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GALACTOSE MONOACRYLATE AS A NEW MONOMER IN GELCASTING PROCESS

MONOAKRYLAN GALAKTOZY JAKO NOWY MONOMER W PROCESIE ODLEWANIA ŻELOWEGO

The present work shows the results of following the recently developed trend to design new low toxic monomers which can be applied in gelcasting process. New compound, 6-O-acryloyl-D-galactose (galactose monoacrylate) has been synthesised and its effectiveness as processing agent has been studied. The results are compared with those reported so far regarding applying some other new monomers - 3-O-acryloyl-D-glucose and glycerol monoacrylate in gelcasting technology. The influence of spatial structure of obtained monomers on rheological properties of alumina suspensions and properties of green bodies is discussed as well.

Keywords: gelcasting, alumina, monosaccharides, deflocculants, low-toxic monomers

Artykuł przedstawia wyniki badań dotyczących zastosowania nowozsyntezowanej akrylowej pochodnej galaktozy jako monomeru w procesie odlewania żelowego. Opracowano metodę syntezy 6-O-akryloilogalaktozy oraz zbadano jej rolę i efektywność w procesie. Wyniki porównano z wcześniejszymi pracami z tego zakresu, dotyczącymi zastosowania innych nowych nietoskycznych monomerów – 3-O-akryloiloglukozy oraz monoakrylanu glicerolu, szukając wpływu budowy przestrzennej cząsteczek monomeru na właściwości reologiczne mas lejnych z tlenku glinu i właściwości odlanych z nich wyrobów.

1. Introduction

It has been observed recently that shaping of advanced ceramic materials by colloidal processing is conducted more often and more eagerly than by other methods like injection moulding or pressing, due to its few advantages. One of the most important is the possibility to obtain homogenous ceramic bodies of high mechanical strength and complicated shape without application of the external pressure. Moreover it is possible to control the rheological behaviour and stability of ceramic suspension by the use of suitable processing agents such as deflocculants or binders, which results in good properties of final elements. The main problem of colloidal shaping techniques is achieving time-stable suspensions of low viscosity having high solid content of well dispersed powder particles. Here is the pivotal role of processing agents which manipulate the interparticle forces.

Colloidal processing enabled fast development of novel 'near-net-shape' techniques accomplished by direct casting methods. They make use of some inherent properties of ceramic suspensions to transform a slurry into a stiff body. In this way the general concept to retain the homogenous state of the slurry during the green body formation is implemented. This step is also commonly accompanied by the formation of permanent bonds between either the particles or some compounds in the suspension, just as in case of gelcasting technology, which is in great interest of the authors.

In gelcasting process a composition of ceramic powder, organic monomer and initiator in dispersing media is prepared and poured into the mould where the monomer polymerizes *in situ* around the particles. Thus a polymer network is created holding the particles together and the desired shape is retained.

The processing agents of gelcasting technology should be responsible not only for good properties of green bodies obtained, but also should follow the 'green chemistry' trend. The less toxic and the less harmful for the environment they are, the more attractive they are to apply. Nowadays acrylamide, methacrylamide or 2-hydroxyethyl acrylate are the most commonly applied monomers in the gelcasting process which is implemented by the radical polymerization mechanism conducted at room temperature [1]. Those monomers need some replacements because the most effective acry-

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lamide is a neurotoxin and probably carcinogenic substance. Besides it contains nitrogen atom in the molecule which results in releasing harmful nitrogen oxides into the atmosphere during burnout process, while 2-hydroxylethyl acrylate is much less toxic but is also much less effective as monomer. Following above reasons, first low-toxic monomer named glycerol monoacrylate (mixture of 2 isomers: 1,2-dihydroxypropyl acrylate and 2,3-dihydroxypropyl acrylate) was synthesized few years ago at Warsaw University of Technology and successfully applied in shaping of alumina powders by gelcasting method [2]. Not only it effectively plays the role of monomer in the process, but also it does not need the addition of external cross-linking agent like N,N'-methylenebisacrylamide, which is indispensable in the case of acrylamide or 2-hydroxyethyl acrylate. Having two hydroxyl groups in the molecule, glycerol monoacrylate is able to create hydrogen bonds in the polymer network making it cross-linked. As a result the obtained green bodies have a mechanical strength value high enough to enable green machining. Glycerol monoacrylate plays therefore double role: the organic monomer and the self-cross-linking substance, thus the amount of organic agents added to the ceramic slurry is reduced.

Continuing this research route, another concept appeared. The idea was to select and synthesize a processing agent that could be capable of playing triple role in the process, not only as the monomer and as the cross-linking additive but also as a dispersing medium for the ceramic powder and would still follow the 'green chemistry' issues. Here the monosaccharides as basic compounds were chosen due to few reasons. They are water-soluble, non-toxic, renewable thus inexpensive substances and they have more than two hydroxyl groups in the molecules. Therefore the creation of hydrogen bonds is possible. Moreover they can be easily removed from the green samples during the burnout process and they have been reported to be effective dispersants for alumina nanopowders and to have a positive influence on rheological properties of those slurries [3]. Therefore few acryloyl derivatives of monosaccharides such as glucose and galactose have been synthesised and their multifunctional role have been studied and compared with results concerning application of previously mentioned monomers, such as glycerol monoacrylate and commercial 2-hydroxyethyl acrylate. The present paper introduces the topic of synthesis of a new derivative, its influence on ceramic suspensions and shows that the choice of monosaccharide plays important role in its further application.

2. Experimental

2.1. The synthesis of galactose monoacrylate

The synthesis route of 6-O-acryloyl-D-galactose (6-Akr-Gal) is shown in Fig. 1. The aim of the synthesis, having the monosaccharide as its first substrate, was to obtain derivative where one certain hydroxyl group was replaced by acryloyl group able to polymerize. It was carried out in three stages. In the first stage (Fig. 1a) four from the five hydroxyl groups in monosaccharide molecule are blocked due to the chemical reaction with acetone in acidic medium. Then the esterification reaction of one free hydroxyl group is held by acryloyl chloride in the presence of amine, so that the acryloyl group is introduced to the molecule (Fig. 1b). The final stage (Fig. 1c) is an acidic hydrolysis that unlocks remaining four hydroxyl groups. The final product is ready to use as an aqueous solution ($10\%_{wt}$) or as a pure monomer after evaporating the solvent.
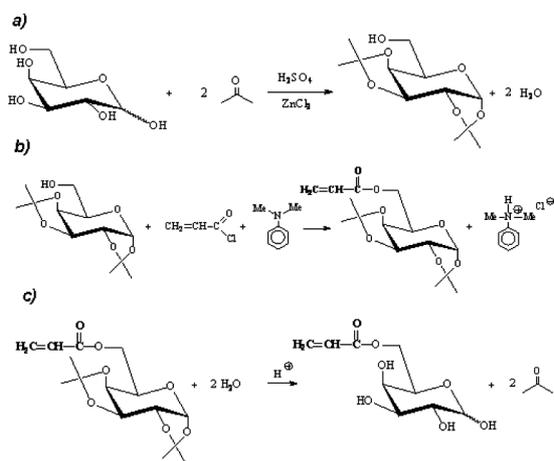

Fig. 1. The three-step synthesis of 6O-acryloyl-Dgalactose

2.2. Initial components

The ceramic powder used in the research was α-Al_2O_3 Nabalox 713-10 (Nabaltec, Germany) of mean particle size $D_{50} = 0.70\mu m$ and specific surface area = 8.0 m^2/g. Diammonium hydrocitrate, DAC (POCh, Poland) and citric acid, CA (Sigma) were used as dispersants, as well as ammonium polycarboxylate A6114 (TOAGOSEI, Aron Dispersant Series). N,N,N',N'-tetramethylethylene-diamine, TEMED (Fluka) played the role of activator and ammonium persulfate, AP (Aldrich) used in the form of $1\%_{wt}$ aqueous solution, was the initiator of polymerization.

2.3. Gelcasting procedure

Alumina aqueous suspensions with monomer additive were prepared in redistilled water at room tempera-

ture. The contents of alumina were $55\%_{vol}$. The concentration of the monomer was $3\%_{wt}$ (based on the alumina powder) and of TEMED $2\%_{wt}$ (based on the monomer). The dispersing mixture of DAC and CA, which was used in former studies, was not effective, as they were reacting with 6-Akr-Gal solution, so A6114 was used in amount of $2\%_{wt}$ (based on the alumina powder). Suspensions were mixed in alumina container in a planetary ball mill PM100 (Retsch) for 60 minutes with a speed of 300 RPM. Then the slurries were deaerated for 30 min under reduced pressure in a vacuum desiccator supplied with magnetic stirrer. After that rheological properties were tested using Brookfield DV+II-Pro rheometer (Brookfield Engineering Laboratories Inc. Massachusetts, USA).

Having the viscosity of the slurries measured, the initiator of polymerization AP was added (0.30.5 $\%_{wt}$) based on the monomer) and the mixture was cast into identical plastic moulds at room temperature. The access of the fresh air was cut off. After thick gelled green bodies were obtained, the specimens were removed from the mould and dried for 24 hours at $50^{o}C$.

The densities of green specimens were measured by the Archimedes' method in kerosene. The tensile strength of the green bodies was determined by the 'Brazilian test', so that 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. 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 microstructure of the specimens was observed using scanning electron microscope SEM JEOL JSM-6500F.

3. Results and Discussion

3.1. Characterization of the monomer

The synthesis of 6-Akr-Gal proceeds in similar way to reported synthesis 3-O-acryloyl-D-glucose (3-Akr-G) [4], although there are some differences in purification of particular intermediate products and each monomer requires different hydrolysis time. Fig. 2 shows chemical formulas of synthesized compounds. 3-Akr-G was reported to be a resinous substances of high viscosity so it was used and stored as 50% aqueous solutions prepared from pure products. It is difficult to obtain 6AkrGal as a pure product because it tends to crystallize or polymerize while evaporating the solvent even though phenothiazine is added as an inhibitor of spontaneous polymerization. $10\%_{wt}$ aqueous solution is gained as a hydrolysis product and so it is stored.
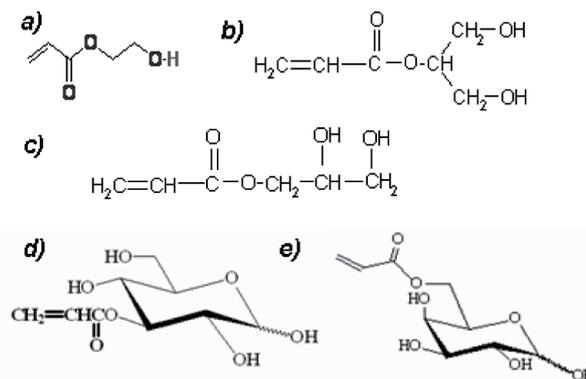

Fig. 2. Chemical formula of a) 2-hydroxyethyl acrylate, b) 1,2-dihydroxypropyl acrylate, c) 2,3-dihydroxypropyl acrylate, d) 3-O-acryloyl-D-glucose and e) 6-O-acryloyl-D-galactose

The selection of above monosaccharide is not random. Among large group of monosaccharides which differ the spatial distribution of hydroxyl groups, only few have the structure that allow to receive monoacryloyl derivatives. The positions and orientations of hydroxyl groups in a molecule determine the ability of saccharide to pass through shown in Fig. 1 synthesis steps. For example the spatial structure of sorbose does not allow blocking four hydroxyl groups and conduct the esterification reaction of one free -OH group. On the other hand, the selection of glucose and galactose allow to see whether the location of acryloyl group in molecule ring (at carbon 3 and 6 respectively) and the spatial orientation of hydroxyl groups does influence the rheological properties of ceramic suspension, the polymerization process, the properties of green bodies, etc. These differences would help in answering the question whether acryloyl derivatives of monosaccharides are universal when applied in ceramic processing or if only some of them are favorable.

3.2. Rheological properties of the ceramic slurries

Fig. 3 shows viscosity curves of alumina slurries with 6-Akr-Gal compared with reported values of the slurries with 3-Akr-G, glycerol monoacrylate and commercial monomer 2-hydroxyethyl acrylate [4-6]. The amounts of DAC and CA used as dispersants were $0.14\%_{wt}$ and $0.10\%_{wt}$ respectively (based on alumina content) in all cases except from 6-Akr-Gal, where A6114 (2.0 $\%_{wt}$) was used. Solid content in all slurries was 55 $\%_{vol}$. All of them exhibit slight shear thinning behaviour, but their viscosities differ much while pH value is similar. Nevertheless the viscosity is low enough to fill precisely the mould in all cases.
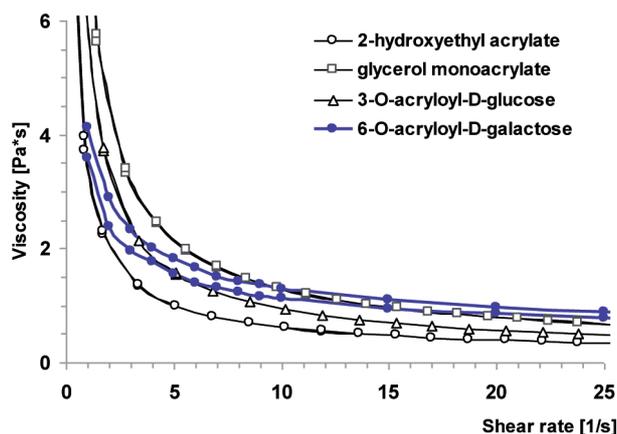
Fig. 3. Viscosity curves for alumina slurries containing 3 %$_{wt}$ of 6-O-acryloyl-D-galactose compared with the reported values for the slurries containing 2-hydryxethyl acrylate, glycerol monoacrylate and 3-O-acryloyl-D-glucose [4-6]

Comparing the idle time (the time after which the gelation process starts) the differences between synthesized compounds were also observed. It was found that very slight differences in addition of initiator can drastically change the time after which the whole system starts to polymerize, so there is a necessity to establish indi-

vidual optimum quantity of initiator for each monomer (Fig. 4). Optimum quantity for 6-Akr-Gal is 0,2-0,3%$_{wt}$ (based on monomer content). The idle time depends also on the amount of activator TEMED which together with AP forms redox system. This information enable to control the time of the gelation process.
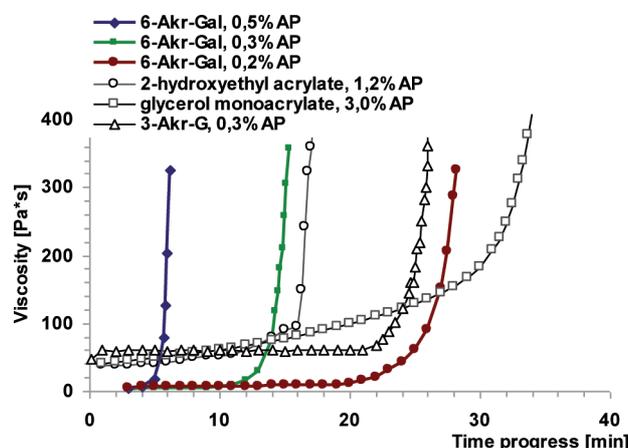

Fig. 4. Influence of initiator (AP) concentration on the idle time for the slurries containing 6-O-acryloyl-D-galactose compared with the reported values for the slurries containing 2-hydryxethyl acrylate, glycerol monoacrylate and 3-O-acryloyl-D-glucose [4-6]

TABLE 1

The properties of ceramic bodies obtained by gelcasting where 6-Akr-Gal was applied compared with the reported values for the samples where 3-Akr-G, glycerol monoacrylate and 2-hydroxyetyl acrylate were applied [4-6]

Monomer	Properties of slurries and green bodies			Properties of sintered in 1600°C ceramic bodied		
	Solid loading [vol %]	Green density [% TD]	Tensile strength [MPa]	Sintered density [%TD]	Linear shrinkage [%]	Bending strength [MPa]
2-hydroxy-ethyl acrylate	55	58.8	0.41 ± 0.03	98.8	13.2 ± 0.2	312 ± 55
glycerol monoacrylate	55	58.3	1.22 ± 0.16	99.2	16.0 ± 0.1	642 ± 47
3-Akr-G	55	59.7	1.23 ± 0.18	99.1	13.9 ± 0.1	488± 65
6-Akr-Gal	55	63.5	6.52 ± 0.42	99.8	15.4 ± 0.1	762± 60

3.3. Characterization of ceramic bodies

Table 1 lists the values of selected properties of green and sintered bodies obtained by gelcasting where 6-Akr-Gal was applied compared with reported values for samples where 3-Akr-G, glycerol monoacrylate and 2-hydroxyethyl acrylate was applied. It can be noticed, that samples containing 2-hydroxyethyl acrylate and glycerol monoacrylate have slightly lower green density than those containing monomers based on saccharides, even though they were gelcasted from the slurries of the same solid loading. Moreover green density of the specimen when 6-Akr-Gal was applied is a little higher than with 3-Akr-G.

Tensile strength of all green bodies is high in comparison to commercial monomer. Thus the machining process in green state is facilitated and specimens are not damaged during it. The strength values are similar for samples gelcasted with the use of 3-Akr-G and glycerol monoacrylate while it is much higher in case of 6Akr-Gal. Such a result may appear due to some differences in spatial structures of those molecules. The molecule of 6Akr-Gal is flat and the acryloyl group in position C6 is not as hidden as in case of 3-Akr-G. That makes the steric hindrance to access this acryloyl group much smaller, so the polymerization process may occur more easily and effectively. As a result the polymers created may be stronger.
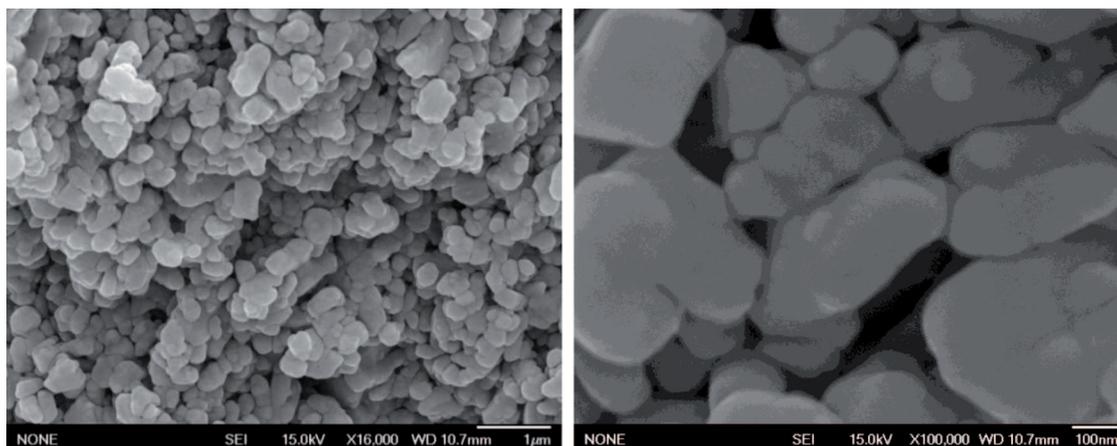
Fig. 5. SEM views of microstructure of green body obtained with the use of 6-Akr-Gal

Fig. 5 presents the SEM microstructure of green body obtained with the use of 6-Akr-Gal. It indicates the homogeneity of the specimen. No clusters of polymeric chains are visible what means that 6-Akr-Gal wets the alumina grains well enough and doesn't form polymeric bridges.

Sintering process was conducted up to 1600°C for 1 h with a rate of heating of 3°C/min. Samples with 6-Akr-Gal present the highest value of relative density and bending strength, a little bit higher that with 3-Akr-G. Nevertheless, linear shrinkage of those samples is quite high in comparison with the other ones.

4. Conclusions

The synthesis route of acryloyl derivatives of monosaccharides was elaborated and it appears to be effective way of synthesis of different monomers. 6-O-acryloyl-D-galactose can play double role in gelcasting process, as applying this derivative as a monomer in gelcasting process allows to obtain ceramic bodies without an addition of any external cross-linking agent. The specimens are characterised by very high values of relative densities or tensile strength of green bodies, what makes 6-Akr-Gal very promising processing agent.

The properties of ceramic slurries, green bodies as well as polymerization process are different for each monomer what indicates that the spatial structure of the molecules and the location of acryloyl group in the saccharide ring have important influence on the whole shaping process.

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