

Gelcasting of alumina with a new monomer synthesized from glucose

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Abstract

Synthesis of a new low-toxic monomer obtained from glucose is reported and its application in gelcasting process is presented. The new monomer named 3-O-acrylic-D-glucose is an interesting alternative for the commercially available acrylic monomers. The presence of many hydroxyl groups in the monomer molecule allows to create hydrogen bonds in the polymer network. The resulting network does not need any external cross-linking agent to obtain a rigid ceramic part. The present paper describes the properties of ceramic slurries, green and sintered elements obtained from two alumina powders of different grain size (0.21 μm and 0.70 μm) with the use of the new monomer 3-O-acrylic-D-glucose and commercially available 2-hydroxyethyl acrylate.

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1. Introduction

Colloidal processes are recently willingly applied in fabrication of high-quality ceramic elements of complicated shape in order to overcome the limitations and high costs of commonly applied moulding methods such as slip casting or injection moulding. The gelcasting, which combines conventional moulding from slips with polymer chemistry, has become recently one of attentively studied forming methods.^{1,2} The gelcasting process allows to obtain high-quality, complex-shaped ceramic elements by means of *in situ* polymerization, through which a macromolecular network is created, to hold the ceramic particles together. The key role in the whole process is played by suitable selection of an organic monomer, which should be able to provide high mechanical strength of the gelled part. There exist some commercially available monomers commonly applied in gelcasting process, such as acrylamide, methacrylamide or 2-hydroxyethyl acrylate,^{3–5} but they still present some disadvantages, such as excessive toxicity. Furthermore, they must be used together with cross-linking monomers, otherwise the received green bodies would not be tough enough. N,N'-

methylenbisacrylamide is the most often used as a cross-linking agent.⁶ In recent years many research has been concentrated on replacing toxic acrylamide by other substances, e.g. by agarose.⁷ In previous works^{8–10} the synthesis and application of a new monomer named glycerol monoacrylate has been reported. The monomer, synthesized from acrylic acid and glycidol, can successfully replace commercial monomers because its toxicity is low and it does not require addition of any external cross-linking agent to a ceramic slurry. This fact is due to the presence of two hydroxyl groups in monomer molecule. They allow to form hydrogen bonds in the polymer network, thus reducing the amount of organic additives needed in the suspension, and to achieve identical results without increasing the amount of the main monomer used.

The following interesting alternative for acrylic monomers has been provided in the form of compounds obtained on the basis of monosaccharides, e.g. glucose. Monosaccharides are water-soluble, non-toxic and, owing to the presence of many hydroxyl groups in molecule, hydrogen bonds can be formed in polymer network like in the case of glycerol monoacrylate.

The present article reports the results of synthesis of 3-O-acrylic-D-glucose, a new monomer based on glucose, and of its application in gelcasting of alumina. Ceramic slurries were prepared from two different alumina powders of grain size 0.21 μm and 0.70 μm . The properties of the elements produced were

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compared with those obtained with the use of commercially available 2-hydroxyethyl acrylate monomer. The rheological properties of the obtained ceramic slurries and the properties of both green and sintered elements have been also presented in the paper.

2. Experimental procedures

2.1. Materials

Two different alumina powders were used. One of them was Al₂O₃ TM-DAR (Tamei Chemicals, Japan) of mean particle size $D_{50} = 0.21 \mu\text{m}$ and specific surface area $14.1 \text{ m}^2/\text{g}$. In former works the powder was used for obtaining textured alumina-related compounds by colloidal processing¹¹ and in electrophoretic deposition of alumina suspensions in high magnetic field.^{12,13} In the present work the authors were highly interested in the possibility of application of TM-DAR alumina in the gelcasting process. The other alumina powder used was Al₂O₃ NABALOX 713-10 (Nabaltec, Germany) of mean particle size $D_{50} = 0.70 \mu\text{m}$ and specific surface area $8.0 \text{ m}^2/\text{g}$. This material was previously successfully applied in gelcasting, that is why in this study it was used as a comparison for TM-DAR. Two monomers were tested in the gelcasting process of the above powders. One of them was a commercially available 2-hydroxyethyl acrylate (Fluka). The other one named 3-O-acrylic-D-glucose was synthesized at our laboratory. Diammonium hydrocitrate (POCH, Poland) and citric acid (Sigma) were used as dispersants in the ceramic slurries. N,N,N',N'-tetramethylethylenediamine (Fluka) played the role of activator and ammonium persulfate (Aldrich), used in the form of 1 wt% aqueous solution, was the initiator of polymerization. In the case of the commercial monomer N,N'-methylenebisacrylamide (Fluka) was used as external cross-linking agent.

2.2. Synthesis of the new monomer

The aim of the synthesis was to obtain, from glucose, an organic monomer named 3-O-acrylic-D-glucose (AkrG), in which one of the hydroxyl groups is replaced by acrylic group (Fig. 1). This group has a double bond between the carbons, that enables polymerization of the molecules. The synthesis of the new monomer was carried out in three stages. In the first stage 1,2:5,6-di-O-isopropylidene-D-glucofuranose was obtained in order to block four from the five free hydroxyl groups in glucose molecule. In the second stage esterification reaction was carried out to obtain 3-O-acrylic-1,2:5,6-diisopropylidene-D-glucofuranose. In the third stage four hydroxyl groups were

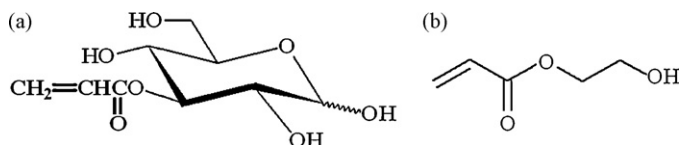


Fig. 1. Molecular structure of (a) 3-O-acrylic-D-glucose and (b) 2-hydroxyethyl acrylate.

unlocked by hydrolysis and the newly obtained monomer could be used in gelcasting process. The monomer is a colourless and odourless resinous substance. In the gelcasting processes it was used in the form of a 50% aqueous solution.

2.3. Gelcasting process

The mixture of the gelcasting components was prepared in several steps. First, the components of the ceramic slurry were dissolved in distilled water. The dispersant used as a mixture of diammonium hydrocitrate (0.14 wt% in the case of NABALOX powder and 0.30 wt% in the case of TM-DAR powder) and citric acid (0.10 wt% in case of both powders) was then added followed by 3.0 wt% of monomer and 2.0 wt% of activator (all with respect to the amount of monomer). The cross-linking agent (1.0 wt% with respect to the quantity of monomer) was used only in the case of the commercial monomer 2-hydroxyethyl acrylate (2-ha). Alumina powder was then added and the slurry was ball-milled for 1.5 h for good homogenization. The viscosity of the slurries was measured, then initiator of polymerization was added and the slurry was mixed by magnetic stirring. The initial solid contents in the prepared suspensions were between 50 and 55 vol% till the optimum quantities of dispersant (mentioned above) and powders (Table 1) were found. In the next stage the slurries were deaerated for 20 min under reduced pressure in a vacuum desiccator supplied with magnetic stirrer. The mixture was then cast into identical plastic molds. The slurry with applied monomers is able to gelate at room temperature. After a thick gelled body was obtained, the specimen was unmoulded and dried for 24 h at 50 °C. Then the properties of the green bodies obtained were examined. The polymer burnout process and sintering were performed at a single stage with a heating program established on the basis of TG/TDA measurements.

2.4. Characterization techniques

The zeta potentials of pure powders, of the powders mixed with the monomers and of all the components of the ceramic slurry were measured by a Zeta-potential Analyser (LSPZ-100 Photal Otsuka Electronics). The rheological behavior of ceramic slurries was examined using a cone/plate Brookfield CAP 2000 Viscometer. The viscosity was measured as a function of shear rate before the addition of polymerization initiator in order to determine optimum quantities of each component of the slurry, especially those of dispersant and solid phase content. Then, the viscosity of the slurry with initiator was measured as a function of time at a constant shear rate of 0.08 s^{-1} with the use of a rotational Brookfield DV + II– Rheometer in order to find the appropriate amount of initiator, so that the time needed for gelling of the specimen was within the range of 20–90 min.

The densities of green and sintered specimens were measured by the Archimedes' method in kerosene and water, respectively. The TG/DTA measurements of specimens composed of Al₂O₃ TM-DAR with addition of 3 wt% of monomers 2-hydroxyethyl acrylate and 3-O-acrylic-D-glucose were carried out using a Thermo Plus TG 8120 (Rigaku) device. The tensile strength of the green bodies was determined by the "Brazilian test"¹⁴ using

Table 1
Properties of green bodies.

Sample	Solid loading (vol%)	pH of slurry	Green density (% TD)	Tensile strength (MPa)
Al ₂ O ₃ TM-DAR + AkrG	53	7.66	60.1	1.0 ± 0.1
Al ₂ O ₃ TM-DAR + 2-ha	53	7.96	59.0	0.9 ± 0.1
Al ₂ O ₃ NABALOX + AkrG	55	8.36	59.7	0.58 ± 0.04
Al ₂ O ₃ NABALOX + 2-ha	55	9.03	58.8	0.41 ± 0.03

a Universal Testing Machine Shimadzu AG-IS. In the Brazilian tension test, a circular disk was placed between two platens and compressed producing a nearly uniform tensile stress distribution normal to the loaded (vertical) diametral plane, leading to the failure of the disk by splitting. This tensile stress is estimated from the elastic theory.¹⁵ The Universal Testing Machine recorded the value of force causing the first cracks in the samples. The tensile strength was calculated as $\sigma_t = (2P/\pi TD)$, where P is force, and T and D are the thickness and diameter of the disk. The diameter of the obtained samples was 20.1 ± 0.1 mm and their thickness was 4.1 ± 0.2 mm. The measurements were performed for 10 samples prepared from each powder.

The microstructure of sintered, polished and thermally etched (1200 °C/1 h) specimens was observed in scanning electron microscope SEM JEOL JSM-6500F. Moreover, the Vickers hardness was measured on Akashi MVK-E hardness tester for sintered and polished samples prepared from both powders obtained with each monomers. The hardness was determined with the use of a Vickers indenter and calculated as $H = 1.8544F/d^2$, where d is the half-diagonal indentation impression and F is the indentation load (20 kG = 1.98 MPa). Further, the fracture toughness was calculated using the indentation method for central cracks $K_{IC} = 0.067H^{3/5}E^{2/5}a^2c^{-3/2}$. Here, $2a$ represents the Vickers indent diagonal length, $2c$ is the resultant crack length, H is the Vickers hardness and E is the Young Modulus (380 GPa for Al₂O₃).

3. Results and discussion

3.1. Characterization of suspensions

Fig. 2 shows the zeta potential values of pure alumina powders and of powders containing other components of the ceramic slurries (monomers and dispersants). It can be seen that the new monomer AkrG almost does not shift the isoelectric point (IEP) of alumina in either TM-DAR and NABALOX. Commercial acrylic monomer 2-hydroxyethyl acrylate also has no effect on the position of IEP. The dispersant (mixture of diammonium hydrocitrate and citric acid) was found to affect the zeta potential changes of the suspension. In this case the IEP of slurry with TM-DAR is shifted from pH 8.4 to 4.4 and of the slurry with NABALOX from pH 7.8 to 4.6. Table 1 shows the pH values of the ceramic slurries prepared. It can be found that the slurries with 2-hydroxyethyl acrylate have higher pH than slurries with AkrG. Comparison of the results obtained for zeta potential with the pH values of the ceramic slurries prepared shows that the suspensions were effectively dispersed at pH 7.5–8 in the case of TM-DAR and at pH 8.3–9 for NABALOX.

The viscosity of the applied monomers was analysed (Fig. 3a). The viscosity of 2-hydroxyethyl acrylate monomer was lower than that of a 50 wt% aqueous solution of AkrG. Such a difference in viscosity of the monomers was to be expected as 2-hydroxyethyl acrylate is a liquid and AkrG is a resinous substance. The difference in viscosity of the monomers results in differences of viscosity of the obtained ceramic slurries. As shown in Fig. 3b both slurries (with 2-hydroxyethyl acrylate and AkrG) exhibit a shear-thinning behavior. Despite of high solid contents, which is 53 vol% for the TM-DAR slurry and 55 vol% for that with NABALOX, the viscosity of both slurries is low enough to fill precisely the mould. One of the advantages of gel-casting process is a possibility to control the time, after which the gelation occurs, by adding a suitable amount of activator and initiator of polymerization. The amount of activator in ceramic slurry was constant and fixed as 2.0 wt% based on monomer content. The quantity of initiator was therefore matched. Fur-

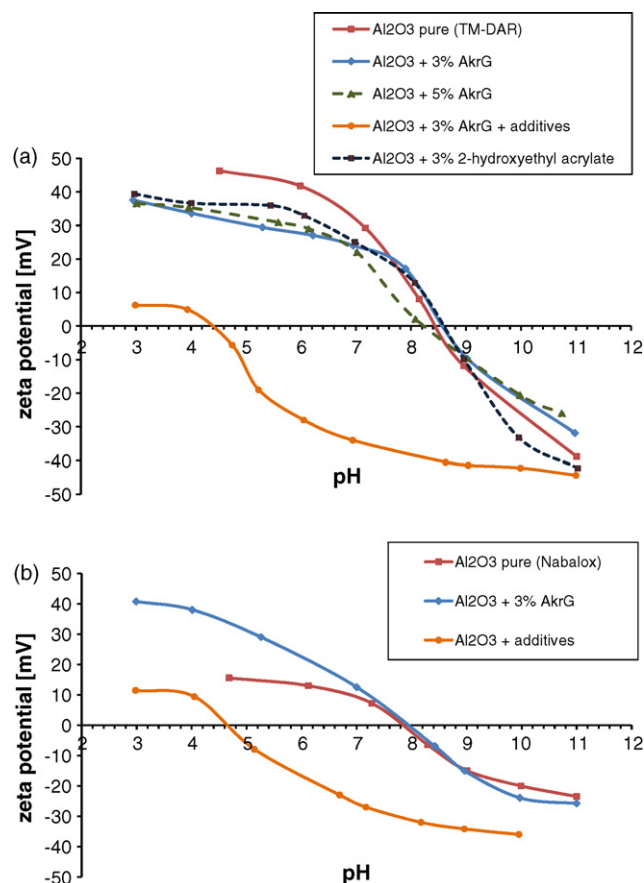


Fig. 2. Zeta potential of Al₂O₃ (a) TM-DAR and (b) NABALOX with and without additives.

ther experiments were carried out for the elaborated optimal solid loadings, dispersants and monomer contents. As shown in Fig. 4 an addition of 0.5 wt% of initiator, as calculated for the monomer content, results in a rapid gelation of the entire system. The lower the quantity of initiator, the longer is the time needed to start the polymerization. However, even very slight differences in the amount of initiator added can drastically change the time after which the whole system starts to polymerize. A precise determination of the idle time is very important for industrial use. Too short idle time (e.g. 5 min) can result in gelation during the mixing of initiator with the slurry, whereas an excessively long time (e.g. 90 min) is inadvisable from economical point of view. For this reason the optimum amount of initiator added to the ceramic slurry with Akrg is about 0.3 wt% for both powders, as can be seen from the results obtained (Fig. 4). This amount of initiator assures at least 20 min delay time before the slurry starts to polymerize. For the initiator contents of 0.5 and 0.4 wt% there were only slight differences in idle time for both powders. The fact can be attributed to different distribution of initiator in the slurry. For lower initiator contents it was possible to extend the time of mixing initiator with the slurry. Fig. 4a and b show also, that an insufficient amount of initiator, in this case 0.2 wt%, causes that the polymerization reaction does not proceed to the end, because not enough active centers are initiated. Similar experiments were carried out with 2-hydroxyethyl acrylate and initiator amounts

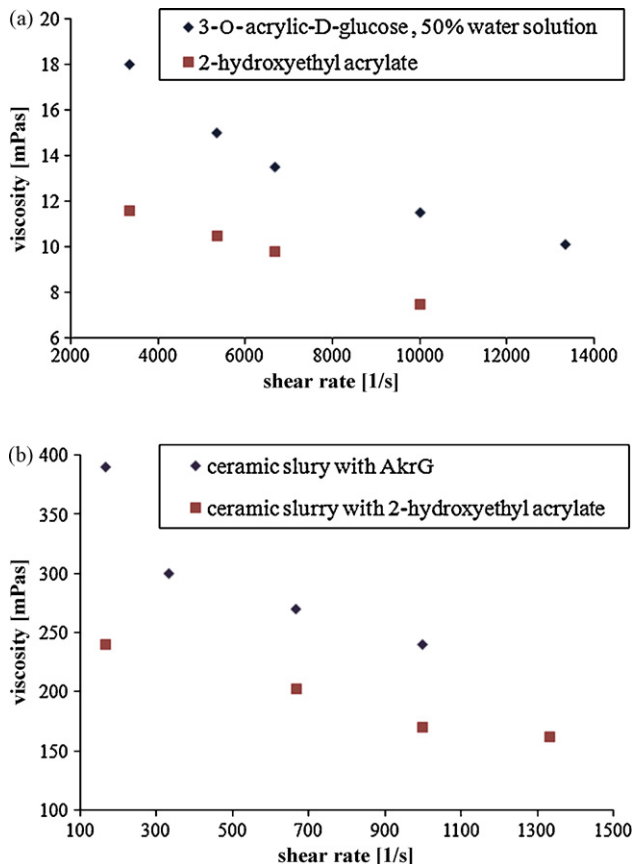


Fig. 3. Viscosity of ceramic slurries with (a) pure monomers Akrg and 2-ha (b) Al_2O_3 TM-DAR slurry with both monomers.

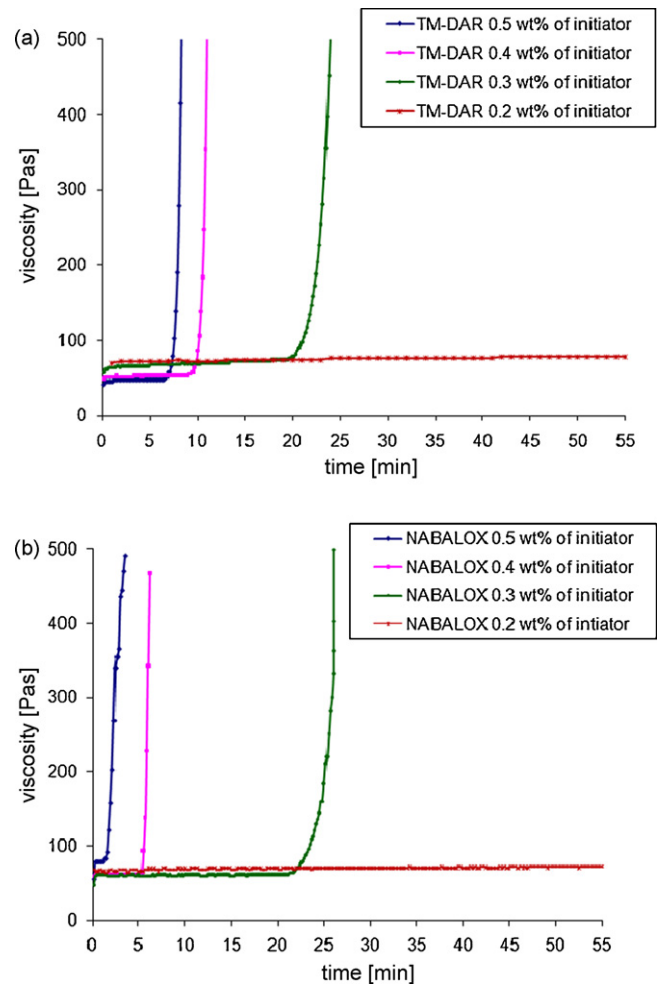


Fig. 4. Influence of quantity of initiator on viscosity of slurries with (a) Al_2O_3 TM-DAR with 3-O-acrylic-D-glucose and (b) Al_2O_3 NABALOX with 3-O-acrylic-D-glucose.

of 0.5 wt%. The differences between Akrg and 2-hydroxyethyl acrylate show that each monomer requires an individual quantity of initiator.

3.2. Characterization of green bodies

Table 1 lists the values of solid loading, density and tensile strength of green bodies obtained. It was possible to obtain suspensions with concentration of TM-DAR alumina of 53 vol%. The concentration of NABALOX was a little higher (55 vol%) but the average particle size of this powder was over 3 times as high as and the specific surface area almost 2 times as low as those of TM-DAR. For that reason, the achieved solid loading for TM-DAR can be regarded as very good.

For both TM-DAR and NABALOX the highest green density was obtained with Akrg (ca. 60%). The SEM microstructure of green bodies shows a very high homogeneity of specimens with Akrg (Fig. 6a and c), while in the specimens with 2-ha clusters of polymeric chains are visible (Fig. 6b and d). This indicates that the commercial monomer does not wet the alumina grains well enough and it forms polymeric bridges which are not homogeneously distributed. Apart from that, a slightly higher tensile

strength measured by the Brazilian test was obtained for specimens with the new monomer. This can confirm that the monomer based on the monosaccharide – Akrg can form a strong polymer network and, as a result, a strong gelled ceramic with no need of adding any external cross-linking agent. According to some other investigations of gelcasting, the tensile strength of alumina TM-DAR with Akrg and initiator content 0.3 wt% is similar or a little higher than those obtained with the use of commercial methacrylamide with N,N'-methylenebisacrylamide¹⁶ as the cross-linking agent or with poly(vinyl alcohol).¹⁷ The hydrogen bonds formed between polymer chains are strong enough to provide a well cross-linked network without additional binding agents. Furthermore, the specimens containing Akrg did not exhibit any exfoliation layer, contrary to the specimens with 2-hydroxyethyl acrylate. The presence of exfoliation layer in case of NABALOX with 2-ha could be the reason of similar cracks formation and low standard deviation for the whole population of specimens measured, as shown in Table 1. The specimens containing TM-DAR exhibit a higher homogeneity and a smaller number of places, where cracks can be initiated.

The pyrolysis of the applied monomers in the dried green alumina TM-DAR samples occurring on sintering in air was determined by thermal analysis. The results are shown in Fig. 5. The DTA curve of Akrg (a) has two exothermic peaks, which can be attributed to gradual burnout of polymer: one connected with the glucose ring and the other with the acrylic group. As results from the TG curve total mass loss is 3.8%, corresponding to the quantity of monomer and other additives (dispersant, activator, initiator) in the ceramic slurry. The DTA curve of 2-hydroxyethyl acrylate (b) also has two exothermic peaks but they are situated at higher temperatures. These peaks can be ascribed to the burnout of the cross-linked polymer network in the presence of an external agent. The total mass loss shown by TG is 4.1%, what corresponds to the higher quantity of additives in the ceramic slurry, especially the organic ones, because of the presence of external cross-linking substance. It can also be found that for both monomers the total burnout of organic compounds is completed at about 520 °C. On the basis of the thermal analysis data a sintering program was developed for each powder. For the TM-DAR the heating rate was 1 °C/min in temperature range 30–550 °C, then till 1300 °C it was 5 °C/min. The product was held at this temperature for 5 h and then cooled down. The TM-DAR alumina powder was of high purity of >99.99% and of a very fine particle size of 0.21 μm, that is why the specimens were densified at a low temperature of 1300 °C. For NABALOX the sintering temperature was 1600 °C at a holding time of 1 h.

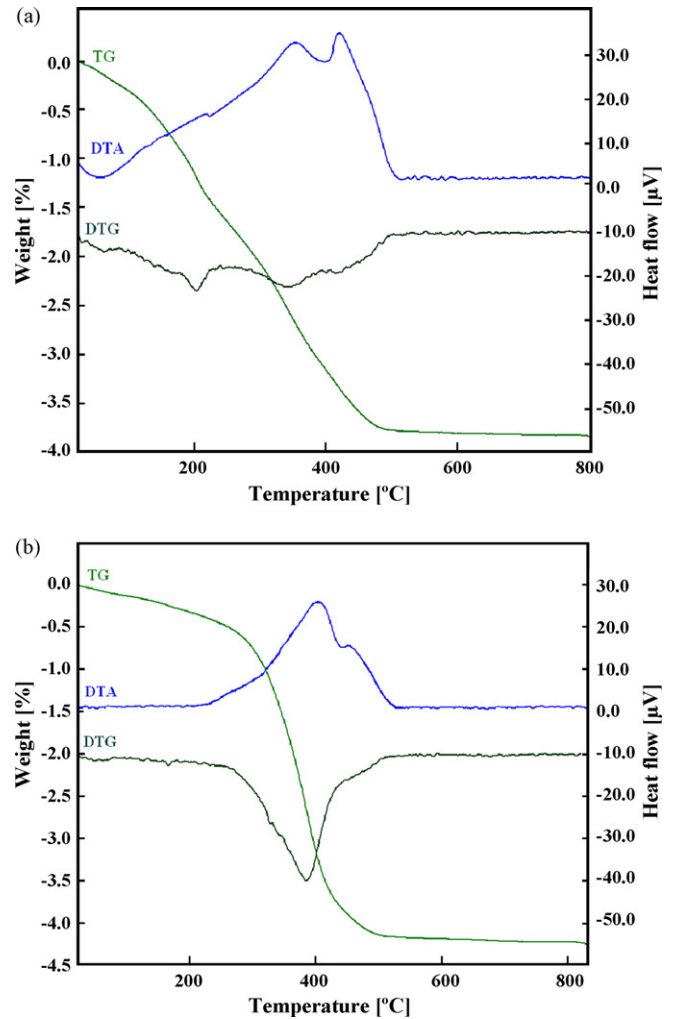


Fig. 5. DTA/TG of Al₂O₃ TM-DAR with (a) Akrg and (b) 2-ha.

3.3. Characterization of sintered bodies

The values of sintering temperature, relative density, Vickers hardness and fracture toughness of alumina ceramics are presented in Table 2. The TM-DAR samples and NABALOX samples casted with Akrg exhibit a similar, high relative density, above 99% of the maximum theoretical value. The density of NABALOX samples with 2-hydroxyethyl acrylate is lower (93%) probably due to lower homogeneity of the green bodies because of the particle agglomeration, as can be seen on the SEM photograph (Fig. 6d). The samples prepared with TM-DAR alumina exhibit also a higher Vickers hardness, which was slightly higher for samples,

Table 2
Properties of sintered bodies.

Sample	Firing temperature (°C)	Sintered density (% TD)	Vickers hardness (GPa)	Fracture toughness (MPa m ^{1/2})
Al ₂ O ₃ TM-DAR + Akrg	1300	99.2	18.9 ± 0.1	2.3 ± 0.3
Al ₂ O ₃ TM-DAR + 2-ha	1300	99.1	19.8 ± 0.4	2.5 ± 0.4
Al ₂ O ₃ NABALOX + Akrg	1600	99.1	16.4 ± 0.3	4.7 ± 0.9
Al ₂ O ₃ NABALOX + 2-ha	1600	93.0	15.9 ± 0.2	2.9 ± 0.7

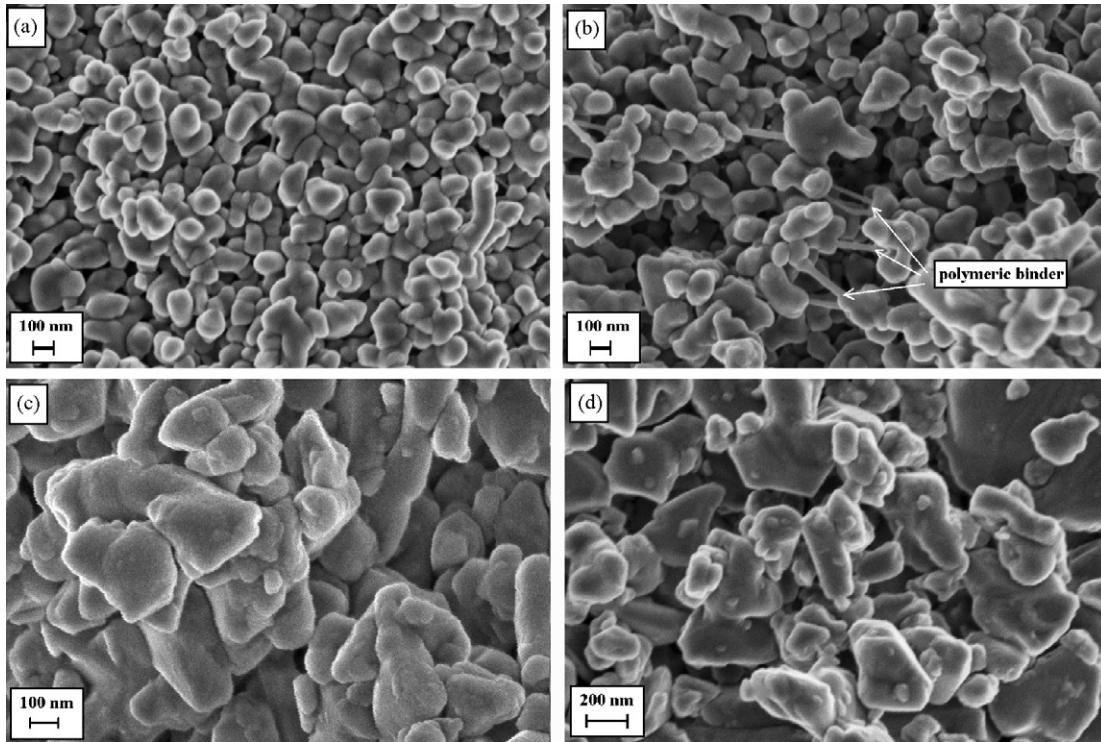


Fig. 6. SEM of green body of (a) TM-DAR with Akrg, (b) TM-DAR with 2-ha, (c) NABALOX with Akrg and (d) NABALOX with 2-ha.

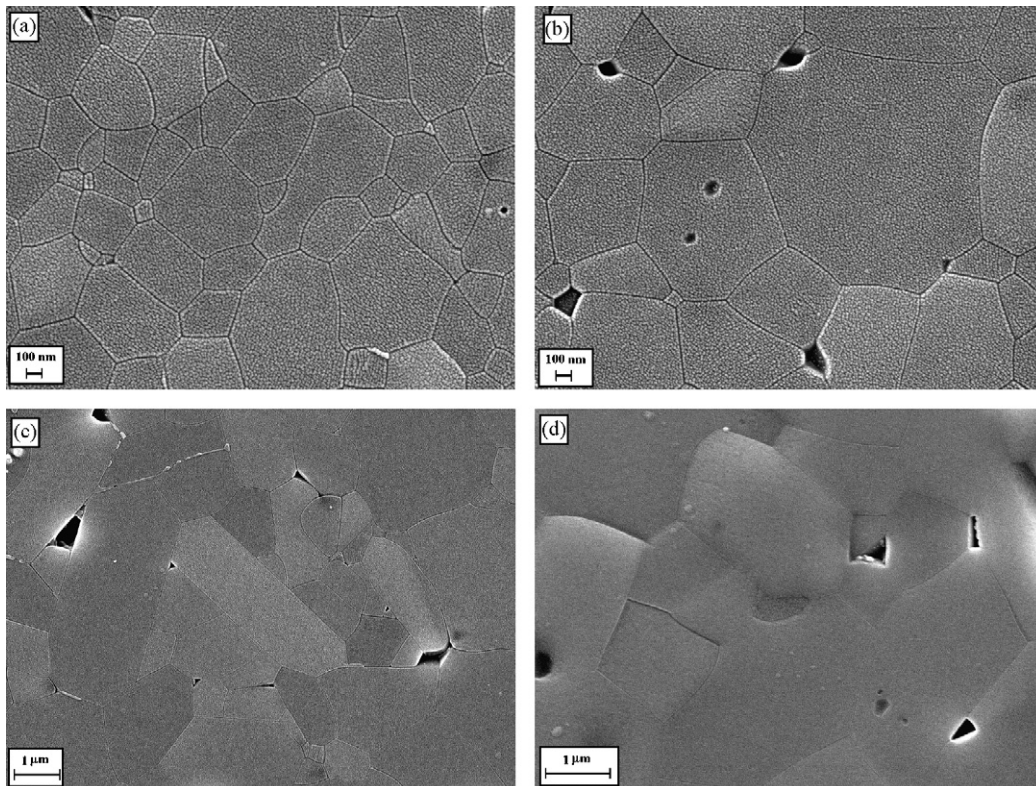


Fig. 7. SEM of sintered body of (a) TM-DAR with Akrg, (b) TM-DAR with 2-ha, (c) NABALOX with Akrg and (d) NABALOX with 2-ha.

where the polymer network was due to 2-hydroxyethyl acrylate.

The samples containing TM-DAR exhibit a higher Vickers hardness (at the average 19.4 GPa) than those with NABALOX (at the average 16.2 GPa), hence the fracture toughness for TM-DAR (at the average $2.4 \text{ MPa m}^{1/2}$) is lower than that for NABALOX (at the average $3.8 \text{ MPa m}^{1/2}$). Nevertheless, the obtained results of fracture toughness for particular samples do not exhibit such a correlation between the Vickers hardness and fracture toughness because of considerable measuring error. The error arises mainly from the measuring method which was combined with the Vickers hardness determination. More precise results would be obtained from the measurement of residual bending strength of the bars with preliminarily cut V-notch. Besides, there is an inaccuracy in specifying the end of propagated cracks in optical microscope being a part of the hardness tester.

The differences in mechanical properties between the TM-DAR and NABALOX ceramics are certainly related with the differences in microstructure, as shown in Fig. 7. Although the mean grain size calculated on the basis of SEM microstructures of sintered specimens exhibits almost no grain growth, it is visible that a such growth appears in both powders. The TM-DAR alumina grains (sintered at 1300°C) have a rather spherical shape and the visible grain growth is about twofold. NABALOX grains (sintered at 1600°C) exhibit oblong shape with the longer diagonal of few microns. There were also visible pores in some places of sintered powders, where the applied monomer was 2-hydroxyethyl acrylate (Fig. 7b and d). It is possible to conclude that in green bodies (Fig. 6b and d) in some places the monomer formed clusters of polymeric chain. The distribution of monomer in the whole ceramic slurry was not homogenous enough, the monomer did not properly surround the ceramic grains. It may be due to a higher wettability angle of alumina in 2-hydroxyethyl acrylate than in 3-O-acrylic-D-glucose. On the other hand, the holes visible on sintered NABALOX powder (Fig. 6c), where the applied monomer was 3-O-acrylic-D-glucose, are caused by mechanism of sintering of larger grains rather than by a not homogenous distribution of the monomer, as in green bodies with AkrG (Fig. 6a and c) such clusters of polymer are not visible as in the case of 2-ha.

4. Conclusions

The new synthesized low-toxic monomer based on glucose (3-O-acrylic-D-glucose) can successfully replace the commercially available 2-hydroxyethyl acrylate in the manufacture of ceramic elements by gelcasting method. The measurements performed have shown that the new monomer has no negative effect on rheological properties of alumina slurries and enables the obtaining of dense and rigid green bodies without adding any external cross-linking agent as needed in the case of commercial 2-hydroxyethyl acrylate. The use of TM-DAR alumina powder allows to obtain well densified final elements at much lower

sintering temperatures than needed for NABALOX Al_2O_3 . The elements made of TM-DAR have also higher Vickers hardness.

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