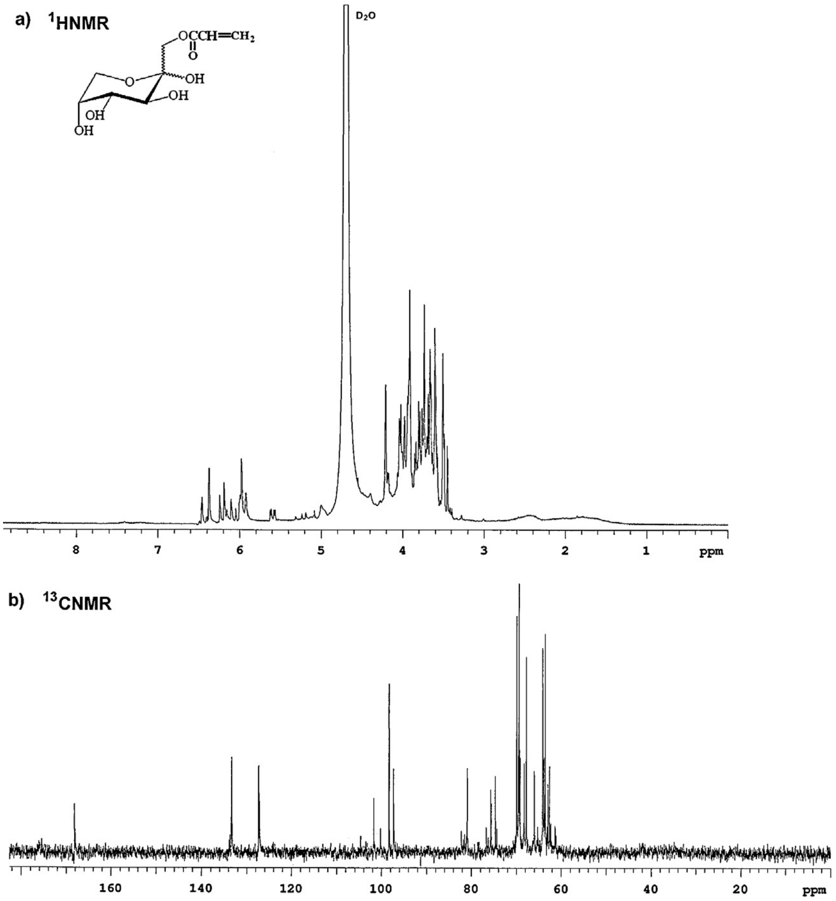

Fig. 3. (a) ^{1}HNMR and (b) ^{13}CNMR spectra of 1-O-acryloyl-D-fructose.

followed by monomer and activator. The composition of prepared ceramic suspensions is given in Table 2. Alumina powder was then added and the suspensions were mixed in an alumina jar in a planetary ball mill PM100 (Retsch) for 90 min with a speed of 300 RPM. Next the slurries were deaerated for 20 min under reduced pressure in a vacuum desiccator supplied with magnetic stirrer. After that the initiator of polymerization was added and the slurry was mixed for additional 5 min. Slurries with applied monomers are able to gelate at room temperature. The mixture was then cast into identical PVC moulds of internal diameter 20 mm and height 5 mm. After a thick gelled bodies were obtained, specimens were unmoulded and dried for 24 h at 50 °C. The sintering process (1600 °C, 1 h for Al_2O_3 Nabalox and 1550 °C, 1 h for Al_2O_3 TM-DAR) of ceramic samples obtained by gelcasting was then conducted in Carbolite furnace

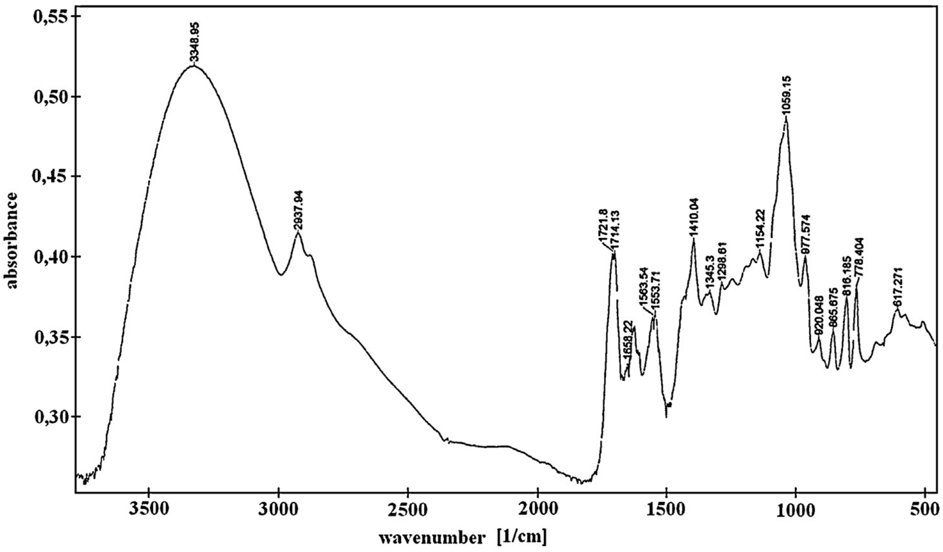

Fig. 4. FTIR spectrum of 1-O-acryloyl-D-fructose.

Table 2
The composition of prepared ceramic suspensions with the use of Al_2O_3 Nabalox, monoacryloyl esters of carbohydrates and 2-hydroxyethyl acrylate.

Monomer	3-O-acr-G	1-O-acr-F	HEA
Concentration of Al_2O_3 [vol%]	55.0	50.0	55.0
Concentration of Al_2O_3 [wt.%]	82.7	79.7	82.7
Monomer content [wt.% wrt Al_2O_3 powder]	3.0	3.0	3.0
Dispersant DAC content [wt.% wrt Al_2O_3 powder]	0.14	0.14	0.14
Dispersant CA content [wt.% wrt Al_2O_3 powder]	0.10	0.10	0.10
Activator TEMED content [wt.% wrt monomer]	1.0	1.0	1.0
Initiator ammonium persulfate [wt.% wrt monomer]	0.4	1.0	0.5

in air. SEM images of ceramic samples in a green state and after sintering were done on Ultra Plus (Zeiss, Germany).

Rheological properties of synthesized esters and 2-hydroxyethyl acrylate (used comparatively) were determined on Kinexus Pro rheometer (Malvern Instruments, UK) in the parallel plate geometry with a gap of 0.5 mm. The shear rate increased from 0.1 to 35 s^{-1}. Parallel plate geometry requires small sample volume (ca. 2 ml). The influence of the synthesized compounds on the viscosity of ceramic suspensions was examined by using Brookfield RVDV + II – Pro Viscometer (Brookfield Engineering Laboratories Inc., USA) in the coaxial cylinders geometry. The shear rate increased from 0.1 to 35 s^{-1} and back to 0.1 s^{-1}. For this measurement a spindle S34 was used. In case of coaxial cylinders sample volume is 20 ml; however measurements of ceramic slurries in parallel plate geometry would cause problems with water evaporation.

3. Results and discussion

3.1. Properties of monoacryloyl esters of carbohydrates

Fig. 1 shows the molecular structure of 3-O-acryloyl-D-glucose and 1-O-acryloyl-D-fructose respectively. The acryloyl group in the molecule of 1-O-acryloyl-D-fructose is substituted at the first carbon in the fructose ring unlike 3-O-acryloyl-D-glucose, where the —OH group at third carbon in the glucose ring has been replaced. This was due to differences in the spatial structure of D-glucose and D-fructose. It means that in case of D-glucose the —OH group at third carbon could not be blocked by isopropylidene groups and therefore underwent esterification reaction, whereas the spatial structure of D-fructose let to leave —OH group at first carbon not blocked. The use of compounds with different spatial structure allowed estimating the impact of different configuration of hydroxyl and acryloyl groups on the properties of colloidal alumina suspensions (such as viscosity of slurries) and ceramic samples, what is the important aspect in ceramic technology.

Fig. 3a presents ^{1}HNMR spectrum of synthesized 1-O-acryloyl-D-frucose: wide multiplet at 3.6 ppm (10H) corresponds to protons of OH and CH bonds, multiplet at 6.2 (1H) corresponds to protons of vinyl group. 1-O-acryloyl-D-fructose was the mixture of α and β anomers. Fig. 3b presents ^{13}C NMR spectrum of synthesized 1-O-acryloyl-D-frucose: 61.9; 65.4; 74.2; 72; 81.9; 97.8 ppm–signals from C atoms of saccharide fragment; 126.5; 133.7 ppm – signals of C atoms of vinyl group; 168.1 ppm – signal of C atom of carbonyl group. Fig. 4 shows FTIR spectrum of 1-O-acryloyl-D-fructose: O—H stretching (wide peak 3349 cm^{-1}), C=O stretching (1722 and 1714 cm^{-1}), C=C (1658 cm^{-1} and 920 cm^{-1}), aliphatic C—H stretching (2938 cm^{-1}), —CH_2— (1410 cm^{-1}), O—H bending (1297 cm^{-1}), C—O (1154 cm^{-1}).

One of the most important points during the synthesis is to receive the pure monomer, with as low as possible oligomer and polymer impurities. The evidence for receiving the expected monomer is that the product (high viscosity liquid) is very well soluble in water, whereas the polymer is completely insoluble. Secondly, ^{1}HNMR spectra of product (measured a couple of days after the synthesis) reveal no signals in region of $\delta = 1/3$ (for the polymer and the oligomers the signals of —CH_2—CH_2— groups should be visible in the mentioned region). Accuracy of those measurements allows us to suppose that the content of oligomers would be less than 5%. Finally, in case of 3-O-acryloyl-D-glucose, authors obtained in last experiments the crystalline monomer in 81% yield. The filtrate still contained the monomer (which is visible in ^{1}HNMR spectrum).

Table 1 lists the values of wetting angle of alumina substrate and glass transition temperature of polymers obtained from examined compounds. The best wettability of ceramic substrate exhibits 3-O-a cryloyl-D-glucose (wetting angle 11°). Very good wettability exhibits also fructose ester (wetting angle 20°). The wetting angle of commercial monomer 2-hydroxyethyl acrylate was 29°. Nevertheless all investigated monomers much better wet alumina than water (wetting angle 46°). A low value of wetting angle can be related to the development of adhesive coating around ceramic grains. This can facilitate the formation of polymeric network which increases the mechanical strength of a ceramic sample. High mechanical strength of ceramic elements in green state is a very important factor in terms of machining and transportation of ceramic samples before sintering process.

The glass transition temperature of all polymers is below room temperature. This means that in conditions of gelcasting process which is carried out at room temperature polymers have elastic properties. These properties are largely responsible for vesting the ceramic products required mechanical strength before the sintering process. The highest T_g value amounting 5.5 °C has polymer obtained from 3-O-acryloyl-D-glucose, the lowest has commercial polyhydroxyethyl acrylate (−27.4 °C). Nevertheless all investigated compounds have beneficial elastic properties for application in shaping of ceramic materials.

3.2. Application of monoacryloyl esters of carbohydrates as organic monomers in gelcasting process

The synthesis of monoacryloyl esters of carbohydrates was initially performed for certain application in ceramic technology. First of all viscosity measurements of ceramic suspensions and fabrication of Al_2O_3 elements by using the in situ polymerization was done. Table 2 presents the composition of prepared ceramic suspensions. One of the advantages of gelcasting process is a possibility to control the time, after which the gelation occurs, by adding a suitable amount of activator and initiator of polymerization. For this reason the quantities of the activator (TEMED) and initiator of polymerization (ammonium persulfate) have been experimentally chosen in order to assure at least 15 min delay time before the slurry starts to polymerize. The amount of activator in ceramic slurries was constant for all suspensions and fixed as 1.0 wt.% based on monomer content. The quantity of initiator was individually matched in order maintain 15 min idle time. For this reason the optimum amount of initiator added to the ceramic slurry with 3-O-acryloyl-D-glucose was about 0.4 wt.%, for 1-O-acryloyl-D-fructose 1.0 wt.% and for commercially available 2-hydroxyethyl acrylate 0.5 wt.%. This indicates that the chemical structure of monoacryloyl derivatives of carbohydrates may have the influence on the polymerization rate and the amount of the initiator needed to start the polymerization.

Fig. 5 presents flow curves and viscosity curves of synthesized esters of carbohydrates and 2-hydroxyethyl acrylate used comparatively. 3-O-acryloyl-D-glucose is a solid, therefore 50% aqueous solution has been prepared in order to examine the rheological properties of this substance. In case of 1-O-acryloyl-D-fructose a fully crystallized product was not obtained, therefore again 50%

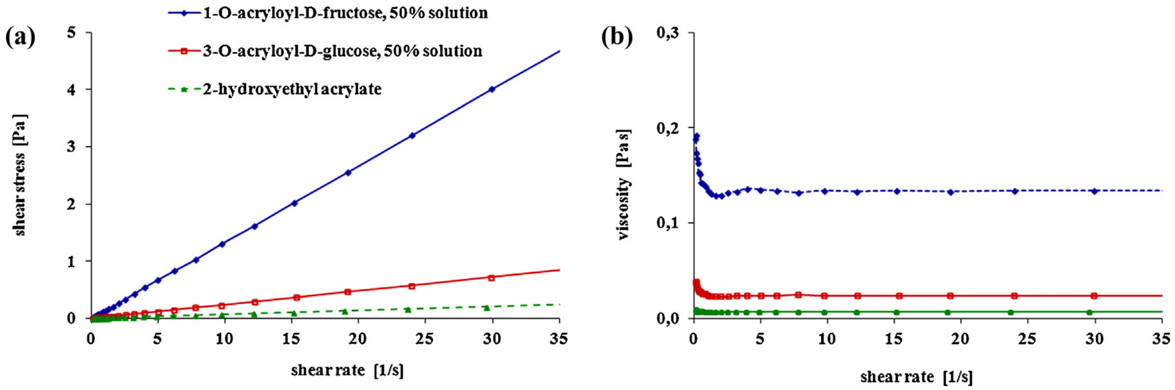

Fig. 5. (a) Flow curves and (b) viscosity curves of synthesized esters of carbohydrates and 2-hydroxyethyl acrylate.

aq solution has been also prepared. On the basis of rheological measurements it can be stated that the lowest viscosity has 2-hydroxyethyl acrylate, it is a Newtonian fluid. Slight shear thinning behaviour is observed for the 1-O-acryloyl-D-fructose. The viscosities of 1-O-acryloyl-D-fructose, 3-O-acryloyl-D-glucose solutions and 2-hydroxyethyl acrylate at shear rate $5.0\,s^{-1}$ were 135 mPas, 24 mPas and 7 mPas, respectively. It means that viscosities of the monomers are very low. In the successive measurements rheological properties of ceramic suspensions composed of alumina powder and examined substances were measured.

Fig. 6 shows flow curves and viscosity curves of ceramic slurries with the synthesized monoacryloyl derivatives of carbohydrates and with the commercially available 2-hydroxyethyl acrylate. The measurements were performed for slurries of 50 vol% (79.7 wt.%) solid loading. The lowest viscosity had slurry with commercial 2-hydroxyethyl acrylate, the apparent viscosity at shear rate $5.0\,s^{-1}$ was 1.13 Pas. Slightly higher viscosity amounting 1.56 Pa s had slurry with 3-acr-G. The highest viscosity 4.03 Pas had suspensions with 1-acr-F, nevertheless it was still low enough to fill precisely casting moulds. All investigated ceramic suspensions are shear thinning fluids.

On the basis of flow curves, yield points (that is stresses at which a solid material begins to flow) of slurries can be determined. The lowest yield point 2.4 Pa was observed for the slurry with 2-hydroxyethyl acrylate, higher yield point 4.1 Pa was noted for slurry with 3-acr-G and the highest stress at which slurry begins to flow was observed for the suspension with 1-acr-F (12.5 Pa). For that reason the maximal solid content which ensures good fluidity of slurries with 1-acr-F was fixed at 50 vol%, while for slurries with two other monomers the solid content could be raised to 55 vol%, as indicated in Table 2.

The differences in viscosities of suspensions can be explained in two ways. Firstly, viscosities of pure monomers may affect viscosities of ceramic slurries. As shown in Figs. 5 and 6 the lowest viscosity has 2-hydroxyethyl acrylate and alumina slurry containing this monomer, the highest viscosity has 1-O-acryloylo-D-glucose and corresponding alumina slurry. The slurry with 2-hydroxyethyl acrylate has the lowest viscosity probably due to the fact that HEA is a liquid, therefore the total amount of liquid phase in suspensions is higher than in case of carbohydrates esters. On the other hand, the differences in viscosities of pure monomers are insignificant, while of slurries are considerable. The second explanation of this phenomenon is that the position and orientation of hydroxyl and acryloyl groups in a molecule have an influence on the viscosity of ceramic slurries. In this case, more favourable chemical structure has 3-acr-G than 1-acr-F. The influence of the conformation and structure of saccharides on the viscosity of nanoalumina suspensions have been discussed by Falkowski, Szafran, and Temeriusz (2008).

Fig. 7 presents the proposed chemical structure of polymer formed from 3-O-acryloyl-D-glucose. There are hydrogen bonds marked with red. The main polymeric chains are formed owing to the presence of double bond between carbons in acryloyl group. The hydrogen bonds are created between glucose units in the main polymeric chain and between neighbouring chains. Hydrogen bonding in the polymer is probably analogous to those in cellulose structure. The similar structure and hydrogen bonding can be formed in the polymeric network of 1-O-acryloyl-D-fructose. Thus the polymers developed from carbohydrate esters are cross-linked owing to the presence of hydrogen bonds unlike commercial acrylic monomers such as presented in the paper 2-hydroxyethyl acrylate. Acrylic monomers in ceramic technology are always used together with the external cross-linking agent, for example N,N′-methylenebisacrylamide or poly(ethylene glycol) diacrylate. The use of external cross-linking agents ensures high mechanical strength of ceramic bodies in green state. The polymers based on monoacryloyl carbohydrates combines advantages of both polysaccharides and acrylic polymers. They are environmentally friendly and opposite to polysaccharides can gel at room temperature. Additionally they do not strongly increase the viscosity of ceramic suspensions and on the contrary to acrylic monomers they do not need the use of external cross-linking agent. As a result both the amount of organic additives needed in the suspension and the amount of gases released to the atmosphere during binder burnout are reduced.

Authors have investigated the influence of three monoacryloyl esters of carbohydrates on the polymerization idle time of alumina powder Nabalox 713-10 and on density and mechanical strength of ceramic samples in a green state (Szafran, Wiecinska, Szudarska, & Mizerski, 2013). The analyzed esters were 3-O-acryloyl-D-glucose, 1-O-acryloyl-D-fructose and 6-O-acryloyl-D-galactose. The results showed that polymerization rate and mechanical strength of ceramic samples is different for each ester. Additionally, synthesized monoacryloyl esters of carbohydrates ensure higher mechanical strength of ceramic green bodies than for example commercially available 2-hydroxyethyl acrylate (Bednarek, Sakka, Szafran, & Mizerski, 2010). This indicates that there is a need to recognize the differences between described in this paper carbohydrate esters (taking into consideration their spatial structure, viscosity, glass transition temperature of polymers, etc.) in order to estimate what type of acryloyl ester would be the most favourable in ceramic technology.

Ceramic samples have been obtained by gelcasting method which is schematically presented in Fig. 8. The basic stage of shaping is the preparation of time-stable ceramic suspension of low viscosity and high concentration of solid phase. In gelcasting process, at the beginning a composition of ceramic powder, dispersant, organic monomer, activator and initiator of polymerization is

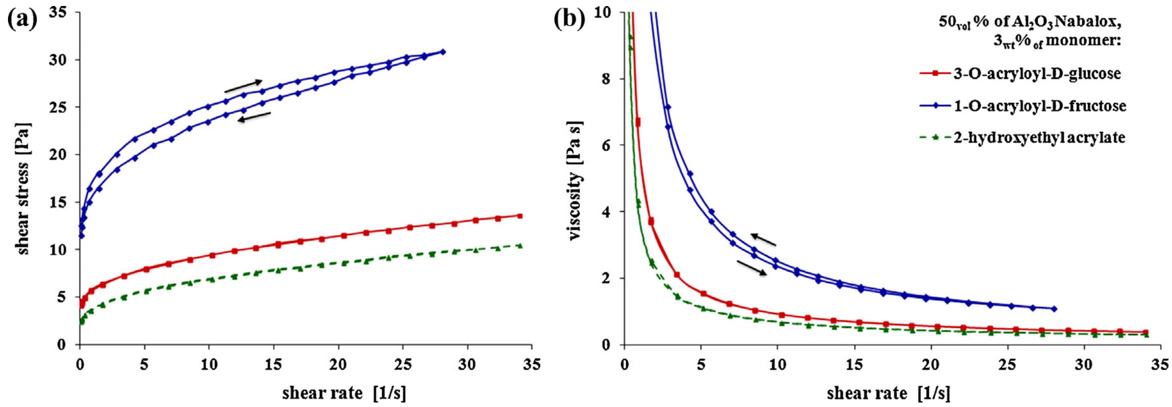

Fig. 6. (a) Flow curves and (b) viscosity curves of Al_2O_3 Nabalox suspensions with examined monomers.

prepared in aqueous medium and poured into the moulds. Then the entire system gel in situ around the particles, creating the network that holds the ceramic grains together. Thus the desired shape of the product is retained. Before the addition of the initiator of polymerization the suspension is degassed because oxygen is a well known inhibitor of radical polymerization. When gelation process is finished, the obtained green body can me unmoulded, dried and sintered. During sintering process all organic additives are burned out, nevertheless they are very important processing agents in the whole shaping process.

Decomposition of the organic additives used in ceramic technology is usually investigated by thermal analysis (DTA/TG measurements). Authors have examined thermal decomposition of synthesized monoacryloyl esters of carbohydrates in comparison to commercial substances by using thermal analysis coupled with mass spectrometry (Bednarek & Szafran, 2012). The results showed that during thermal decomposition of polymers formed from 1-O-acryloyl-D-fructose and 3-O-acryloyl-D-glucose no harmful gases are released to the atmosphere. These substances decompose with the release of H_2O and CO_2. While the application of commercial

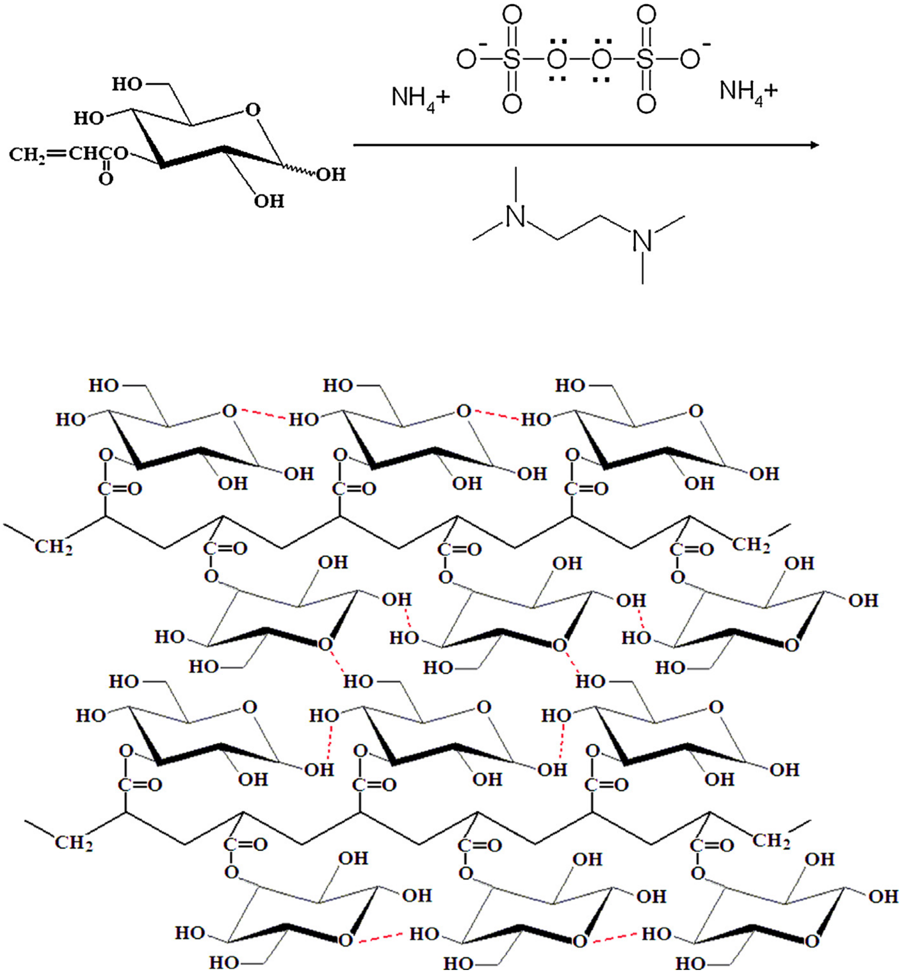

Fig. 7. Proposed structure of polymer formed from 3-O-acryloyl-D-glucose, hydrogen bonds between glucose units are marked with red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

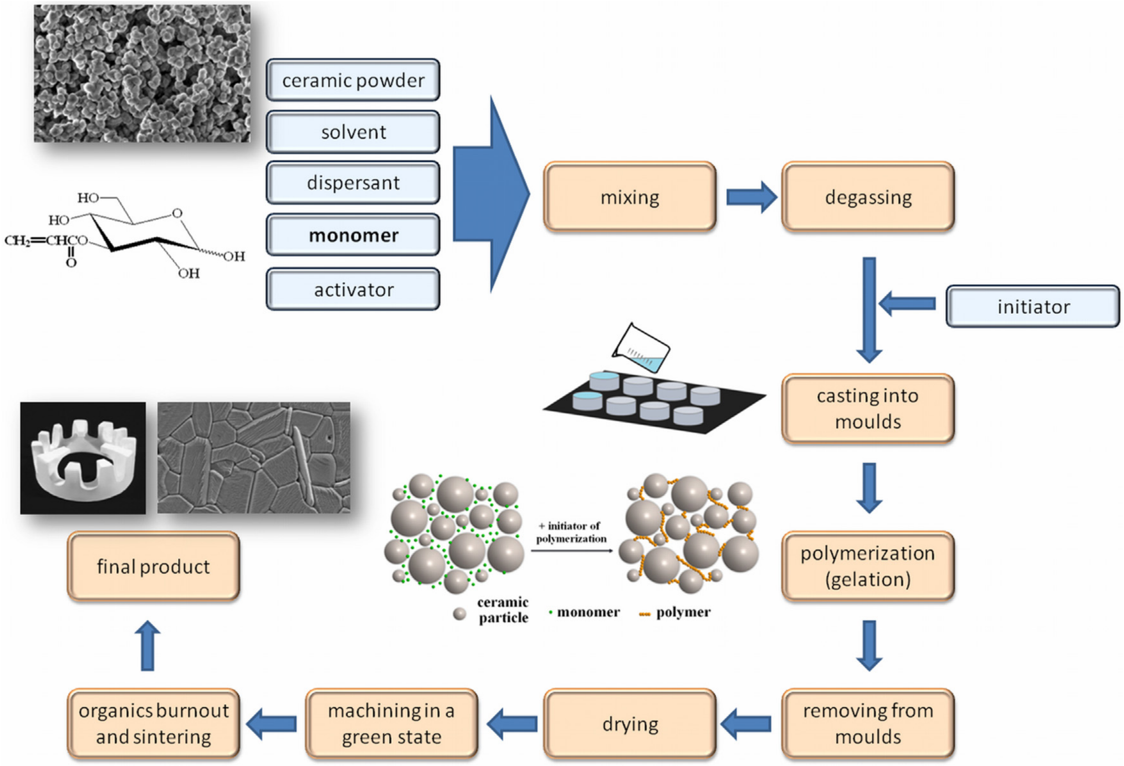

Fig. 8. Scheme of fabrication of ceramic elements by using the in situ polymerization.

monomers such as acrylamide and cross-linking substances e.g. N,N′-methylenebisacrylamide results in releasing of harmful NO_x.

The presented in Fig. 9a SEM micrograph of Al_2O_3 TM-DAR green body shows that the obtained by gelcasting ceramic specimens are homogenous. Polymeric bridges, formed due to the in situ polymerization of 3-O-acryloyl-D-glucose, between ceramic grains are marked with red. It is much easier to recognize polymeric bridges on SEM when ceramic powder of finer particles is used, therefore for the microstructure observations Al_2O_3 TM-DAR was chosen instead of Al_2O_3 Nabalox. Based on SEM image of sample after the sintering process (Fig. 9b) one can observe the high degree of densification what is substantial in ceramic technology. Carbohydrate polymers which had formed during gelcasting process did not disturb the sintering process. The detailed properties of ceramic specimens in green and sintered state obtained with the use of 3-O-acryloyl-D-glucose we described elsewhere (Bednarek et al., 2010; Falkowski, Bednarek, Danelska, Mizerski, & Szafran, 2010).

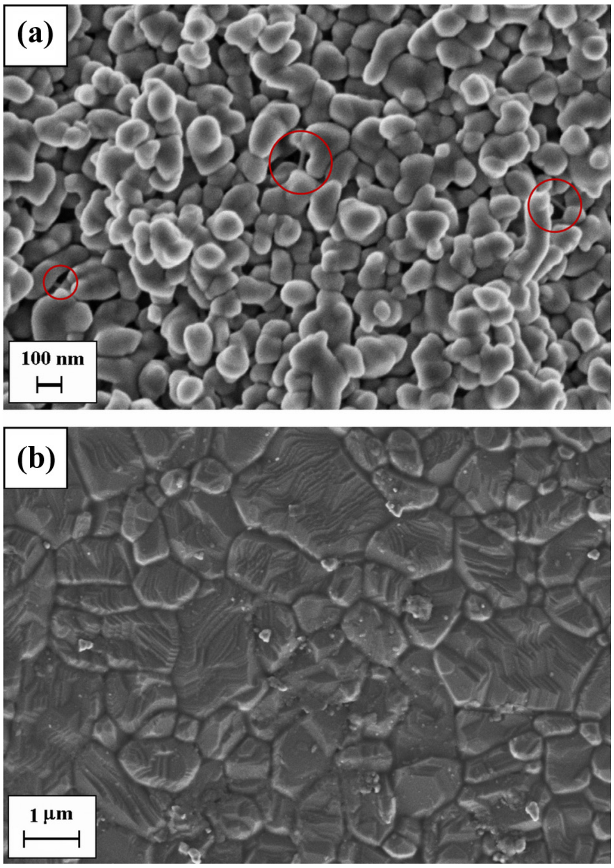

Fig. 9. SEM images of Al_2O_3 TM-DAR samples obtained by gelcasting with the use of 3-O-acryloyl-D-glucose (a) green body and (b) sintered sample.

4. Conclusions

The synthesis of monoacryloyl esters of carbohydrates 3-O-acryloyl-D-glucose and 1-O-acryloyl-D-fructose was described. The compounds can polymerize by using N,N,N′,N′-tetramethylethylenediamine and ammonium persulfate as redox initiating system. Acrylol esters of carbohydrates have been used as organic monomers in fabrication of Al_2O_3 ceramics by gelcasting technique. The obtained polymers are characterize by low glass transition temperature what is very beneficial for ceramic applications. They have also very good wettability of ceramic substrate. Viscosities of alumina suspensions composed of synthesized compounds are low, what ensures obtaining high quality ceramic parts. SEM images of alumina bodies in green and sintered state showed that the application of new compounds allows to obtained homogenous ceramic bodies. The synthesized compounds are therefore the good alternative for the commercially available acrylic monomers such as 2-hydroxyethyl acrylate used in the fabrication of ceramic elements by using the in situ polymerization, mainly because they do not need the use of external cross-linking agent.

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