

Monomer systems for the gelcasting of foams

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Abstract

The association of the gelcasting process with the aeration of ceramic suspensions allowed the development of a novel category of porous ceramics with unprecedented mechanical properties. One of the critical points in the processing of porous ceramics by this route involves the setting of the foams, which is based on a gelling reaction by the in situ polymerization of organic monomers dissolved in the liquid phase. A variety of monomeric systems that are known to be suitable gelling agents for setting ceramic suspensions into dense forms were investigated in this work, with a view to the production of ceramic foams. These systems, namely ammonium acrylate, *N*-hydroxymethylacrylamide, methacrylic acid, methacrylamide and methylene-bisacrylamide, were studied considering the main requirements to produce ceramic foams, which include short setting time and high wet green strength. The effects of monomer type on powder dispersion, reaction kinetics, and green strength of wet and dried gelled bodies were investigated. The results revealed that the chemical characteristics of each system can affect the dispersion and rheological properties of suspensions. Polymerization kinetics and wet and dry mechanical strength varied markedly, depending on the type of monomer used. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years, several consolidation techniques have been developed to manufacture ceramic bodies with refined microstructure,¹ complex shapes,^{2–5} and minimum need for machining. Some of these advances have led to the development of new technologies, such as the solid freeform fabrication methods^{6,7} and have been gradually transferred to industry.⁸ Many of these techniques are based on a gelation process, which converts a concentrated colloidal suspension from the liquid to the solid state after being moulded in the required shape.

The use of gelling systems has also been successfully applied in the manufacture of porous ceramics.^{4,9–11} The emphasis in this work is given to the gelcasting of foams route,^{10,11} which was shown to provide porous ceramics with unprecedented properties, such as high mechanical strength,¹² high permeability¹³ and low thermal con-

ductivity.¹⁴ The process is based on the aeration of a colloidal suspension in the presence of foaming agents, and setting by the in situ polymerization of water-soluble organic monomers. The production of porous bodies with porosity levels up to 90%, spherical pores in the range of 40–200 μm, and dense struts was reported.^{12,15} The properties can be controlled by producing pore fractions and pore sizes in various ranges.

The most critical factor in successfully producing porous bodies comprises the choice of gelling substances and the control of gelling reactions. Initially, the gel precursors should not affect the state of powder dispersion and the stability of suspensions, in order to allow the production of homogeneous microstructures and highly dense struts. Also, the monomer addition should not cause a significant increase in the suspension viscosity, which would limit the ability of foam generation. After foam generation, the gelation must be sufficiently fast to prevent foam collapse, which occurs due to liquid drainage by capillary and gravitational forces.¹⁶ Finally, the polymeric network formed must be sufficiently strong to support the porous structure, even at the typically low solids loading used in the process. In spite

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of its large porosity, the gelled foams must withstand demoulding, handling, drying and machining without damage.

Originally, the gelcasting system was developed with the use of acrylamide as the main gelling substance.⁸ Alternative gelling systems have been investigated in order to substitute acrylamide because of its hazards. Janney et al.¹⁷ demonstrated that a range of monomers, such as ammonium acrylate, *N*-hydroxymethylacrylamide, methacrylic acid, methacrylamide and methylene-bisacrylamide can be applied to set ceramic suspensions.

In this work various gelling systems were investigated, considering that the requirements to setting of foams are more strict than those found in dense ceramics production. The study reports the influence of monomer type on the rheological behavior of ceramic suspensions, polymerization kinetics, and on green strength of wet and dry specimens. These properties are essential to optimize the properties of the end-material.

2. Materials and methods

The process of gelcasting ceramic foams consists of preparing a suspension containing the ceramic powder, water, dispersants and monomers, prior to foaming and setting.^{10,11} Calcined alumina (A-1000 SG, Alcoa, specific surface area of 8.4 m²/g) 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 and coworkers for production of dense ceramics.¹⁵ Ammonium acrylate monomer, which has been extensively employed in the gelcasting of foams,^{10–15} was also tested for comparison.

All monomers were diluted in distilled/deionized water at a concentration of 25 wt.%. Solutions were prepared either with one single type of monomer or

associating two types of monomers at a 1:1 weight ratio. An aliquot of 1 mol% crosslinking agent (MBAM) was added to all monomer solutions, except to the solutions containing HMAM, which do not require a crosslinker for gelation.

Methacrylic acid (MA) was neutralized with NH₄OH up to a pH of 7.0 prior to its use in order to increase the reactivity. This procedure was employed because most generally the polymerization reaction is inhibited in the acidic pH range.¹⁵ Moreover, a higher pH is more suitable for the dispersion of alumina suspensions with the addition of polyelectrolytes.¹⁸ Methacrylamide monomer (MAM) was not tested on its own due to its low solubility in pure water.

2.2. Rheology of ceramic suspensions

Calcined alumina was slowly added to each monomer solution under agitation to prepare suspensions at 40 vol.% solids. Suspensions with higher solids loading are avoided in the gelcasting of foams due to their low foaming ability under agitation.¹⁵ Ammonium polyacrylate (Dispex A40, MW = 10,000 g/mol, Ciba, England) was used as the dispersing agent, in various concentrations to determine the amount for optimum dispersion, i.e. the point of minimum viscosity. Each sample was ultrasonicated for 2 min. The pH of all suspensions was adjusted to 8.5 before the rheological measurements, with the addition of either NH₄OH or HCl. Rheological measurements were carried out with help of a Brookfield LV-DV III viscometer equipped with a small sample adapter. The shear stress versus shear rate curves were recorded in up and down sweep cycles, with shear rate varying between 0.2 and 330 s⁻¹. The measured curves were fitted to Casson's model,¹⁹ given by the equation:

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta \cdot \dot{\gamma}} \quad (1)$$

where τ is the shear stress (Pa), τ_0 is the yield stress (Pa), η is Casson's viscosity (Pa.s) and $\dot{\gamma}$ is the shear rate (s⁻¹).

Table 1
Monomer systems tested for setting of ceramic suspensions

Monomer	Symbol	Chemical formula	Function
Methacrylic acid ^a	MA	H ₂ CCCH ₃ COOH	Monomer
Methacrylamide ^b	MAM	H ₂ CCCH ₃ CONH ₂	Monomer
<i>N</i> -hydroxymethylacrylamide ^a	HMAM	H ₂ CCHCONHCH ₂ OH	Monomer
Ammonium acrylate ^c	AA	H ₂ CCHCOONH ₃	Monomer
Methylenebisacrylamide ^d	MBAM	(H ₂ CCHCONH) ₂ CH ₂	Crosslinker

^a Merck, Germany.

^b Sigma, USA.

^c Allied Colloids, England.

^d Pharmacia, Sweden.

2.3. Suspension preparation and gelation procedure

Alumina suspensions were prepared to study the polymerization kinetics and to produce samples for the evaluation of wet and dry green strength after gelation. Suspensions containing the optimum amount of defloculant were ball milled for 30 min, using an equal volume of suspension and alumina spheres as grinding media. The pH was then adjusted to 8.5 using either NH_4OH or HCl .

The redox pair composed of ammonium persulfate (APS, $\text{NH}_4\text{S}_2\text{O}_8$, Sigma, USA) as the initiator and N,N,N',N' -tetramethylethylenediamine (TMED, $(\text{H}_3\text{C})_4\text{N}(\text{CH}_2)_2\text{N}$, Sigma, USA) as the catalyst was used to induce polymerization in ceramic suspensions. Ammonium persulfate aqueous solutions were prepared at a concentration of 33.3% w/w prior to use. A new solution was prepared before each test to avoid ageing influence on the polymerization kinetics. An optimized²⁰ 1:1 molar ratio of APS and TMED was used. The catalyst was always added before the initiator, to avoid premature polymerization.

In order to study the polymerization kinetics, varied concentrations of the initiator and catalyst were tested for each monomeric system. The gelation of suspensions was monitored by measuring the raise in viscosity along time. For this purpose, a Brookfield LV DV-III 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 15 s. The initial temperature was fixed at $28.0 \pm 0.5 \text{ }^\circ\text{C}$.

2.4. Determination of wet and dry green strength

Samples for mechanical evaluation were prepared following the same procedure described above, using various initiator and catalyst concentrations. After the addition of reagents and homogenization, the suspensions were poured into cylindrical moulds with 20 mm in diameter and 50 mm in height to accomplish gelation.

Samples for wet green strength evaluation were stored in water-saturated atmosphere immediately after gelation to avoid moisture loss. A few instants before the test being carried out a sharp blade was used to cut each sample into shorter cylinders with 12 mm height. Wet green strength was inferred from the load required to intrude a steel rod ($\phi = 3 \text{ mm}$) 8 mm in depth into the samples at a displacement rate of 5 mm/min. This procedure was adapted from the gum industry, due to the lack of standardized tests for ceramic gels.²¹ The experiments were conducted in a universal testing machine (MTS-810).

For dry green strength, gelled specimens were previously dried at $100 \text{ }^\circ\text{C}$ and then cross-sectioned into smaller cylinders with the help of a diamond disc, having a height to diameter ratio between 0.2 and 2. These

cylinders were submitted to the diametral compression, or Brazilian test, at a displacement rate of 0.5 mm/min.²² In this test, the fracture starts under tension at the center of the sample, providing characterization of both gel strength and adhesion between polymer and ceramic particles. Moreover, effects due to poor surface finishing are negligible. The strength was calculated as follows,

$$\sigma = \frac{2F}{\pi hD} \quad (2)$$

where: σ is the strength (Pa), F is the fracture load (N), h and D are the specimen's height and diameter (m). Results were an average of at least four samples.

3. Results and discussion

3.1. Rheology of ceramic suspensions

The influence of monomer type on the dispersion of alumina suspensions is seen in Fig. 1, where Casson's viscosity [Eq. (1)] is plotted as a function of the defloculant concentration.

The rheological behavior of suspensions can be divided into two classes, according to the influence of monomer type on viscosity. One group of monomers, including HMAM and MAM-HMAM pair, caused negligible changes to the system viscosity and to the amount of defloculant required for stabilization, compared to pure alumina suspension. The minimum viscosity in this first group was of approximately 40–70 mPa.s, with defloculant concentration in the range of $2\text{--}3 \times 10^{-4} \text{ g/m}^2$. The other group, containing MA, MA-MAM and MA-HMAM pairs, required an amount of dispersant $\cong 10$ times higher ($2\text{--}3 \times 10^{-3} \text{ g/m}^2$) to reach minimum viscosity in the range of 1000–2000 mPa.s.

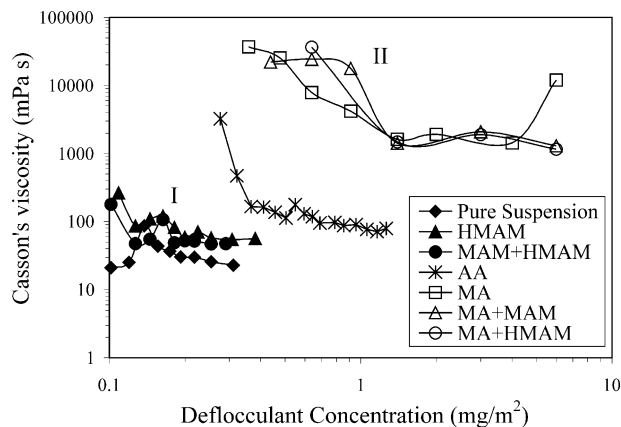


Fig. 1. Casson's viscosity of suspensions containing different gelling systems as a function of defloculant concentration (ammonium polyacrylate, Dispex A-40).

Suspensions containing AA monomers displayed an intermediate deflocculant consumption ($6\text{--}7 \times 10^{-4}$ g/m²) and minimum viscosities in the range of 100 mPa s.

It is believed that the influence of monomer addition on the dispersion state is a consequence of interactions between monomers and alumina surface, which depend on the chemical structure of monomers. The monomer systems that caused viscosity increase and higher deflocculant consumption contained either methacrylic acid (MA) or ammonium acrylate (AA), which have a carboxylate group in their structure. Positive sites at the surface of alumina particles in aqueous media attract the anions derived from the ionization of carboxylate groups, causing its specific adsorption onto the particles surface. The carboxylate group is also present in the ammonium polyacrylate used to deflocculate the suspensions, and causes the anchoring of some chain segments on the surface of alumina particles. However, in this case other chain segments form negatively charged loops and tails, producing a strong electrostatic repulsion between particles covered with deflocculant.²³ An additional stabilization mechanism occurs due to steric repulsion between alumina particles covered with polyelectrolytes, which rises from a local increase in the osmotic pressure caused by the interpenetration of these highly hydrophilic macromolecules.²⁴ A competition exists between the adsorption of ionized monomers and ionized polyelectrolytes. As the bulk concentration of the former is much higher, the particles surface becomes predominantly covered with monomers. Therefore, the interparticle repulsion is not enough to stabilize the suspension against flocculation, at conventional deflocculant concentrations. As the bulk concentration of deflocculant increases, a larger fraction of particles surface is covered with polyelectrolyte and the surface potential increases, producing a more stable suspension. Additional experiments are currently being carried out to clarify the reason for the difference in behavior between MA and AA, in spite of their similar structures. Nevertheless, the rheological behavior suggests that the interparticle potential energy of the systems containing either MA or AA present a secondary minimum at the region of minimum viscosity, causing weak flocculation of the suspension. The changes in the rheological behavior of alumina suspensions containing AA have been previously reported for alumina systems containing ammonium acrylate in gelcasting of foams.¹⁵

Considering the production of foam from monomer-containing suspensions, the high viscosity of suspensions containing monomers with carboxylated groups, MA in particular, limits foam generation by means of aeration. Nonetheless, high viscosity is usually associated to a yield stress, which imparts higher stability to the foam and prevents it from the collapse and from lamella-thinning processes before gelation.²⁵ Suspensions with low yield stress and low viscosity may be

easily foamed to produce samples with very high porosity. However, in this case the gelation kinetics must be well controlled to produce fast reaction onset because the foam structure changes rapidly. Since the degradation of foam alters the properties of the final product, it is believed that rheological properties are of prime importance to control properties like permeability and mechanical strength.

3.2. Kinetics of polymerization

After the addition of catalyst and initiator, the variation of viscosity along time generally followed a well-defined pattern. For most systems, the viscosity remained nearly constant during a period of time, called induction time, and then increased rapidly as gelation took place. The induction time varied according to catalyst/initiator concentration. The only exception to the previous behavior was detected for the MA-MAM system, which displayed a continuous viscosity increase from the moment of initiating reagents addition. Fig. 2 shows the viscosity variation with time for the MA-MAM system, which revealed an abnormal behavior. A typical polymerization behavior is also shown in Fig. 2 for the MAM-HMAM system, at various initiator/catalyst concentrations. For the production of ceramic foams, it is important to fix a short induction time followed by fast gelation. Under these conditions, foaming and molding can be accomplished with success prior to the viscosity increase, which ceases changes in foam structure.

Fig. 3 shows the influence of the concentration of initiator/catalyst on the induction time for gelation of suspensions containing different types of monomer. The system MA-MAM was not included, since it did not present an induction time. It may be noticed that monomers containing carboxylate group—AA and MA—showed shorter induction times than those containing the amide group. This suggests that the carboxylate

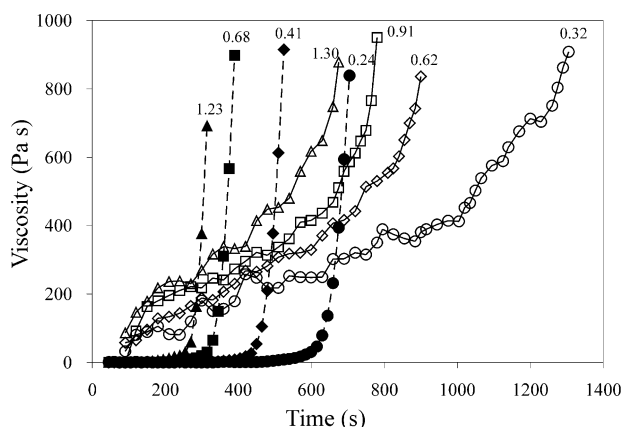


Fig. 2. Variation in viscosity of alumina suspensions containing MA + MAM (hollow symbols) and MAM + HMAM (solid symbols) during gelation. The numbers near each curve refer to the concentration of initiator used to promote the polymerization.

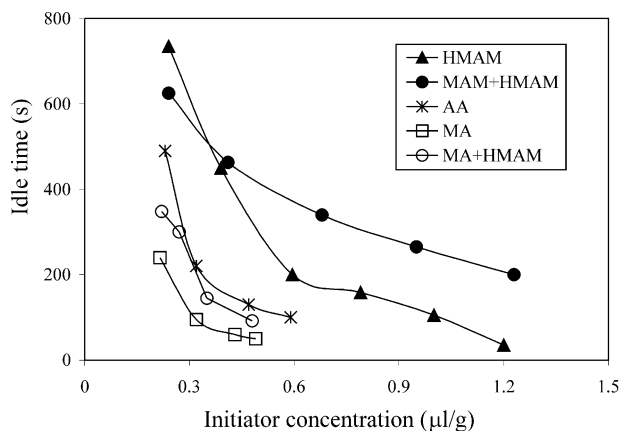


Fig. 3. Effect of initiator concentration on the induction time for gelation of suspensions containing different monomers. Catalyst was added previously in a 1:1 molar ratio to the initiator.

group may have a favorable influence on the polymerization kinetics. In fact, each monomer has specific enthalpy (H_p) and entropy (S_p) of polymerization that determine the free energy of polymerization, $\Delta G_p = \Delta H_p - T\Delta S_p$. However, thermodynamic characteristics are frequently overridden by other factors, such as the polarity and size of substitute groups,²⁶ what impedes any attempt to make clear-cut generalizations.

The polymerization experiments also revealed that the combination of different monomers may be a useful tool to control the polymerization kinetics. For example, HMAM presented local gelation when initiator was added to the suspension. This resulted in a heterogeneous gel, leading to the formation of defects in the final body. Nevertheless, when HMAM was combined with MAM the gelation reaction was homogeneous, well controlled, and local gelation was avoided. It is important to note that other parameters such as pH and temperature strongly influence the polymerization kinetics.^{15,28} For this reason, the results shown here are mainly comparative.

3.3. Wet gel strength

Typical wet strength curves of gelled samples using different monomer systems are shown in Fig. 4. The loading curves for all monomer systems displayed a large region of either elastic or plastic deformation. Some specimens fractured at a given load, while others exhibited only extensive plastic deformation without fracture. A fitting applied to the initial linear part of the curves provided the slope, which was associated with the gel rigidity, i.e. the resistance offered against the rod intrusion. The gel rigidity values are plotted as a function of initiator concentration in Fig. 5.

In general, the rigidity of all gels decreased as the initiator concentration increased. Gels produced with HMAM showed the highest rigidity values (1.4–1.9 N/m)

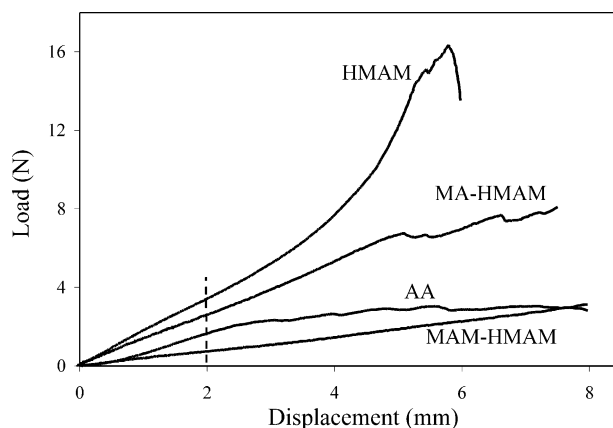


Fig. 4. Examples of typical load versus displacement behaviors observed during the evaluation of wet strength. The linear trend up to a displacement of 2 mm was considered for calculations.

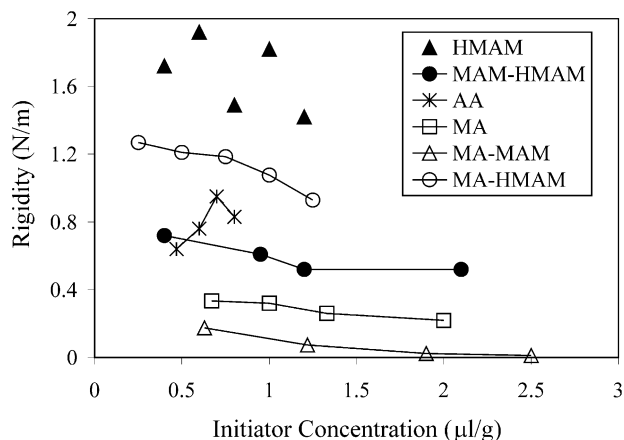


Fig. 5. Rigidity of wet alumina gels produced with different gelling systems using varied initiator concentrations. Catalyst concentration was maintained at 1:1 molar ratio with initiator.

for any concentration of initiator, although the results were scattered. Additionally, all the compositions produced with HMAM fractured. The compositions containing HMAM combined with other monomers (MA-HMAM and MAM-HMAM) displayed comparatively high values of rigidity, in the range of 0.9–1.3 and 0.6–0.8 N/m, respectively. The gels prepared with AA revealed rigidity in the same level as those prepared with the pairs of monomers including HMAM. Contrarily, samples containing MA, either on its own or in combination with MAM, showed very low values of rigidity (0.05–0.35 N/m). In particular, the ceramic gels prepared with the MA-MAM pair behaved like viscoelastic materials as they were easily deformed and had their shape partially restored after pressure release. This behavior may be related to the gel structure resulting from different polymerization rates, since the average chain length is strictly related to the concentration of free radicals along the reaction.²⁷ However, when copolymerization is considered, the tendency of each

monomer to self-propagate, that is, to react with other monomer of the same kind, or to cross-propagate, which means to react with monomer of another kind, may result in different structures.²⁶ Depending on the reactivity ratios, a specific kind of monomer may predominate at the copolymer structure, that determines the properties of the gel.

It is important to emphasize that a high wet strength is essential for foam production. Because of the high porosity that is usually incorporated in foams (>90%), green samples are often quite fragile, and further mechanical damage can be induced as they are demoulded and handled.

3.4. Dry gel strength

Fig. 6 shows the results of diametral compression of dry green specimens produced with different monomers at various initiator/catalyst concentrations.

The green strength of samples was generally high and increased as the initiator concentration increased for all monomer systems except MA-HMAM. The largest strength values were observed for suspensions gelled using AA (15–20 MPa). The lowest values of diametral strength were obtained for specimens prepared with the MA-MAM monomer system (3–12 MPa). This was attributed to the presence of flaws such as cracks and large voids, which appeared during the drying process, as the wet gel was too weak to support the stresses developed during this step (Fig. 5).

The tendency of dry green strength to increase with initiator concentration is probably related to changes in the gel structure resulting from the polymerization kinetics, similarly to what was observed for the rigidity of wet ceramic gels.

For some specimens large concentrations of initiator caused a decrease in green strength. This could be a

consequence of local gelation, which was observed during the preparation of some samples. As large amounts of initiator were added to catalyst-containing suspensions, high local concentrations led to very fast reactions even under vigorous agitation. As a result, lumps were immediately formed resulting in defects that lowered the mechanical strength. In fact, an examination of the fracture surface revealed the detachment of lumps in some samples produced with large amounts of initiator. On the other hand, samples produced with small additions of initiator showed a smooth and flawless fracture surface. The presence of a maximum in strength values of specimens prepared with HMAM and MAM-HMAM could be a result of both effects discussed above. At first, the mechanical strength increases with initiator concentration as a result of changes in gel structure. Above a given initiator concentration, lump formation due to local gelation weakens the sample, and the strength decreases. For these samples, lowering either the concentration of the initiator solution or the suspension temperature might avoid lump formation.

4. Conclusions

In this work, various monomer systems were tested for gel formation in ceramic suspensions with the purpose of ceramic foam production. The analysis aimed at the selection of systems that display fast and easily controllable gelation, giving a gel sufficiently strong to support the structure of foamed ceramic suspensions. Suspensions containing monomers with the carboxylate group in their structure showed high viscosity and required large amounts of deflocculant to be dispersed. This behavior was more pronounced for MA monomers than for AA monomers, and was attributed to the high affinity between the carboxylate group and the surface of alumina particles. Monomers containing amide groups caused negligible effects on the dispersion state compared to pure alumina suspensions. The polymerization kinetics in general exhibited an induction time, which depended on the initiator concentration and was followed by fast gelation. This behavior is advantageous for production of ceramic foams, since it allows the homogenization and molding of the samples before gelation takes place. The wet strength of gelled specimens depended on the polymerization kinetics and was higher for gels produced with lower initiator concentration. The highest wet strength was obtained with HMAM, whereas quite low wet strength was noted for systems containing MA and MA-MAM. Dry strength was high for most systems and in general decreased as initiator concentration increased. The dependence of the gel strength on the initiator concentration occurs because the gel structure depends on the polymerization kinetics. Suspensions with pure *N*-hydroxymethylacrylamide

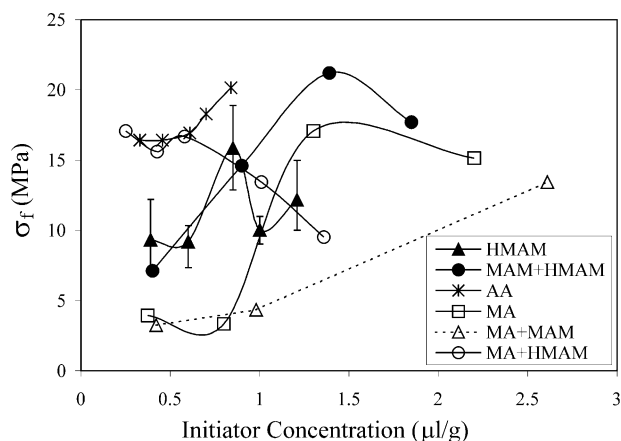


Fig. 6. Dry strength of samples containing different gelling systems produced with varied initiator concentrations. Typical standard errors were the same for all systems, and are indicated in bars for the system containing HMAM.

showed a tendency to form lumps due to fast gelation when initiator was added. Ammonium acrylate and *N*-hydroxymethylacrylamide, either pure or combined with methacrylamide, presented the best wet and dry strength results and showed little or no influence on the dispersion state. According to these results, the production of foams may be successfully accomplished with using AA monomers, due to its high strength and a tendency to impart a yield stress to the suspension, giving more stable foams. The system MAM-HMAM was also satisfactory, but the low yield stress of the suspensions containing this system requires a very good control of the reaction. Alternatively, processing additives may be used to impart a yield stress to the suspensions, and make the foam structure less dependent on the polymerization kinetics.

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