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A catalytic effect of alumina grains onto polymerization rate of methacrylamide-based gelcasting system

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Abstract

Gelcasting is a promising new technology for manufacturing of advanced ceramic components. However, up to now few articles have been published on the catalytic effect of ceramic filler onto polymerization rate of monomeric systems used in gelcasting. In this work the stress viscosimetry was used to study the catalytic effect of alumina filler onto polymerization rate of methacrylamide–*N*,*N*′-methylenebisacrylamide (MAM–MBAM) monomers as a function of alumina volume fraction (0.1–0.5), temperature (20–50 °C) and initiator concentration (0.4–1.3 wt.% on the monomers base). The initiation time of gelcasting suspensions of constant MAM–MBAM volume fraction decreased with increasing initiator/accelerator concentration, temperature and the volume fraction of solids. The alumina effect on the initiation time was more visible at lower initiator concentration, suggesting that ceramic microenvironment is favorable for the gelling process. The calculated activation energies of methacrylamide premix and 50 vol.% ceramic suspension were 32.5 and 21.7 kJ/mol, indicating a catalytic effect of the ceramic filler.

Keywords: A. Suspensions; D. Al_2O_3; Gelcasting; Methacrylamide

1. Introduction

Gelcasting is a near-net shape forming method of advanced ceramic materials that combines polymer chemistry, colloidal chemistry and ceramic technology. In this method, a slurry of ceramic powder in a solution of gel-formers is placed into a mould. Gel-formers polymerize and create a strong polymer hydrogel, which permanently immobilizes the ceramic slurry in desired shape of mould cavity. The original study on gelcasting involved polymerization of acrylamide monomers, as gel-formers. Monofunctional acrylamide and difunctional *N*,*N*′-methylenebisacrylamide were used as the reactive organic monomers [1]. The main disadvantage of this gelling system is that acrylamide is a neurotoxin [2]. Therefore, many new gel formers, especially consisting of monomers of low toxicity or environmentally friendly biopolymers are extensively studied [3–7].

In spite of abundant literature on various gelling systems used in gelcasting technology as well as various ceramic materials manufactured by this technique, few papers have been published on the catalytic effect of ceramic filler on the polymerization rate of monomeric systems. In their original work on gelcasting, Young et al. [1] pointed out that the idle time of acrylamide–*N*,*N*′-methylenebisacrylamide system was reduced by the presence of alumina powder. The chemorheological study of this gelling system performed by Babaluo et al. [8] showed that the presence of alumina powder caused reduction of activation energy of suspensions, hence shorter idle times were observed. Morissete and Lewis [9] investigated chemorheology of a gelcasting system based on aqueous-based alumina–poly(vinyl alcohol) (PVA) suspensions cross-linked by an organometallic coupling agent. Additions of Al_2O_3 particles kept reducing the critical cross-link concentrations, suggesting that solid filler was not inert. Chu and Halloran [10] studied the curing kinetics of Al_2O_3 and hydroxyapatite suspensions in a liquid mixture of acrylates (propoxylated neopentoglycol diacry-

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late and isobornyl acrylate). The calculated activation energies for the acrylate premix and the two ceramic suspensions (alumina and hydroxyapatite) were 133, 74 and 78 kJ/mol, indicating the catalytic effect of the ceramic filler.

In this work, the stress viscosimetry was used to investigate the catalytic effect of alumina filler onto polymerization rate of methacrylamide–*N*,*N*′-methylenebisacrylamide (MAM–MBAM) monomers as a function of alumina volume fraction (0.1–0.5), temperature (20–50 °C) and initiator concentration (0.4–1.3 wt.% on the monomers base). This gelling system is of reduced toxicity as well as of low cost. It was already used by several researchers [3,11,12] for manufacturing various ceramic materials, such as Si_3N_4, Al_2O_3 and hydroxyapatite. Therefore, the study of the catalytic effect of ceramic grains seems justified.

2. Materials and methods

2.1. Materials

The alumina powder CT 3000 SG (Alcoa Chemie, Germany) with a specific surface area of 7.0 m^2/g and purity of 99.97% was used as the ceramic raw material. Ammonium polyacrylate (40 wt.% solution) (Darvan 821A, R.T. Vanderbilt Company Inc., USA) was a dispersant. Monomer was monofunctional methacrylamide (MAM), $CH_2{=}C(CH_3)CONH_2$ (Fluka, Switzerland). Cross-linker was difunctional *N*,*N*′-methylenebisacrylamide (MBAM), $(CH_2{=}CHCONH)_2CH_2$ (Aldrich, Germany). The redox pair used to initiate polymerization consisted of ammonium persulfate (APS), $(NH_4)_2S_2O_8$ (Aldrich, Germany) as initiator and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (Fluka, Switzerland) as accelerator. Ammonium persulfate aqueous solutions were prepared at a concentration of 10 wt.% prior to use.

2.2. Solution and suspension preparation

The premix solutions were made as 15 wt.% solutions in distilled water of monomer and cross-linker combination. The weight ratio of monomer to cross-linker was 6:1.

Alumina powder was slowly added to the monomer solution with dispersant under agitation to prepare suspensions of solids volume fraction ranging from 0.1 to 0.5. The dispersant concentration was 0.5 wt.% per dry powder. All the slip components were further homogenized for 2 h by ball-milling.

2.3. Kinetics of polymerization

Before adding the initiator and accelerator the premix solutions and ceramic suspensions were de-aired to avoid the effect of oxygen inhibiting polymerization process. The premix solutions for idle time measurements were de-aired by bubbling nitrogen. The ceramic suspensions were de-aired in vacuum at 5 °C to avoid excess evaporation of water. The polymerization reactions were initiated by adding of APS and TEMED. The actual concentrations of APS were in the range 0.4–1.3 wt.% in relation to monomers base. A weight ratio of APS to TEMED was 1:1. The pH of ceramic suspensions and monomer solutions was adjusted to 9.5 using NH_4OH.

The gelation of premix solutions and 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 subjected to a constant 0.1 s^{-1} shear rate and the viscosity value was registered every 5 s. The measurements were made at the temperature range of 20–50 °C in N_2-filled chamber. The polymerization rate of a relatively toxic acrylamide monomer (Aldrich, Germany) was also tested for comparison.

3. Results and discussion

3.1. Gelation of premix solutions

In the radical polymerization systems, it is common to observe a period of inactivity between the time of introduction of initiator and activator and the actual beginning of the polymerization reaction. This period is known as the induction period or idle time. In the processing of ceramics, the induction period represents the time available for casting the slurry into the mould. For most systems, the viscosity remains nearly constant during the idle time, and then increases rapidly as gelation takes place. Fig. 1 illustrates the viscosity variation versus time for 15 wt.% MAM–MBAM solutions with respect to the amount of initiator and accelerator. The reduction of

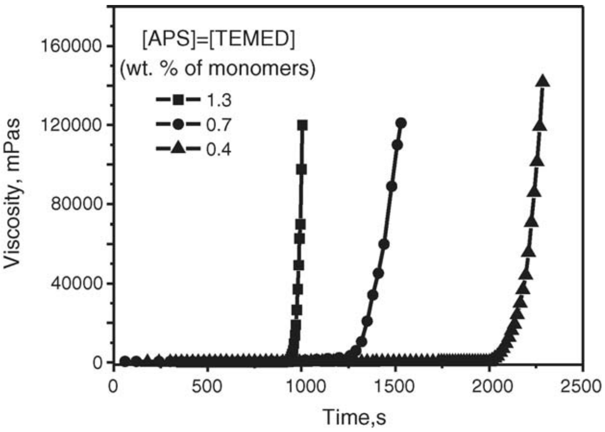

Fig. 1. The apparent viscosity as a function of time of MAM–MBAM solutions for various concentrations of initiator and accelerator at temperature of 20 °C.

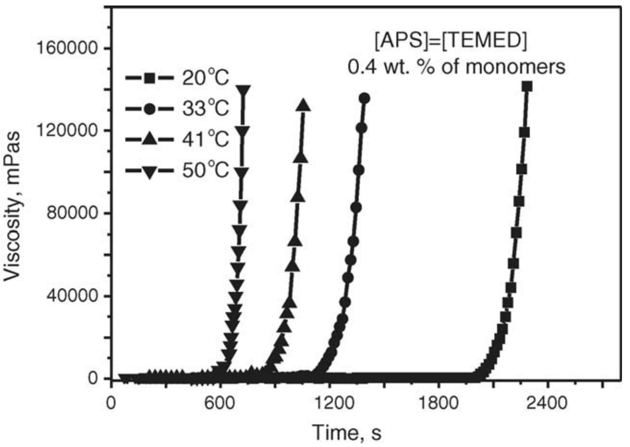

Fig. 2. The apparent viscosity as a function of time of MAM–MBAM solutions held in various temperatures.

initiator concentration increases the idle time, since the polymerization rate is of the order of 0.5 for initiator concentration in the chain polymerization [13].

The variation of viscosity with premix solution temperature is shown in Fig. 2. As can be seen in Fig. 2 the idle time becomes shorter as temperature increases. The idle time is inversely proportional to the rate of production of free radicals, which is related to the solution temperature, T. This relationship may be expressed by an Arrhenius-type equation:

$$t_{\text{idle}} \propto \frac{1}{r} = A \exp\left(\frac{E_{\text{A}}}{RT}\right)$$

where r is reaction rate, R the gas constant, and E_{A} the activation energy of the free radicals generation process.

Fig. 3 is an Arrhenius plot of the idle times for MAM–MBAM solutions with initiator concentration of 0.4 wt.% on the monomers. The calculated activation energy was 32.5 ± 0.9 kJ/mol. The activation energy calculated from viscosimetric measurements represents the process of free radical generation only, because the free-radical polymerization is a complex multi-step reaction. The first step is the decomposition of initiator molecule with the rate constant, k_{i} into two species carrying unpaired electrons called free radicals. A free radical can then react to open double bond of a vinyl monomer. In a few seconds or less, many more monomers add successively to the growing chain with the propagation rate constant, k_{p}. Finally two radicals react with each other and terminate the growth activity yielding one or two polymer molecules [14]. This bimolecular process is called termination and is identified with the rate constant k_{t}.

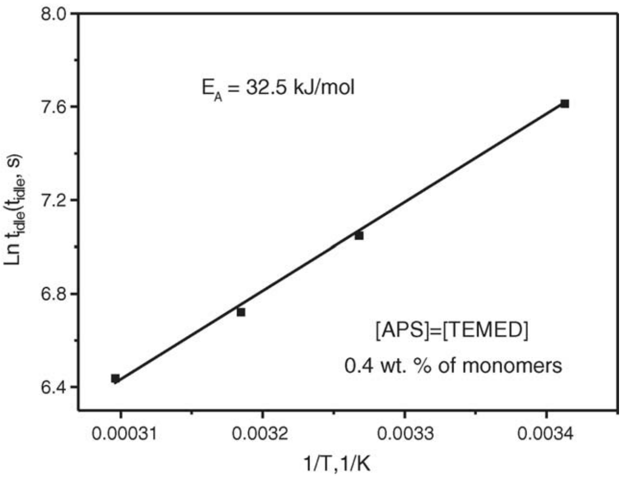

Fig. 3. Semi-log plot of idle times vs. inverse of temperature for MAM–MBAM solutions.

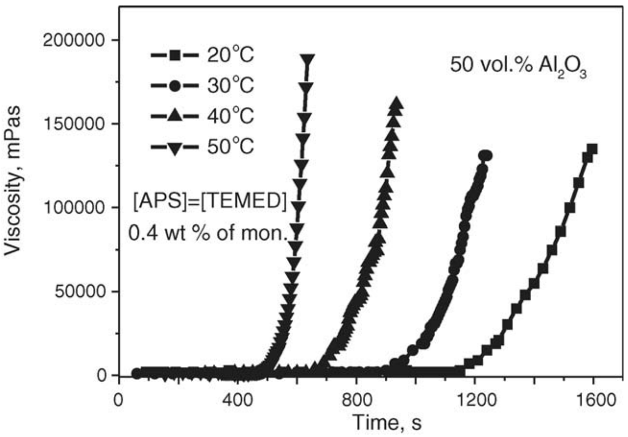

Fig. 4. The apparent viscosity as a function of time of 50 vol.% alumina suspensions held in various temperatures.

3.2. Gelation of ceramic suspensions

The dependence of polymerization rate versus temperature for 50 vol.% Al_2O_3 suspensions in 15 wt.% MAM–MBAM solutions with initiator concentration of 0.4 wt.% (on the monomers base) is shown in Fig. 4. The trends are similar to those observed for premix solutions (Fig. 2), i.e., idle time decreases with increasing temperature. However, for the same temperature and the same amount of initiator

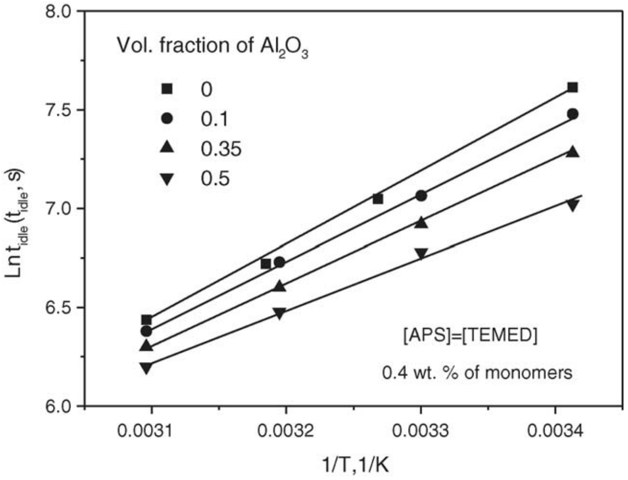

Fig. 5. Semi-log plot of idle times vs. inverse of temperature for suspensions with various alumina loading levels.

Table 1
Apparent activation energies of premix solution and ceramic suspensions

Volume fraction of Al_2O_3	Activation energy (E_A, kJ/mol)
0	32.5 ± 0.9
0.10	28.6 ± 0.6
0.35	25.6 ± 0.9
0.50	21.7 ± 1.0

and accelerator, the idle time of the ceramic suspension is shorter than that of the premix solution. These results indicate the catalytic effect of Al_2O_3 filler on the polymerization process of MAM–MBAM monomers.

Fig. 5 is an Arrhenius plot of initiation times versus inverse of temperature, for ceramic suspensions with alumina loadings from 0.1 to 0.5 volume fraction. The data concerning MAM–MBAM premix solutions are also presented in Fig. 5, for comparison. The calculated values of activation energies of free radical generation process, depicted in Table 1, detect the catalytic effect of ceramic powder on the gelation kinetics of suspensions, e.g. the activation energy of free radical generation process decreases with increasing the alumina loading level.

The viscosity variation versus time for suspensions with various volume fractions of alumina at constant temperature of 20 °C is shown in Fig. 6. From Fig. 6, it is seen that the idle time of polymerization is influenced by the volume fraction of Al_2O_3. The more volume fraction of ceramic grains, the shorter initiation time is observed. Fig. 7 is a collective plot of initiation times as a function of alumina volume fraction for the suspensions for which gelation was promoted by two different amounts of initiator and accelerator, e.g. 0.4 and 1.3 wt.% on the monomers. For both initiator concentrations the catalytic effect of Al_2O_3 is visible as nearly linear decreasing of idle time with increasing volume fraction of alumina powder. The stronger slope of linear fitting is observed for suspensions with gelation promoted by a lower amount of initiator. This is because at a given temperature the gelation rate is dependent on initiator concentration and volume fraction of alumina powder. For the low amount of initiator, the alumina powder plays a more significant role in the initiation process.

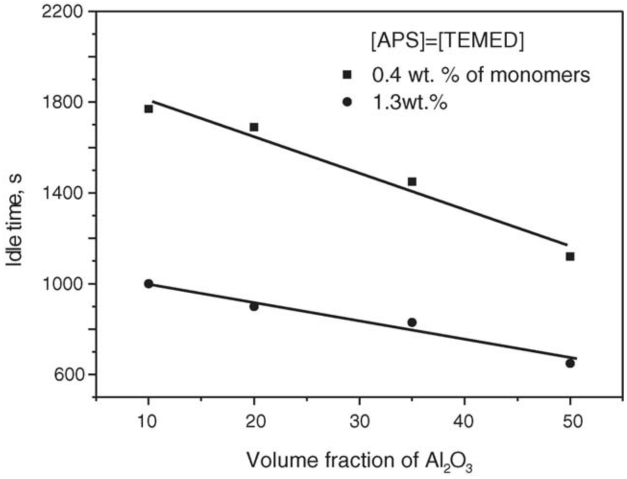

Fig. 7. Idle time of suspensions for various alumina loading levels and various initiator concentrations at temperature of 20 °C.

To clarify the catalytic effect of alumina grains on polymerization of MAM–MBAM monomers, a gelation of premix solutions and alumina suspensions were promoted at room temperature by the use of initiator only without accelerator. Ammonium persulfate has a half-life decomposition of 10 h at 80 °C, so it is practically inactive at room temperature without accelerator because the free radicals cannot be generated at a sufficient rate. Therefore, as expected, gelation of premix solutions were not observed within several days. On the other hand, gelation of alumina suspensions were observed within hours, as shown in Fig. 8. This gelation rate is not useful for gelcasting technology because of too long idle time, but it clearly indicates that polymer initiation in the alumina microenvironment is favored. The gelation of ceramic suspensions taking place at room temperature without accelerator means that alumina grains participate in the in decomposition of initiator into

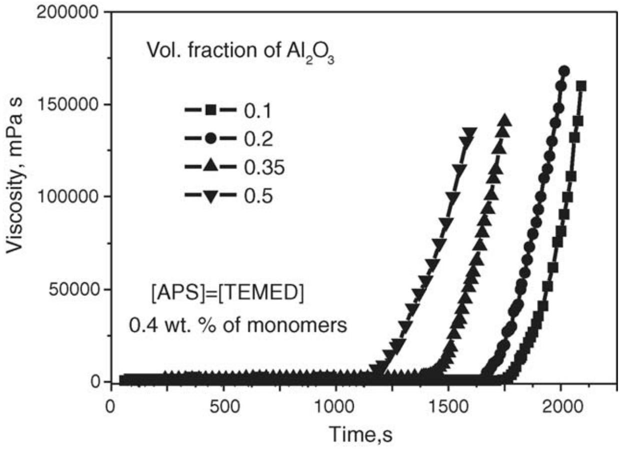

Fig. 6. The apparent viscosity as a function of time of suspensions with various alumina loading levels at temperature of 20 °C.

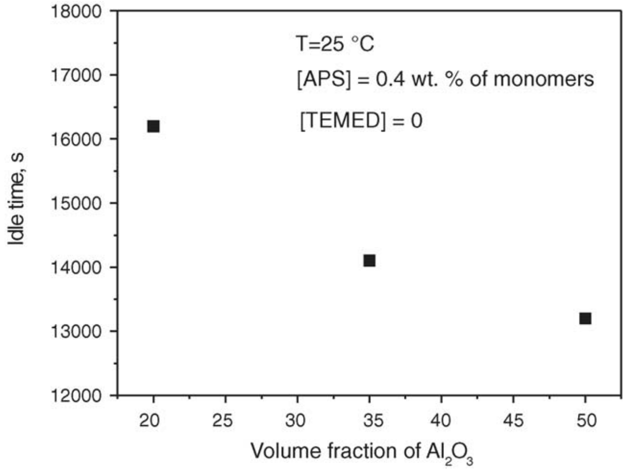

Fig. 8. Idle time of suspensions for which gelation was promoted by the use of initiator only without accelerator at temperature of 25 °C.

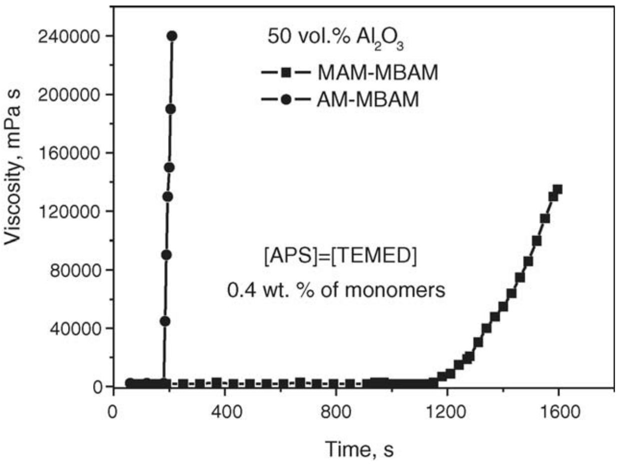

Fig. 9. Comparison of polymerization kinetics of 50 vol.% Al_2O_3 suspensions containing MAM–MBAB and AM–MBAM monomers.

free radicals. The surface of alumina acts as Lewis acid or Lewis base sites [15]. Hence, the interaction of alumina powders with inactive initiator molecules can be viewed as a Lewis acid–base reaction occurring at the surface of powders. Electrons from base-sites at alumina surface may participate in decomposition of initiator molecules ($S_2O_8^{2-}$) into free radicals ($SO_4^{\bullet -}$ + SO_4^{2-}). However, the experiments made so far are inconclusive with regard to the effect of ceramic grains on the later stages of polymerization reaction, e.g. propagation and termination.

3.3. Comparison with acrylamide

Acrylamide–*N*,*N*′-methylenebisacrylamide system is the best-known system in gelcasting technology. Fig. 9 presents a comparison of viscosity variation versus time for 50 vol.% alumina suspensions containing methacrylamide monomer (MAM) and acrylamide monomer (AM). In both cases the cross-linker is *N*,*N*′-methylenebisacrylamide (MBAM). From Fig. 9, it can be seen that the polymerization rate of the high solid loading alumina suspension containing acrylamide monomer is much higher than that observed for the slurry containing methacrylamide monomer. In both types of monomers, the amide group is the functional group, but other factors such as steric factor strongly affect on the kinetics of polymerization. In acrylamide, $CH_2{=}C(H)CONH_2$, the carbon atom responsible for polymerization is more uncovered that in methacrylamide, $CH_2{=}C(CH_3)CONH_2$, so the radical attack is easier for more uncovered carbon atom of AM. Additionally, the reactivity of monomers can be predicted on the base of *Q* and *e* values [16]. *Q* value represents the general reactivity of the monomer and macroradical. The *e* value is proportional to the residual electrostatic charges in the respective reaction groups, e.g. it represents induction effects of substituents on the double bond and radical. The *Q* and *e* values for methacrylamide are 0.40 and −0.05, while these values for acrylamide are 0.23 and 0.54, respectively [16]. The high and positive *e* value is observed for monomers showing strong donor induction effect, while monomers showing strong accepting induction effect have a high and negative *e* parameter. The *e* parameter for acrylamide is high and positive, while this parameter for methacrylamide is very low and negative. This means that electron density distribution in acryl macroradicals is more favoured for polymerization than in methacryl macroradicals.

3.4. Impact on gelcasting process

Methacrylamide gelcasting system is a valuable alternative to that based on a neurotoxic acrylamide system. For the typical gelcasting suspension containing high volume fraction of solids (0.5 or higher), the dependence of idle time on temperature is very important because the suspension temperature is varied during gelcasting process. At the deairing stage, the suspension temperatures have to be kept below 5 °C to prevent excess evaporation of water. At this stage, the initiator and accelerator are added and the idle time should be then sufficiently long. The temperature dependence of gelation kinetics is considered advantageous, because one can overcome the accelerating effect of solid additions on gelation rates by handling the systems at low temperatures prior to casting. Apart from the idle time, the total processing time (e.g. time interval, which begins immediately after addition of initiator and catalyst to the suspension and terminates when viscosity becomes very high) is another important parameter. The total processing time is important for de-moulding operation because gelcast compacts have to be geometrically stable and possess sufficient mechanical strength. Therefore, after the casting operation, the mould is kept at temperature of 50 °C or higher in order to decrease the period of time between casting and de-moulding.

The polymerization rate of the gelcasting suspension containing methacrylamide is relatively low. For this reason the methacrylamide gelcasting system is useful for production of dense ceramics only. It should not be used for manufacturing of ceramic foams where the requirements are stricter than those found in dense ceramic production. One of these requirements is that after foam generation, the gelation must be sufficiently fast to prevent the foam collapse [17].

4. Conclusions

At a constant temperature, the idle time of gelcasting suspensions was a function of initiator/accelerator concentration and alumina volume fraction. The higher alumina volume fraction, the shorter was the initiation time, suggesting that alumina microenvironment was favorable for gelling process. The alumina effect on initiation time was particularly well pronounced at low initiator concentration.

A reduction in the activation energy of free radical generation process in gelcasting suspensions with increasing alumina volume fraction proves the catalytic effect of ceramic filler on the polymerization reaction in methacrylamide–*N*,*N*′-methylenesbisacrylamide premix.

Although the alumina grains reduced initiation times, the raise in viscosity after the initiation time was a relatively slow process due to relatively low reactivity of methacrylamide macroradicals.

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