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Initiator effect on the gelcasting properties of alumina in a system involving low-toxic monomers

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Abstract

Various low-toxicity gelling systems based on monofunctional monomers: methacrylamide, poly(ethylene glycol) methyl ether methacrylate, and 1-vinyl-2-pyrrolidone, difunctional monomers: *N*,*N*′-methylenebisacrylamide and poly(ethylene glycol) dimethacrylate were studied for powder dispersion and gel formation in 55 vol.% alumina suspensions. At optimum dispersant level the viscosity of aqueous slurries consisting of alumina and organic monomers at the shear rate of 20 s^{-1} was less than 1.5 Pa s, i.e., convenient for gelcasting slips. The storage and loss moduli, and complex viscosity of pure hydrogels were characterized as a function of initiator concentration. The effect of the initiator concentration on idle times of gelation of ceramic suspensions as well as on green flexural and tensile strengths of gelled bodies were determined. The idle times varied markedly, depending on the chemical character of monomer used. The monomers containing ester and ether groups exhibited shorter idle times than those containing amide groups. The green flexural and tensile strengths of gelled bodies for individual monomers were functions of initiator concentration. For each monomer system an optimum initiator concentration was found, at which the highest green strength was measured. This was due to more polymerization degree of hydrogel, as was revealed by dynamic rheometry.

Keywords: A. Suspensions; D. Al_2O_3; Gelcasting; Low-toxic monomers

1. Introduction

Gelcasting is a near-net-shape forming method of advanced ceramic materials that combines polymer physical chemistry, colloidal chemistry, and ceramic technology. Aqueous gelcasting has been widely studied and extensively used in recent years because water is the most environmentally friendly raw material for wetting ceramic powders. In the beginning of the process, a small amount of organic gel-formers are dissolved in water to obtain the so-called premix solution. Next, ceramic powders are dispersed in the premix solution and then cast in a nonporous mold. By acting of temperature or/and chemical cross-linking agents the gel-formers create a strong polymer hydrogel, which permanently immobilizes the ceramic slurry in the desired shape of the mold cavity. After removal from the mold, the part is dried, then the polymer is burned out, and the sample is sintered to a high density. Gel-cast green bodies also have a high green strength, which allows them to be easily machined before sintering.

The original study on gelcasting involved polymerization of acrylamide monomers, as gel-formers. Monofunctional acrylamide, $CH_2{=}CHCONH_2$ and difunctional *N*,*N*-methylenebisacrylamide, $(CH_2{=}CHCONH)_2CH_2$ were used as the reactive organic monomers [1,2]. The industry, however, has been reluctant to use gelcasting because the main component of the gelling system, acrylamide, is a neurotoxin [3]. Hence, processes of reduced toxicity were searched for, and many alternative gelling systems based on low-toxicity monomers were demonstrated by Janney et al. [4]. On the other hand, gelcasting techniques utilizing environmentally friendly polymers or biopolymers as gel-formers can be categorized as the cross-linking of poly(vinyl alcohol) polymers by metal ion complexation [5], cross-linking of biopolymers, for example, chitosan cross-linked by glutaraldehyde [6], thermoreversible gelation of slips containing biopolymers such as gelatin [7], agarose [8] and carrageenans [9], and temperature activated cross-linking of biopolymers such as proteins [10], and

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ovalbulins [11]. Many new gel-formers especially from biopolymers are being still studied.

The subject of present consideration are low-toxic monomers only. In spite of abundant literature on acryloamide—*N*,*N*′-methylenebisacrylamide system there is much less experimental data published on the monomers constituting low-toxic systems [4,12,13]. In this work, various gelling systems based on the monofunctional monomers: methacrylamide (MAM), methoxy-poly(ethylene glycol) monomethacrylate (MPEGMA), and *N*-vinyl pyrrolidone (NVP), difunctional monomers: *N*,*N*-methylenebisacrylamide (MBAM) and poly(ethylene glycol) dimethacrylate (PEGDMA) were investigated to determine the effect of the type of monomer used on powder dispersion and gel formation in 55 vol.% alumina suspensions. The powder dispersion was characterized by viscosity measurements. The gel formation was evaluated by kinetics of polymerization of suspensions with gelling systems as well as by the green tensile and flexural strengths of gelled samples. The dynamic modulus of pure low-toxicity hydrogels have also been evaluated and discussed.

2. Materials and methods

The alumina powder CT 3000 SG with a specific surface area of 7.0 m^2/g (Alcoa Chemie, Ludwigshafen, Germany) was used as the raw material.

2.1. Monomer systems

The types of monomers investigated in this work, depicted in Table 1, were selected based on work done by Janney et al. [4].

The premix solutions were made as 15 wt.% solutions in distilled water of each monomer and crosslinker combination. The weight ratio of monomer to crosslinker was 6:1 for MBAM and 3:1 for PEGDMA. The higher monomer to crosslinker ratio used with the MBAM gels reflects its lower molecular weight. Therefore, the crosslinking density for all monomer systems studied should be approximately the same. Four different combinations of monomer to crosslinker systems were studied: MAM-MBAM, MPEGMA-MBAM, MAM-PEGDMA, and (MPEGMA, NVP)-MBAM. In preparation of (MPEGMA,NVP)-MBAM solutions the molar ratio of MPEGMA to NVP was 1:1. It should be noted that methacrylamide monomer, MAM, was poorly dissolved in cold water, but lightly warming to temperature not exceeding 30 °C and simultaneous mixing caused successful dissolution during several minutes.

2.2. Apparent viscosity

Alumina powder was slowly added to each monomer solution with dispersant under agitation to prepare suspensions at 55 vol.% of solids. Ammonium polyacrylate (Darvan 821A, R.T. Vanderbilt Company Inc., USA) was used as the dispersant, in various concentrations to determine the point of minimum viscosity. All the slips components were further homogenized for 5 min by ultrasonication. The viscosities of the suspensions were measured using a rotary rheometer (Rheotest R.V.2, Rheotest Messgerate Medingen, Germany) fitted with double concentric cylinder geometry. All rheological measurements were conducted at shear rates ranging from 5 to 160 s^{-1}, at temperature of 20 °C.

2.3. Kinetics of polymerization

The redox pair consisted of ammonium persulfate, (APS), $(NH_4)_2S_2O_8$, (Aldrich, Germany) as the initiator and *N*,*N*,*N*,*N*′-tetramethylethylenediamine, (TEMED), $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (Fluka, Switzerland) as the catalyst was used to induce polymerization in ceramic suspensions. Ammonium persulfate aqueous solutions were prepared at a concentration of 10 wt.% prior to use. An optimized [14] 1:1 molar ratio of APS to TEMED was used. The catalyst was always added before the initiator, to avoid premature polymerization.

In order to determine the idle times, varied concentrations of the initiator and catalyst were tested for each monomeric system. The gelation of alumina suspensions was monitored by measuring the raise in viscosity in time. For this purpose, a Brookfield (RVDII+, Brookfield Eng. Labs. Inc., USA) viscometer equipped with the small sample adapter was used. The suspensions were submitted to a constant 0.1 s^{-1} shear rate and the viscosity value was registered every 30 s. The measurements were made at temperature of 27 °C, in N_2 filled chamber to avoid the effect of oxygen inhibiting polymerization process. The idle time was measured as a

Table 1
Monomer systems tested for ceramic suspensions

Monomer	Symbol	Chemical formula	Function
Methacrylamide[a]	MAM	$CH_2{=}C(CH_3)CONH_2$	Monomer
Poly(ethylene glycol) methyl ether methacrylate[b], $M \cong 300$	MPEGMA	$H_2C{=}C(CH_3)CO_2(CH_2CH_2O)_nCH_3$	Monomer
1-Vinyl-2-pyrrolidone[b]	NVP	C_6H_9NO	Monomer
N,*N*′-Methylenebisacrylamide[b]	MBAM	$(CH_2{=}CHCONH)_2CH_2$	Crosslinker
Poly(ethylene glycol) dimethacrylate[b], $M \cong 875$	PEGDMA	$CH_2{=}C(CH_3)CO(OCH_2CH_2)_nO_2CC(CH_3){=}CH_2$	Crosslinker

[a] Fluka, Switzerland.

[b] Aldrich, Germany.

function of concentration of initiator from 0.15 to 2 wt.% of the monomers. Kinetics of polymerization of a relatively toxic acrylamide monomer (Aldrich, Germany), were also tested for comparison.

2.4. Gel moduli

The premix solution of each monomer system was first degassed for 10 min and then mixed with initiator and catalyst. Next the solution was poured to a glass dish and allowed to gel in N_2 atmosphere at the temperature of 60 °C. Immediately after gelation the specimen wafers measuring 20 mm in diameter were cut from the crosslinked materials with a stamping tool. An oscillatory rheometer (RS 50, Haake, Germany) equipped with 20 mm platens in parallel-plate geometry was used to measure the dynamic rheological properties, such as storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) of the pure gels. To avoid specimen slippage during analysis, 400 fine grit sandpaper was cut to shape and attached to both platens with double-sided tape. The study was done in function of frequency from 0.01 to 10 Hz at constant shear stress of 10 Pa.

2.5. Samples preparation and evaluation of dry green strength and green density

Suspensions containing the optimum amount of dispersant were ball milled for 1 h, using an equal volume of suspension and alumina spheres as grinding media. After homogenization the slips were degassed and catalyst and initiator were added. The concentration of initiator was changed from 0.15 to 2 wt.% of the monomers, which corresponded to 0.004–0.05 wt.% of the total weight of the 55 vol.% ceramic suspension. Next the slips were poured to polyethylene molds and allowed to gel in N_2 atmosphere at 60 °C. After gelation the samples were dried initially in high humid chambers, next in less humid atmosphere. The last stage of drying was performed in oven at 60 °C.

The mechanical strength of green samples after drying process was evaluated by measuring tensile strength and flexural strength. The tensile strength was determined by a diametral compression method so-called 'Brazilian test' [15]. The disk-shaped samples for diametral compression had a diameter of 30 mm and thickness of 10 mm. The flexural strength was determined from three point bending. The gel-cast bars 75 mm × 7 mm × 9 mm were used and the span was 50 mm. The crosshead speed was 0.5 mm/min for all samples. A universal testing machine FP100, TIRA Rauenstein was used.

The tensile strength of samples δ_t was calculated using the following expression:

$$\delta_t = \frac{2F_{max}}{\pi D h} \tag{1}$$

where F_{max} is the load applied at fracture, D and h are the diameter and thickness of the sample, respectively.

The flexural strength δ_f was calculated from:

$$\delta_f = \frac{3F_{max} l}{2h^2 b} \tag{2}$$

where l is the span, h and b are the thickness and width of the bar, respectively.

The reported tensile and bending strengths were the averages of at least five determinations.

The green density was calculated from the weight and dimensions of a minimum of five samples. The dimensions were measured after drying process with a digital caliper accurate to ±0.01 mm. The sample weight was accurate to ±0.0001 g and was corrected in consideration of the organic and moisture content.

3. Results and discussion

3.1. Apparent viscosity

Low viscosity is beneficial for both mixing and casting in the slurry processing. It is, therefore, important to determine the optimum amount of dispersing agent, i.e., the point of minimum viscosity. The dependence of viscosity of the 55 vol.% alumina slurry containing MAM-MBAM monomers as a function of the shear rate for several fixed dispersant levels is shown in Fig. 1. The viscosity can be seen to approach a minimum at 0.5 wt.% (per dry powder) of Darvan 821A. At this concentration of dispersant, the viscosity at the shear rate of 20 s^{-1} was less than 1.5 Pa s, i.e., convenient for gelcasting slips. For each molecular weight of the dispersant, there is a critical amount of polyelectrolyte that has to be added to achieve good stabilization of the suspension and its low viscosity. This corresponds to the saturation limit of polyelectrolytes on Al_2O_3. Further addition of dispersant produces an excess of polymer in solution so the viscosity increases [16]. All the slips prepared in this work revealed a shear thinning. This behavior is characterized by a decrease in viscosity with increasing shear rate

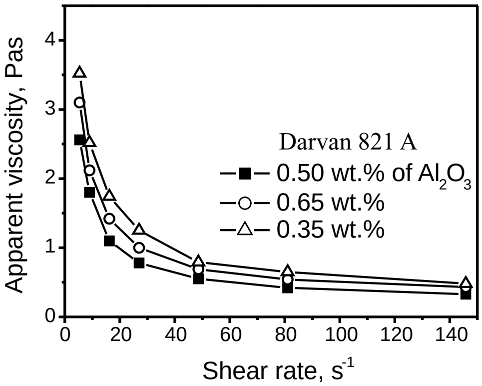

Fig. 1. Effect of deflocculant concentration on the viscosity of 55 vol.% Al_2O_3 suspension in 15 wt.% (per solution weight) MAM-MBAM monomers solution.

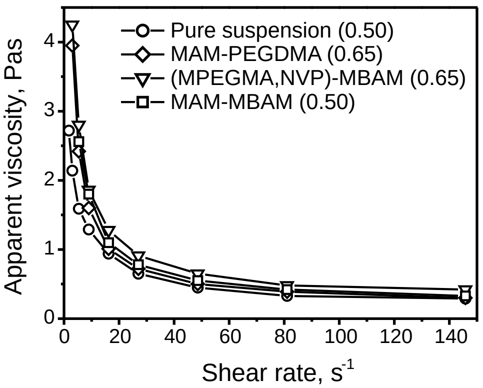

Fig. 2. Comparison of the minimum viscosities of 55 vol.% Al_2O_3 suspensions containing different monomers. The numbers in parenthesis refer to optimum deflocculant concentration.

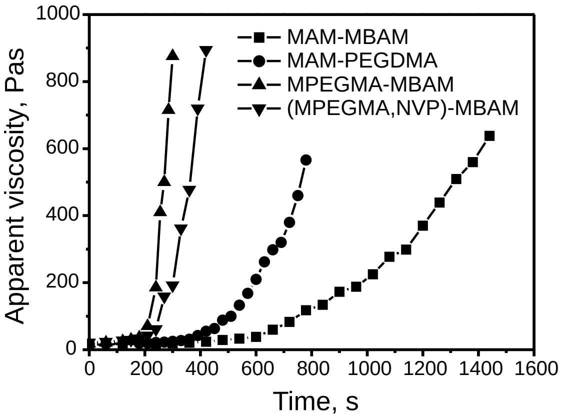

Fig. 3. Polymerisation kinetics of 55 vol.% Al_2O_3 suspensions containing different monomers. The initiator concentration was 1.3 wt.% of monomers.

and is typically found in dispersion of ceramic suspensions containing high percentage of solids.

Fig. 2 illustrates the minimum viscosities of alumina slurries containing different types of monomers, and the minimum viscosity of pure alumina suspension. As can be seen, the studied monomers caused small changes to the system viscosity and to the amount of deflocculant required for stabilization, compared to pure alumina suspension. All slurries containing monomers with amide groups (MAM-MBAM) required 0.5 wt.% of dispersant to achieve a minimum viscosity. A little higher level of dispersant (0.65 wt.%) was required for stabilization of slurry containing monomers with ether and esters groups (MPEGMA, MPEGDMA). It may result from interactions between alumina surface and monomer functional groups. Additionally the MPEGDMA and PEGDMA monomers are not single monomers but oligomers containing long chains in their structure (see Table 1) that affect on their mobility in the suspension.

3.2. Kinetics of polymerization

A mixture of mono- and difunctional unsaturated monomers polymerizes in the presence of free radicals to form a network polymer. The free radicals are generated by initiator, while the catalyst facilitates decomposition of the initiator so that radicals are produced at sufficient rate at low temperature. In the radical polymerization systems, it is common to observe a period of inactivity between the time of introduction of initiator and catalyst and the actual beginning of the polymerization reaction. This period is known as the induction period or idle time. For most systems, the viscosity remains nearly constant during the idle time, and then increases rapidly as gelation takes place. Fig. 3 is a typical representation of the viscosity variation versus time for alumina suspensions containing several low-toxicity monomer systems: MAM-MBAM, MAM-PEGDMA, (MPEGMA,NVP)-MBAM and MPEGMA-MBAM. As can be seen, the monomers containing ester and ether group—MPEGMA or carbonyl group—NVP showed shorter induction time and higher polymerization rate than those containing the amide group—MAM. A collective plot of the idle times of suspensions containing low-toxicity monomers, as a function of initiator concentration, is given in Fig. 4. The idle times of suspensions containing a relatively toxic acrylamide monomer system (AM-MBAM) are also plotted in Fig. 4, for comparison. In whole initiator concentration the suspensions containing low-toxicity monomers exhibited longer initiation time than those containing the acrylamide (AM) monomer. The difference in the idle time is particularly observed in the case of acrylamide (AM) and methacrylamide (MAM) monomers. In both types of monomers the amide group is the functional group, but other factors such as the steric factors strongly affect on the kinetics of polymerization. In acrylamide, $CH_2{=}C(H)CONH_2$, the carbon atom responsible for polymerization is more uncovered than in methacrylamide, $CH_2{=}C(CH_3)CONH_2$, so the radical attack is easier for more uncovered carbon atom of AM. Moreover, formed at the initiation stage methacryl macroradicals are better

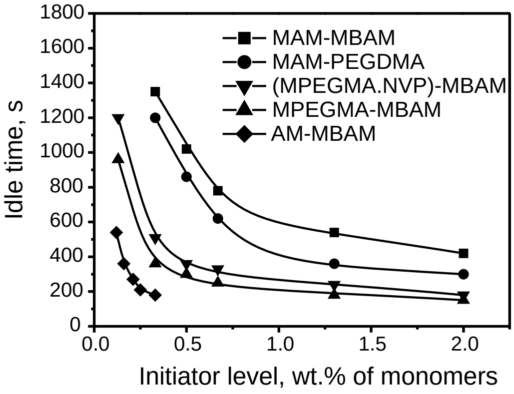

Fig. 4. Effect of initiator concentration on the idle time for gelation of suspensions containing different monomers.

stabilized by slight electrodonor induction effect of methyl group than acryl macroradicals [17].

From Fig. 4 it is seen that the crosslinking monomer affects on initiation time. Methacrylamide crosslinked by *N*,*N*-methylenebisacrylamide (MBAM) exhibited longer initiation time, than the same monomer crosslinked by PEGDMA. The PEGDMA monomer contains the ester and ether group, while the MBAM contains the amide group. Therefore, monomers containing ester and ether group may have a favorable influence on polymerization kinetics.

The polymerization experiments also revealed that the combination of two monofunctional monomers might be a useful tool to adjust the initiation time. The suspensions containing MPEGMA-MBAM system exhibited shorter induction period than those containing (MPEGMA,NVP-MBAM) monomers.

It should be noted that other parameters of polymerization such as pH, temperature, chemical character of the initiator or catalyst influence the polymerization kinetics. For this reason the results shown in Fig. 4 are mainly comparative. These results may change when other initiator would be used instead of ammonium persulfate. Moreover, the effect of ceramic grains on the kinetics of polymerization is important. As it was shown by Chu and Halloran [18], the kinetics of polymerization for alumina and hydroxyapatite suspensions containing the same monomers were different.

3.3. Gel moduli

The mechanical properties of pure hydrogel are the first criterions to estimate its suitability for gelcasting process. The mechanical strength of the pure wet gel influences the wet strength of green ceramic gel-cast body before drying process, which is important for demoulding operation. We characterized the wet gel strength by dynamic mechanical properties, such as G', G'' and η^*, the storage modulus, loss modulus and complex viscosity, respectively. For a pure, homogeneous liquid obeying linear viscoelastic laws, G' may be interpreted as the elastic modulus which is related to the strength of the gel, G'' is an indicator of the viscous nature and η^* may be interpreted as the viscosity [19]. Fig. 5 shows the storage modulus, loss modulus and complex viscosity for (MPEGMA,NVP)-MBAM wet gel made with 1.3 wt.% of initiator level on the monomers base. According to the data presented in Fig. 5, the slope of complex viscosity curve in double logarithm plot is -1, implying that the gel is solid in nature and has substantial yield strength. Another important feature of these data is that G' (and to a lesser extend, G'') exhibits little, if any dependence on frequency, and G' exceeds G'' by more than an order of magnitude. Taken together, these two characteristics—G' independent on frequency and $G' \gg G''$—confirm that the cross-linked gel behaves as a highly elastic material [20]. Similar behavior was observed with regard to the other gels produced in this study. However, although for all studied gels, the G' was always about one order of magnitude higher than G'' and the slope of complex viscosity was -1, the gels showed more or less pronounced dependence on frequency, as is shown in Fig. 6. While G' values for MPEGMA-MBAM and (MPEGMA,NVP)-MBAM gels were independent on frequency, the storage modulus of polymethacrylamide gels (MAM-MBAM and MAM-PEGDMA) showed a weak dependence on frequency. The increase of G' with increasing frequency for MAM gels was probably due to water expulsion from the gel structure. Solvent expulsion after polymerization was particularly notable for MAM gels, where more than 10% of water could be expelled after polymerization [4]. Therefore, the dynamic oscillations could modify the gel structure during G' measurements by accelerating water expulsion and consequently making the gel more rigid.

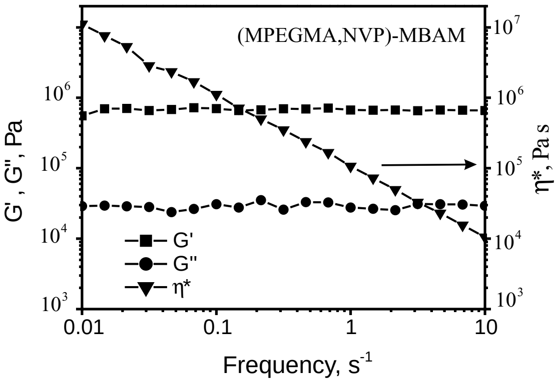

Fig. 5. Storage and loss modulus, and complex viscosity of a hydrogel produced with (MPEG,NVP)-MBAM monomers. The initiator concentration was 1.3 wt.% of monomers.

Fig. 7 illustrates the storage moduli of gels produced with (MPEGMA,NVP)-MBAM monomers at several initiator levels. From Fig. 7 it is seen that the storage modulus increases with increasing initiator level. On the other hand, the storage modulus of a hydrogel is correlated with its crosslinking density [21]. Therefore, from Fig. 7 it follows that the effective crosslinking density of the hydrogel improves with more ammonium persulfate as initiator.

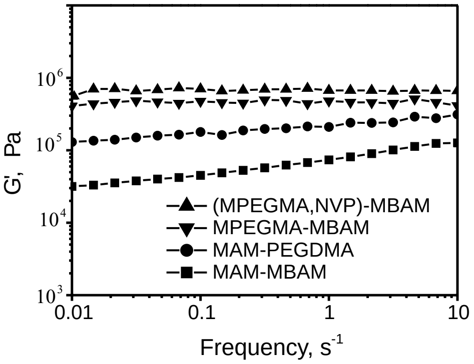

Fig. 6. Comparison of storage modulus of hydrogels produced with different gelling systems. The initiator concentration was 1.3 wt.% of monomers.

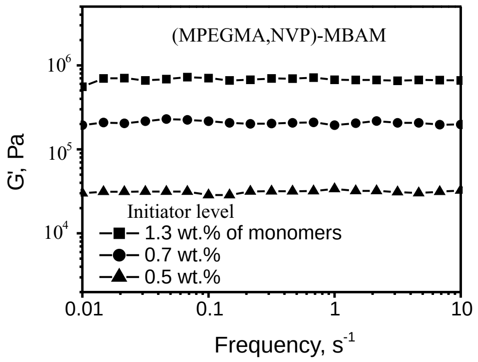

Fig. 7. Comparison of storage modulus of (MPEGMA,NVP)-MBAM hydrogels produced with several different initiator concentrations: 0.5, 0.7 and 1.3 wt.% of monomers.

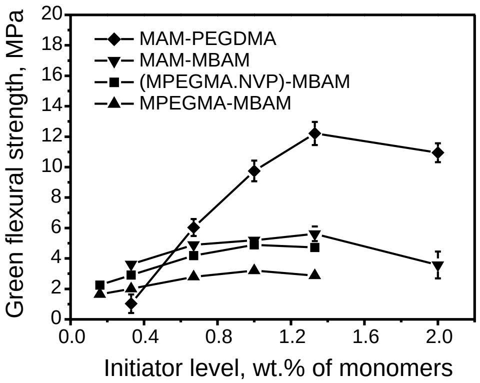

Fig. 9. The green flexural strength of alumina samples containing different gelling systems vs. the initiator concentration.

3.4. Dry green strength and green density

Figs. 8 and 9 show a dependence of the green tensile and flexural strengths of gel-cast samples after drying process as a function of initiator concentration in the ceramic slurry. The concentration of initiator was changed from 0.15 to 2 wt.% of the monomers, which corresponded its level of 0.004–0.05 wt.% of the total weight of the 55 vol.% ceramic suspension. In Figs. 8 and 9 one can see the trend as the green tensile and flexural strengths at first increase with increasing initiator concentration. At the optimum initiator level, the green tensile and flexural strengths reach maximum values. Further addition of initiator causes a decrease of green strength. Although gelation of the slurries could be achieved even at a small concentration of initiator, the gelled bodies showed poor mechanical strength for the lack of sufficient crosslinking of the polymer. Therefore, it was necessary to enhance the degree of polymerization by free-radical polymerization of the monomers using more ammonium persulfate as initiator. The gelled bodies thus prepared showed high mechanical strength. Too much initiator caused a decrease in green strength due to occurrence of a local gelation. As a result of the local gelation, lumps were immediately formed resulting in defects that lowered the mechanical strength. In fact, an examination of fracture surfaces revealed the detachment of lumps in some samples produced with large amount of initiator. However, it should be noted, that even if a local gelation did not occur, by using too much initiator one obtains a weak gel, or no gel at all because of the presence of too many initiation sites, so that the network segments of polymer are too short to form the gel structure.

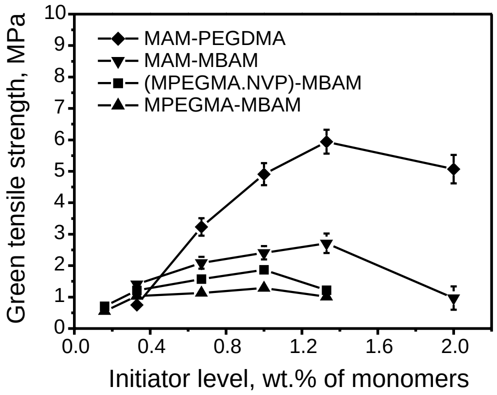

Fig. 8. The green tensile strength of alumina samples containing different gelling systems vs. the initiator concentration.

The highest strength was measured with samples containing MAM-PEGDMA system. For specimens prepared at optimum initiator level, the tensile and flexural strengths were 5.9 and 12.2 MPa, respectively. The lowest values of tensile and flexural strengths (1.3 and 2.4 MPa) were obtained for specimens prepared with MPEGMA-MBAM monomer system. However, the combination of two linear monomers increased the mechanical strength. The strengths obtained for samples prepared with (MPEGMA,NVP)-MBAM monomers were higher than those obtained for MPEGMA-MBMA system, as well as than those for NVP-MBAM system (less than 1 MPa, not presented in Fig. 8). It is worth noticing that the flexural strength of bars was greater than the tensile strength. In bending test the microcracks localized in the thin surface layer influenced the strength. On the other hand, the microcracks localized in whole volume of the sample affected the tensile strength.

It should be noted that the green strength of gel-cast specimens depends on several factors. The important points seem to be the chemical character of monomers, the weight ratio of monofunctional monomer to crosslinker, the amount of monomers in the suspension and the chemical character of the initiator and its concentration. In this work only the green strength dependence on initiator concentration was studied for suspensions with fixed monomers level on 2.5 wt.% per total suspension weight.

The green density was determined for samples prepared in the initiator concentration range where local gelation did not occur. The green density of gel-cast samples varied in the range of 56–57% of the theoretical density of corundum (3.98 g/cm^3) and was approximately the same for all low-toxic monomer systems.

4. Conclusions

In this work various low-toxic monomer systems were tested for powder dispersion and gel formation in 55 vol.% ceramic suspensions containing 2.5 wt.% of monomers (per total suspension weight). The monomers caused a negligible effect on the dispersion state compared to pure alumina suspension. At the optimum concentration of dispersant the viscosity at the shear rate of $20\,s^{-1}$ was less than 1.5 Pa s, i.e., convenient for gelcasting slips.

The study of the kinetics of polymerization showed that low-toxic monomers containing ester and ether groups exhibited higher polymerization rates than those containing amide groups. On the other hand, the relatively toxic acrylamide monomer showed much shorter idle times than the low-toxic methacrylamide, that probably resulted from steric factors. In acrylamide, the carbon atom responsible for polymerization was more uncovered, so the radical attack was easier.

The investigations of storage moduli of pure gels in function of initiator concentration revealed increasing polymerization degree with increasing ammonium persulfate level used as initiator. The polymerization degree affected on green flexural and tensile strengths of gelled ceramic bodies. To achieve high green strength an optimum concentration of initiator was necessary to enhance the degree of polymerization. At the optimum initiator concentration the green strength of gelled bodies depended on the type of monomer used. The highest green strength was obtained for MAM-PEGDMA system. The tensile and flexural strengths were 5.9 and 12.2 MPa, respectively. The ceramic bodies gelled with other monomers had lower tensile and flexural strengths in the range 1.3–2.7 and 3.2–5.6 MPa, respectively.

The green density of gelled bodies was approximately the same for all monomers and was equal to 56–57% of theoretical density of corundum, indicating good compaction behavior.

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