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GELCASTING OF ALUMINA WITH APPLICATION OF NEW MONOMER SYNTHESIZED FROM XYLITOL

ODLEWANIE ŻELOWE TLENKU GLINU Z ZASTOSOWANIEM NOWEGO MONOMERU ZSYNTEZOWANEGO Z KSYLITOLU

A new monomer for application in the gelcasting process has been designed and synthesized, following the green chemistry trend to use non toxic and renewable compounds. Xylitol was the main substrate for the synthesis that included 3 stages. The final product, named 1-O-acryloylxylitol, was tested regarding its effectiveness as the processing agent for fabrication of alumina elements by gelcasting method. Rheological properties of the ceramic slurries were studied as well as the properties of shaped elements before and after sintering. The results are compared to those obtained by applying commercial monomer 2-hydroxyethyl acrylate.

Keywords: alumina, gelcasting, low-toxic monomers, xylitol

Podążając za trendem „zielonej chemii”, zakładającym m.in. wykorzystywanie nietoksycznych i odnawialnych surowców w technologii, zaprojektowano i zsyntezowano nowy monomer przeznaczony do zastosowania w procesie odlewania żelowego. Wyjściowym substratem trój etapowej syntezy był ksylitol, a finalnym produktem 1-O-akryloiloksylitol. Otrzymana pochodna została sprawdzona pod względem efektywności polimeryzacji *in situ* w ceramicznej masie lejącej na bazie tlenku glinu. Zbadano jej wpływ na właściwości reologiczne stosowanych zawiesin. Odlano serie kształtek, dla których wyznaczono podstawowe parametry w stanie surowym oraz po spiekaniu. Wyniki porównano stosując równolegle komercyjnie dostępny monomer akrylan 2-hydroksyetylu.

1. Introduction

The gelcasting technique has been researched for the last two decades due to very attractive possibilities of inexpensive forming of advanced ceramics of complex shape. The idea of the process is to carry out a controlled polymerization *in situ* in the ceramic suspension and create a macromolecular network that holds the ceramic particles together and ensures high mechanical strength of the green bodies before sintering [1-3]. Due to that, the machining of the gelcast is not required and the method can be classified as ‘near-net-shape’ techniques. Originally, the term ‘gelcasting’ referred to the process where the polymerization of acrylic monomer together with a cross-linking agent was initiated by chemical reaction. The constant development of the gelcasting spread the idea to consolidate the suspension by the chemical or physical gelation of many different compounds, initiated chemically, photochemically or thermally. Recent researches concerning the gelcasting, mainly focus on three aspects: (1) the development of low/non-toxic gelating systems that don’t require thermal initiation, (2) the methods that allow one to reduce the possibility of causing some defects, especially during forming products of a large shape, (3) combining it with the other techniques and applying it in new areas (eg. fabrication of porous ceramics) [4]. The first one is the most crucial regarding the possibility

of industrial application, because the most effective systems are highly toxic at the same time (eg. acrylamide as monomer together with N,N’-methylenebisacrylamide as cross-linker). That is one of the main reasons why the process has not been industrialized yet for the large scale production and is often applied only in the laboratories.

Monosaccharides and their acryloyl derivatives have been recently found very promising as a group of compounds and effective processing agents [5-8]. It was reported that the creation of a very strong macromolecular network is possible without the external cross-linking agents due to the presence of many hydroxyl groups in their molecules and hydrogen bonds between them. Moreover, it appeared that they also can be dispersants for alumina nano- and submicropowders. Monosaccharides are polyhydroxycompounds, as well as polyhydroxyalcohols, but no monomer based on polyhydroxyalcohol has yet been synthesized and tested. The only near example could be glycerol monoacrylate, that has two hydroxyl groups in the molecule and was found very effective as monomer in the gelcasting process [8]. That is the reason why xylitol, a polyhydroxyalcohol, was chosen for the present research. It is a non-toxic, renewable, water-soluble and inexpensive substance. The paper presents its synthesis, as well as application in fabrication of alumina elements by gelcasting method. The influence of the monomer content in the suspension is dis-

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cussed and the main results concerning the properties of the suspensions and gelcast elements are compared to those obtained with the application of commercial low-toxic monomer 2-hydroksyethyl acrylate.

2. Experimental

2.1. The synthesis of the new compound

The synthesis route of 1-O-acryloylxylitol (Akr-X) is shown in Fig. 1. The aim of the synthesis, was the selective substitution of acryloyl group instead of hydroxyl group to the xylitol molecule. It was carried out in three stages, analogous to the synthesis route reported for 3-O-acryloyl-D-glucose [5]. In the first stage (Fig. 1a) was aimed at blocking four from the five hydroxyl groups in xylitol molecule by the reaction with acetone in acidic medium. The second stage was the esterification of the only remaining hydroxyl group, done by acryloyl chloride in the presence of amine. It allows to introduce the functional group with the double bond to the molecule. The third stage (Fig. 1c) was focused on acidic hydrolysis that unlocks the hydroxyl groups. The final product is ready to use as an aqueous solution (20%) or as a pure monomer after evaporating the solvent.

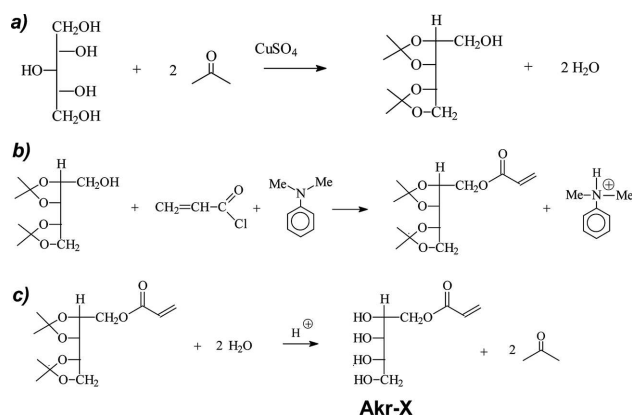


Fig. 1. The synthesis of 1-O-acryloylxylitol (Akr-X)

2.2. Materials and other components of the slurries

The ceramic powder used in the research was a high purity α -Al₂O₃ TM-DAR (Taimei Chemicals Ltd., Japan) of

mean particle size $D_{50} = 0.15 \mu\text{m}$ and specific surface area $S_{BET} = 14.5 \text{ m}^2/\text{g}$. Diammonium hydrocitrate, DAC (POCh, Poland) and citric acid, CA (Sigma) were used as dispersants. 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. Two monomers were applied, newly synthesised Akr-X and commercially available 2-hydroksyethyl acrylate, HEA (Fluka) accompanied with a cross-linking agent, N,N'-methylenebisacrylamide, MBAM (Fluka). The molecules of that gelating system is shown in Fig. 2.

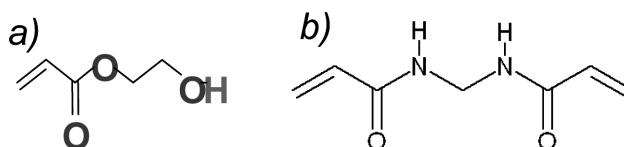


Fig. 2. Chemical formula of a) 2-hydroxyethyl acrylate (HEA) and b) N,N'-methylenebisacrylamide (MBAM)

2.3. Shaping procedure

Firstly, ceramic slurries were prepared at room temperature in the containers made of alumina. The dispersants, the monomer and activator were dissolved in distilled water and the ceramic powder was added at last. The contents of all additives are listed in Table 1. The slurries were mixed in a planetary ball mill (PM100, Retch) for 60 minutes with a speed of 300 rpm. Next, the slurries were degassed under reduced pressure in a vacuum desiccator supplied with a magnetic stirrer. Just before casting the slurries into the round plastic moulds ($\varphi 20$), the initiator was added and they were mixed for 3 minutes by magnetic stirrer. The access of the fresh air was cut off by placing the mould filled with slurries under cover for 6h to complete the gelation process. After the gelled bodies were obtained and removed from the moulds they were dried in air at room temperature for 24h, then at 50°C for 24h. Just before sintering they were dried at 105°C for 1h. The specimens were sintered at 1500°C for 2h.

TABLE 1

The composition of the ceramic suspensions prepared for the gelcasting

Slurry (denotation)	Al ₂ O ₃ powder [vol %]	DAC + CA dispersant [wt % + wt %]*	Akr-X/ HEA monomer [wt %]*	TEMED activator [wt %]**	MBAM cross-linker [wt %]**	APS initiator [wt %]**
TX3	50	0.30 + 0.10	3.0 (Akr-X)	2.0	-	0.3
TX5	50	0.30 + 0.10	5.0 (Akr-X)	2.0	-	0.3
THA3	53	0.14 + 0.10	3.0 (HEA)	2.0	2.0	0.1
THA5	53	0.14 + 0.10	5.0 (HEA)	2.0	2.0	0.1

* amount with respect to the powder content, ** amount with respect to the monomer content

2.4. Characterization techniques

The viscosities of the suspensions after mixing and degassing, but before initializing of the polymerization, were measured by using Brookfield DV+II-Pro rheometer (Brookfield Engineering Laboratories Inc. Massachusetts, USA) as a function of shear rate. The idle time was calculated on the basis of viscosity measurements in time at a constant shear rate 0.1s^{-1} , 3 minutes after addition of the initiator to the suspension. The densities of green and sintered 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 [9]. The microstructure of the specimens was observed in scanning electron microscope ZEISS (Germany).

3. Results and discussion

3.1. Influence of the monomers on viscosity of the slurries

As shown in Fig. 3., all of the viscosity curves reveal the shear-thinning behavior of the suspensions. All of the suspensions present low viscosity, low enough to fill the complex moulds in details, even despite very high alumina content (over $50_{vol}\%$). However some differences are visible. The amount of dispersants were matched individually for the slurries with different monomers, on the basis of viscosity curves obtained for the suspensions where $3_{wt}\%$ of monomers were applied. Both monomers have a positive impact on the viscosity. $5_{wt}\%$ addition of each monomer decreases the viscosity, that is lower than the viscosity of the slurry with $3_{wt}\%$ monomer content. Moreover, the viscosities of the suspensions with HEA are lower than with Akr-X, even despite the higher solid content. That was to be expected, because HEA is a low-viscous liquid whereas Akr-X is a high-viscous resinous substance.

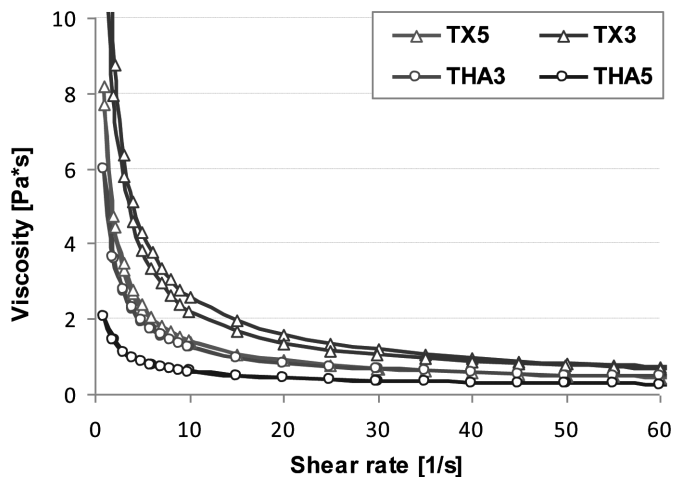


Fig. 3. Viscosity curves for alumina suspensions with HEA and Akr-X (compositions according to Table 1)

The monomer content in the suspension is a crucial issue, because after the polymerization, that macromolecular network is responsible for the mechanical strength of the green elements. Generally, the larger the network is, the stronger the green bodies, so higher content of the monomer in the suspension leads to higher mechanical strength of the specimens before the sintering. However, the more organic substances are added to the suspension, the more difficult it is to burn them out during sintering, so the easier it is to cause any defects. Usually the amount of the monomer in the gelcasting procedure should be not larger that $5_{wt}\%$ and the amount of $3_{wt}\%$ is thought to be the minimum quantity.

3.2. The idle time control

The composition of activator (catalyst) and initiator is essential additive to start the polymerization in situ in the ceramic suspension. Their contents also allow to control the idle time of the process, it means the time interval between adding the initiator to the suspension and the real start of the reaction. The creation of the polymer leads to the rapid and big increase of the viscosity of the slurries. From the technological point of view, the idle time shouldn't be then too quick, as all the operations concerning mixing and filling the suspension to the mould regard some time. However, the idle time shouldn't be too long, because of the simple economical issues – the whole shaping process should be as fast as possible. At the same time, the initiator content has a large influence on the mechanical properties of the green bodies. The mechanism of polymerization assumes creating free radicals and chain reaction. Too high initiator content leads to the creation of too many free radicals that start the polymerization and finally a lot of short polymeric chains are created. On the other hand, too low initiator content might be not efficient. The ideal situation is when only few long polymeric chains are created.

For gelcasting the elements for that research, the polymerization was initialized by 0.3 and 0.1 $_{wt}\%$ of APS for the slurries with Akr-X and HEA respectively, having the idle time around 25 minutes. Table 2 lists the values of the idle time for different amount of initiator.

TABLE 2

The idle time values controlled by the initiator content

monomer	activator content [wt %]	initiator content [wt %]	idle time [min]
Akr-X	2	0.3	25
	2	0.5	20
	2	0.7	18
	2	1.0	14
HEA	2	0.1	23
	2	0.3	9
	2	0.5	6
	2	1.0	4

3.3. Properties of the ceramic bodies

Table 3 shows the results of characterization of the green and sintered gelcast elements. First of all, it has to be noticed that it was not possible to obtain the specimens from the suspension with 3_{wr}% of commercial monomer HEA together with 2_{wr}% cross-linking agent. The exfoliation of the elements was highly visible, especially while demoulding, the elements disintegrated or split off into layers while machining, and the shape of the mould was not reflected at all. Increased amount of the monomer made it possible to get a desired shape. At the same time, the specimens obtained by applying new Akr-X without the external cross-linker for the gelcasting procedure were easy to demould and machine without any damage.

TABLE 3

The properties of the green elements

Slurry (denotation)	Relative density [% TD]	Tensile strength [MPa]
TX3	59.1 ±0.6	4.3 ±0.6
TX5	57.4 ±0.5	5.0 ±0.5
THA3	-	-
THA5	60.1 ±0.4	-

Table 3 lists the values of relative density and tensile strength of the green elements. The densities are comparable, certainly the elements shaped by polymerizing HEA are more densified due to higher solid content of the suspension. However, the tensile strength of the green bodies can't be compared. The 'Brazilian test' used for the calculation of that value assumes that the tensile force causes the split through the diameter of the sample parallel to the direction of the force. That could not be measured for the samples with polymerized HEA, because of the exfoliation. Fig. 3 shows the photographs of the samples after and during the 'Brazilian test' accompanied with the functions of force vs strain. It can be noticed, that even small forces cause exfoliation of the sample containing polymerized HEA, whereas the samples with poly(Akr-X) split properly. Their tensile strengths are then very high, over 4 MPa, comparing to values reported in other papers. Surely, the hydrogen bonds formed between the polymer chains are strong enough to provide a well cross-linked network, without additional binders. Certainly, the higher polymer content in the sample, the higher mechanical strength of the green bodies, but the amount of 3_{wr}% of Akr-X is enough to get satisfactory properties. The homogeneous green microstructure can be seen at SEM photo of a fracture surface (Fig. 5a-b). Moreover, polymeric bridges are visible when 5_{wr}% of monomer is applied.

Table 4 lists the shrinkage and density values after sintering the bodies with poly(Akr-X) at 1500°C for 2h. The densities of the elements are very high, around 99%. It's clearly visible, that the more organic content in the sample, the more difficult it is to get full densification, because more pores are likely to be created, that is also confirmed by the SEM images (Fig. 5c-d).

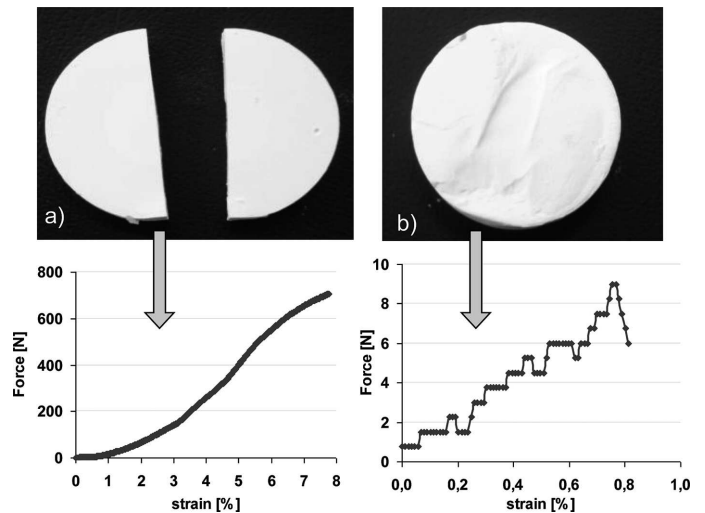


Fig. 4. Photo of the samples after 'Brazilian test' accompanied with the function of force vs strain registered during the test, a) sample with poly(Akr-X), b) sample with poly(HEA)

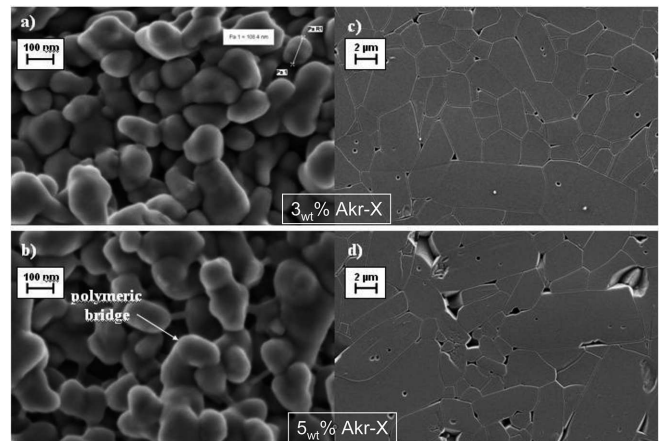


Fig. 5. SEM microstructure of green (a,b) and sintered (c,d) elements, obtained by polymerizing *in situ* 3_{wr}% Akr-X (a,c) and 5_{wr}% Akr-X (b,d)

TABLE 4

The properties of the sintered elements

Slurry (denotation)	Linear shrinkage [%]	Relative density [% TD]
TX3	17.2 ±0.9	99.2
TX5	17.8 ±0.8	98.9

4. Conclusions

Following the synthesis route elaborated for acryloyl derivatives of monosaccharides, similar derivative of xylitol, a polyhydroxyalcohol, was synthesized. This monomer was applied for a gelcasting of alumina powder. It appears that 1-O-acryloylxylitol (Akr-X) is an effective processing agent, it does not only play the role of monomer polymerizing *in situ* in the suspension, but also does not need external cross-linker to create a strong macromolecular network. The specimens

obtained by gelcasting a suspension with Akr-X are characterised by very high values of tensile strength of green bodies, as well as very high densities of sintered elements. The quality of the products is incomparably better than if commercial 2-hydroxyethyl acrylate (HEA) together with MBAM as cross-linking agent is applied for the same procedure. The research shows that not only acryloyl derivatives of monosaccharides, but generally of polyhydroxycompounds are promising group of substances to use in the process.

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REFERENCES

- [1] O.O. Omatete, M.A. Janney, S.D. Nunn, *J. Eur. Ceram. Soc.* **17**, 407 (1997).
- [2] A.C. Young, O.O. Omatete, M.A. Janney, P.A. Menchhofer, *J. Am. Ceram. Soc.* **74**, 612 (1991).
- [3] J. Yang, J. Yu, Y. Huang, *J. Eur. Ceram. Soc.* **31**, 2569 (2011).
- [4] P. Bednarek, Y. Sakka, M. Szafran, T. Mizerski, *J. Eur. Ceram. Soc.* **30**, 1795 (2010).
- [5] P. Falkowski, P. Bednarek, A. Daneliska, T. Mizerski, M. Szafran, *J. Eur. Ceram. Soc.* **30**, 2805 (2010).
- [6] M. Szafran, P. Bednarek, A. Szudarska, *Advances in Science and Technology* **62**, 163 (2010).
- [7] A. Szudarska, T. Mizerski, M. Szafran, *Archives of Metallurgy and Materials* **56**, 1211 (2011).
- [8] C. Tallon, D. Jach, R. Moreno, M.I. Nieto, G. Rokicki, M. Szafran, *J. Am. Ceram. Soc.* **90**, 1386 (2007).
- [9] J.R. Capua Proveti, G. Michot, *Int J Fract.* **139**, 455 (2006).

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