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Chemorheology of alumina–aqueous acrylamide gelcasting systems

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Abstract

Gelcasting is a novel forming method in fabricating complex three-dimensional ceramic parts. A lot of studies have been conducted on the rheological aspects of organic–inorganic suspensions, but up to now few articles have been published on the chemorheological aspects of gelcasting systems. In this work the chemorheology of gelation of aqueous-based alumina-organic monomers suspensions was investigated using stress viscometry techniques. It was concluded from this work that among various variables, such as monomer, crosslinker, initiator and accelerator concentrations, ceramic loading level and temperature, the later parameter has the most significant effect on the idle time and processing time as two critical parameters in the gelcasting of near-net shape articles. The presence of alumina powder has also a catalytic effect. The rheological behaviour of these systems was in good agreement with the original Casson model, too.

Keywords: Al_2O_3; Casson Model; Chemorheological behaviour; Gelcasting; Suspensions

1. Introduction

Gelcasting is a novel forming method in fabricating complex three-dimensional ceramic parts. A macromolecular network is created through in situ polymerisation of monomeric species or crosslinking of polymeric ones, to hold the ceramic particles very close to each other.[1,2] In this method, controllable casting and solidification permits to fabricate green bodies, which not only have high mechanical strength and stiffness, but also low shrinkage during drying and sintering processes.[3,4] Gelcasting is now extensively used in forming complex shape and near-net-shape ceramic parts for electronics, automotive and defence industries,[3] also in producing porous ceramic parts employed in drug delivery systems, bio-ceramics, membranes, membrane reactors and sensors,[5,6] porous support systems,[7] ceramic foams,[8] ceramic powders, and nano-sized ceramics.[9–11]

From the rheological point of view, a lot of studies have been conducted to investigate the effects of various polyelectrolytes on rheological (flow) behaviour of different aqueous ceramic suspensions; such as alumina suspension,[12–19] alumina–zirconia suspensions,[20] suspensions of nano-sized YSZ,[21] and zeolite nanocrystals,[22] colloidal processing of silicon nitride,[23,24] nickel powders,[25] colloidal silica particles suspension,[26] and so on.

But up to now, a few studies have been conducted on the chemorheological aspects of gelcasting systems. Morissette and Lewis,[1] investigated chemorheology of aqueous-based alumina–polyvinyl alcohol suspensions during gelation process. Chu and Halloran,[27] tried to characterise curing kinetics of alumina and hydroxyapatite suspensions in acrylates by differential scanning calorimetry (DSC). They evaluated the activation energy of acrylate pre-mix gelation and indicated the catalytic effect of ceramic fillers therein. But proposed method was very expensive and the idle time, as a very important factor in processing, was undeterminable.

In this work, based on Morissette and Lewis's theoretical effort, the chemorheology of gelation of aqueous-based alumina-organic monomers suspensions was investigated using stress viscometry technique. The effect of various parameters such as monomer, crosslinker, initiator, and accelerator concentrations, ceramic loading level and temperature on the idle time and the processing time were considered and discussed. The

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rheological behaviour of these systems, were also evaluated and compared with the original Casson model to see any agreement between the experimental data and the model which was valid for shear rates up to 400 s^{-1}.[12,18]

2. Experimental details

2.1. Materials

The characteristics of materials used in this work are given in Table 1 and also in Fig. 1.

2.2. Suspension preparation

An appropriate amount of monomers was dissolved in deionised water to make pre-mix solutions. Ceramic suspensions were prepared by adding required volume fractions of ceramic powder, i.e. 20–40% by volume, to the pre-mix solution containing 0.3 ml of APMA [ammonium poly (methacrylate)] per 100 g of Al_2O_3.[19] Suspensions were mechanically stirred for at least 2 h.

Various monomer pre-mix solutions, with different monomer concentrations, were prepared and the behaviour of these systems in the presence or absence of ceramic powder was investigated and compared with each other. Gelation was initiated immediately after adding predetermined amounts of initiator and accelerator.

2.3. The rheological properties measurements

A controllable stress rheometer (i.e. Shanghai balance instrument factory, model NDJ-4, type LVF), was used to characterise the rheological behaviour of pre-mix solutions and suspensions. Most measurements were carried out with spindle numbers 1 and 4 immersed in the liquid in a vessel of infinite dimensions. The time dependency of pre-mix solutions and/or suspensions viscosities during gelation process was also characterised at various temperatures, (i.e. 15–40 °C) at a constant angular velocity (i.e. $\Omega = 12$ rpm). A digital thermometer (i.e. pH-mV-temperature meter with an accuracy of ±0.8 °C, Lutron TM-905, Taiwan), was used to measure the temperature of pre-mix solutions and suspensions during the progress of gelation. A representative process flow diagram is provided in Fig. 2.

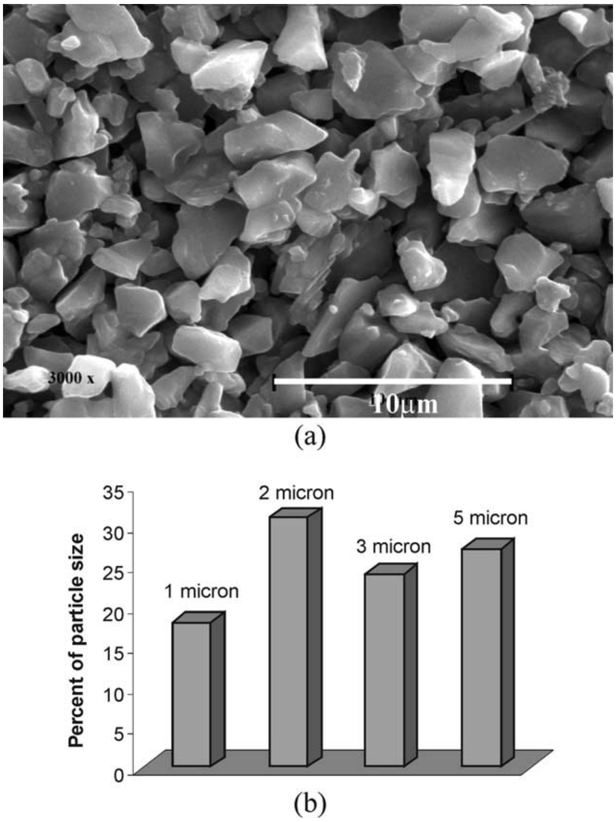


Fig. 1. (a) Shape, and (b) particle size distribution.

Table 1
Characteristics of materials

Materials	Function	Molecular formula	Characteristics	Supplier
α-Alumina	Ceramic phase	α-Al_2O_3	See Fig. 1 (a–c)	Good Fellow[a]
Acrylamide (AM)	Monofunctional monomer	$C_2H_3CONH_2$	Mw 71.08 solid white powder	Merck[b]
N,N′-Methylene bis acrylamide (MBAM)	Difunctional monomer (Crosslinker)	$(C_2H_3CONH_2)\ _2CH_2$	Mw 154.2 solid white powder	Sigma[c]
Ammonium persulfate	Initiator	$(NH_4)\ _2S_2O_8$	Mw 228.2 solid white powder	Merck[b]
N,N,N′,N′- tetramethyl ethylene diamide (TEMED)	Accelerator	$C_6H_{16}N_2$	Mw 116.2 liquid, yellow	Merck[b]
Ammonium poly(methacrylate) (APMA)	Dispersant	$(C_4H_5O_2^-NH_4^+)_n$	Ave. Mw 15,000 aqueous solution 40 wt.%	R.T. Vanderbilt[d]

[a] Cambridge Science Park, Cambridge CB4 4DJ England.
[b] E. Merck, D6100 Darmstadt, F.R. Germany.
[c] Sigma Chemical Co., PO Box 14508 St. louis, MO 63178, USA.
[d] R.T. Vanderbilt Co., Norwalk, CT, USA.

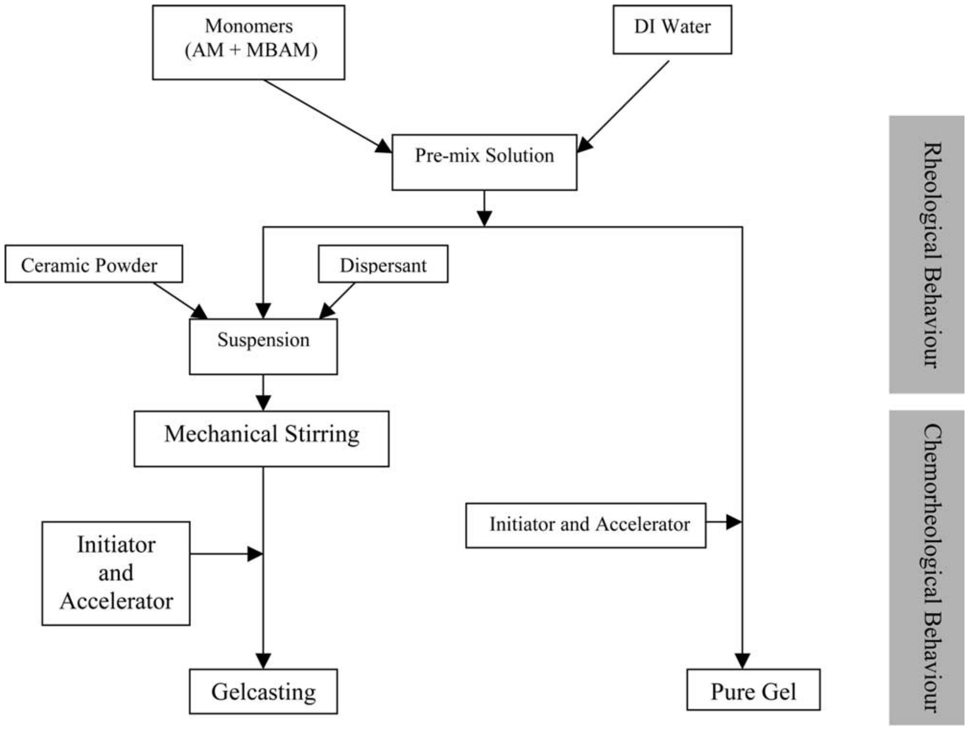


Fig. 2. Rheological and chemorheological behaviour of pure gel and gelcasting systems.

3. Results and discussion

3.1. Rheological properties of suspensions

Fig. 3 shows the flow curves (shear stress versus shear rate) of suspensions for three different ceramic loading levels at constant volume fraction of AM ($\varphi_{AM} = 0.06$) and constant molar concentration of crosslinker ([MBAM] = 0.0526(mol/lit)) at 25 °C. The experimental data were fitted to the original Casson model [Eq. (1)], using the least squares method.

$$\tau^{1/2} = \tau_c^{1/2} + \left(\eta_c \dot{\gamma}\right)^{1/2} \qquad (1)$$

where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), τ_c and η_c are the Casson's yield stress (Pa) and intrinsic viscosity (Pa s), respectively. The R-squared values for all three suspensions are higher than 0.98. It means that the Casson model shows a good agreement with the experimental data. The corresponding rheological parameters of the model were plotted in Fig. 4. As it shows, increasing ceramic loading level increases the Casson yield stress (τ_c) also the Casson intrinsic viscosity (η_c), which are expected (see Fig. 3).

3.2. Chemorheological properties of solutions

The curves of apparent solution viscosity $\left(\eta_{app}^{soln}\right)$ as a function of time with constant crosslinking agent, initiator and accelerator concentrations for various volume fractions of acrylamide at 25 °C, are shown in Fig. 5(a).

$\eta_{app}^{sol\cdot n}$exhibits a relatively slow increase during a certain period of time, then increases rapidly towards infinity. The time scale of this process decreases dramatically with increasing acrylamide volume fraction (φ_{AM}), due to reasons, which will be mentioned later.

The initiation of polymerisation in pre-mix solutions and alumina suspensions was monitored based on changes in solution and/or suspension viscosity or temperature. The process was actually monitored in terms of idle time, t_{idle}, i.e. the time interval between the addition of the initiator, or the initiator/accelerator, and the commencement of polymerisation. This is equivalent to the time available for casting the slurry during processing. The idle time was difficult to quantify precisely from viscometric measurements because of limitations in the minimum measurable viscosity, but could be estimated from the x-axis intercept of the tangent to the viscosity curve at elevated viscosity. In this work, t_{idle} was exactly determined by monitoring the temperature changes in the system.

The idle times of pre-mix solutions decrease with increasing of acrylamide volume fraction (φ_{AM}), as shown in Fig. 5(b). The experimental results are in a good agreement with the previous theoretical work.[28] Therefore the average molecular weight of polymeric chains between junctions, i.e. $\bar{M}_c$, increases rapidly by increasing the AM concentration. Osada [29] and Peppas[30] reported that by increasing AM concentration, the

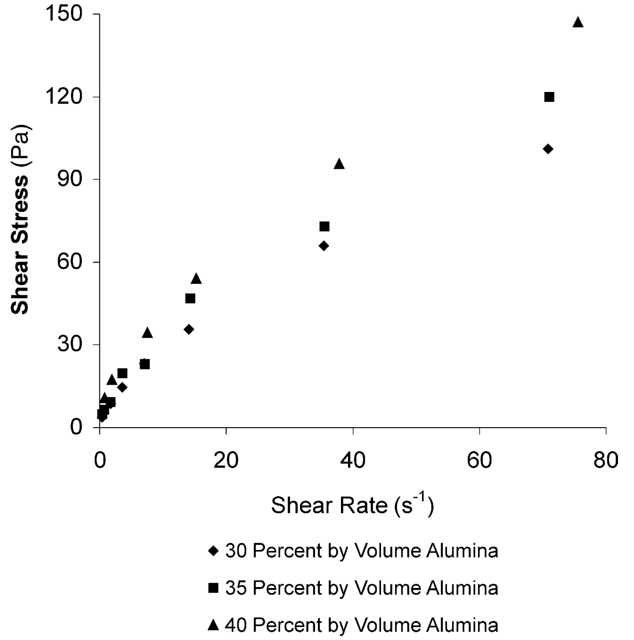


Fig. 3. Flow curves of suspensions for three different ceramic loading levels.

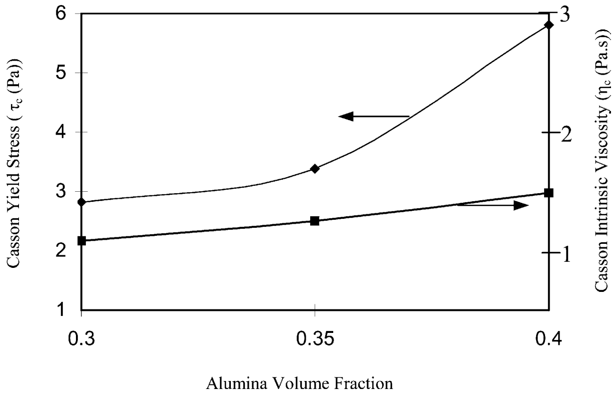
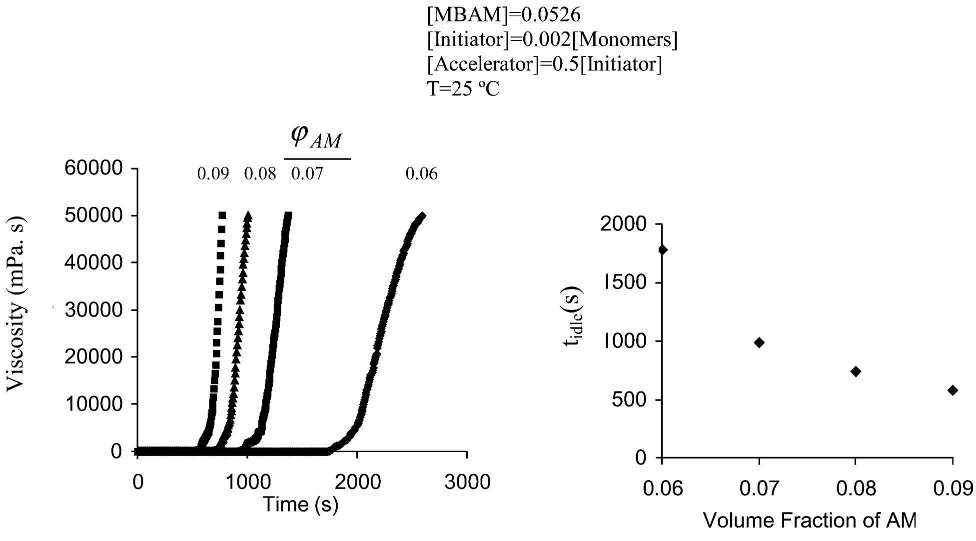


Fig. 4. The variation of rheological parameters of the original Casson model with respect to ceramic loading levels.

quantity of entanglements remains constant, but the chain length between them increases. The significant difference between 0.06 and higher than 0.07 volume fraction of AM is probably due to self-reaction of crosslinkers and formation of somehow ring structures (cyclisation). Melekaslan and Okay[31] reported that cyclisation and multiple crosslinking reactions are known to occur predominantly during the gel formation process of AM and MBAM monomers.

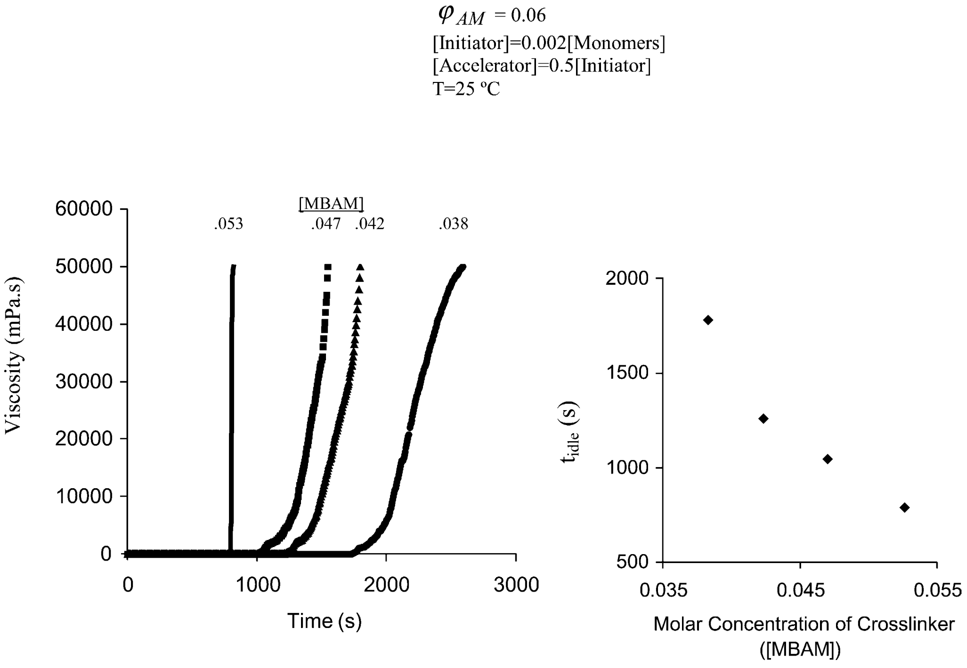
Fig. 6(a) shows η_{app}^{soln} as a function of time at constant concentrations of AM, initiator and accelerator for various crosslinker concentrations at 25 °C. The idle time decreases with increasing crosslinker concentration [Fig. 6(b)]. It is probably attributed to the reaction of crosslinker with the monomer to form a very tight net.[30] It means that by increasing the amount of crosslinker, $\bar{M}_c$ decreases dramatically. But this effect is not linear and at higher concentrations of crosslinker, it becomes weaker due to self-reaction of crosslinkers (cyclisation and multiple crosslinking reactions).[31]

Fig. 7 shows the variation of the idle time (t_{idle}) of pre-mix solutions with respect to the amount of initiator and accelerator. The reduction of initiator concentration increases t_{idle}, since the polymerisation rate is of the order of 0.5 for initiator concentration in the chain polymerisation.[28] The effect of accelerator/initiator ratio is clearly shown in Fig. 8. Increasing of this ratio decreases the idle time dramatically. It also increases



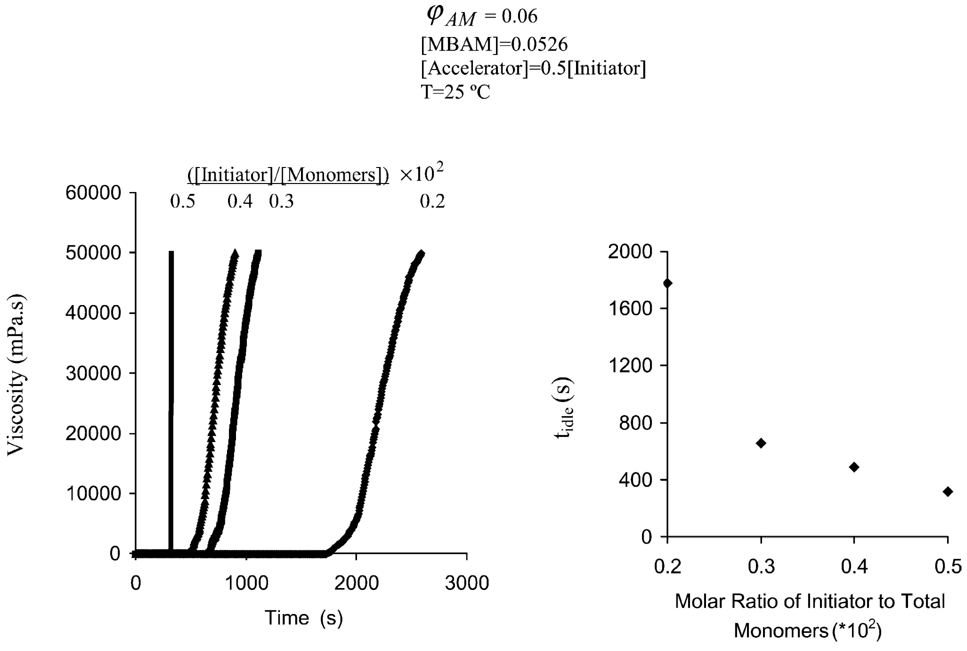
(a) (b)

Fig. 5. (a) The apparent viscosity as a function of time, (b) idle time (t_{idle}) of solutions for various volume fractions of acrylamide (φ_{AM}).



(a) (b)

Fig. 6. (a) The apparent viscosity as a function of time, (b) idle time (t_{idle}) of solutions for various crosslinker concentrations.



(a) (b)

Fig. 7. (a) The apparent viscosity as a function of time, (b) idle time (t_{idle}) of solutions for various concentrations of initiator.

gelation rate, what is due to the reduction in activation energy of reaction.

The variation of idle time with pre-mix solution temperature is shown in Fig. 9. The corresponding data show clearly that the gelation kinetic is retarded when the temperature of pre-mix solutions is decreased. At lower temperatures, i.e. 15 °C, during the course of measurements, a significant gelation did not occurred.

A qualitative evaluation of the results corresponding to the properties of pre-mix solutions and ceramic suspensions are presented in Section 3.4.

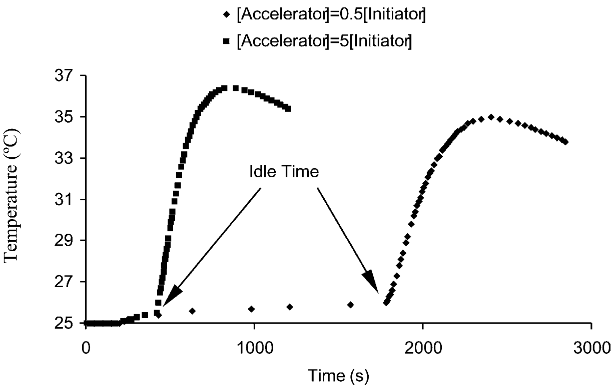


Fig. 8. The effect of accelerator/initiator ratio on the idle time.

3.3. Chemorheological properties of ceramic suspensions

The apparent viscosity as a function of time is plotted in Fig. 10(a), for gelcasting suspensions with constant amounts of reactive monomers, initiator and accelerator, and various ceramic loading levels at 25 °C. The basic features of these curves do not show any alteration due to the presence of the Al_2O_3 filler particles; but the gelation kinetics are influenced by the volume fraction of Al_2O_3 $(\varphi_{Al_2O_3})$. This observation indicates the catalytic effect of ceramic powder. The catalytic effect of Al_2O_3 is probed by the nearly linear decreasing of t_{idle} with increasing volume fraction of alumina powder as shown in Fig. 10(b).

The thermal effects on gelation behaviour of gelcasting suspensions are shown in Fig. 11. In this case the volume fraction of Al_2O_3 and also reactive monomers, initiator and accelerator concentrations, are kept constant. The trends are similar to those observed for pre-mix solutions (Fig. 9); i.e., t_{idle} increases with decreasing temperature. However, unlike the pure solutions behaviour, not only t_{idle} of suspensions (with 0.35 volume fraction of alumina powder) has decreased dramatically, but also an increase in apparent viscosity with gelation time is detected for these suspensions at 15 °C. This behaviour, also confirms the catalytic effect of alumina powder.

The idle time (t_{idle}) is inversely proportional to the rate of gelation reaction; i.e. instantaneous polymerisation and crosslinking, which depends on temperature (T). The relationship may be expressed by an Arrhenius-type equation:

$$t_{idle} \propto \frac{1}{r} = A\exp\left(\frac{E_a}{RT}\right) \qquad (2)$$

where r is reaction rate, R is the gas constant, and E_a is the activation energy of gelation reaction (kJ/mol).Fig. 12, is the semi log plots of t_{idle} versus inverse of temperature (T^{-1}), for both pre-mix solution and ceramic suspensions with 0.2 and 0.35 volume fractions of ceramic powder. These data were fitted to solid lines using the Eq (2). The slope of fitted solid lines yields the amounts of $\left(\frac{E_a}{R}\right)$. The results of curve fitting are summarised in Table 2. The calculated values of activation energy detect the catalytic effect of ceramic powder on the gelation kinetics of suspensions (activation energy of reaction decreases by increasing the ceramic loading level).

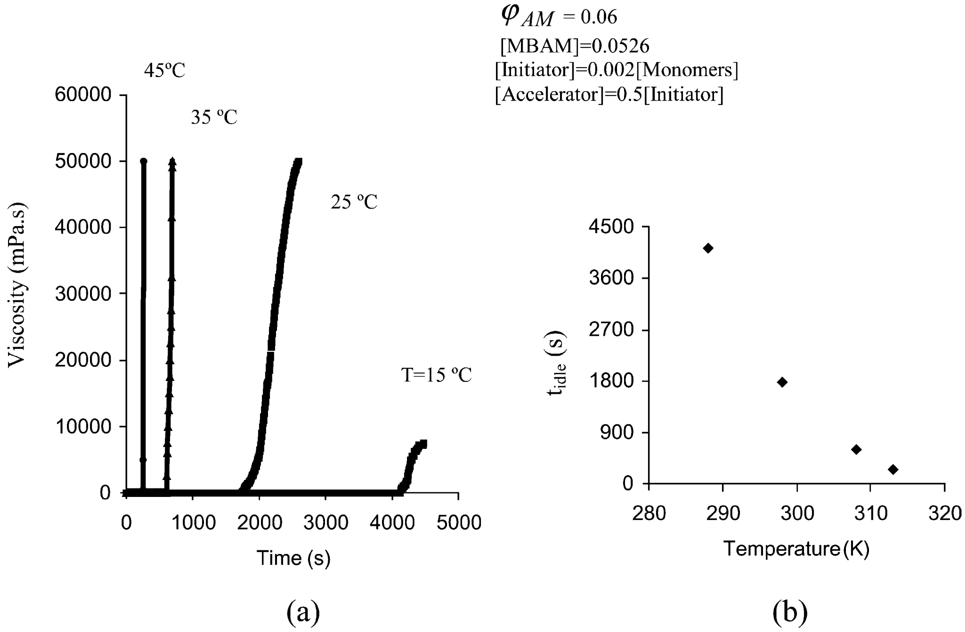
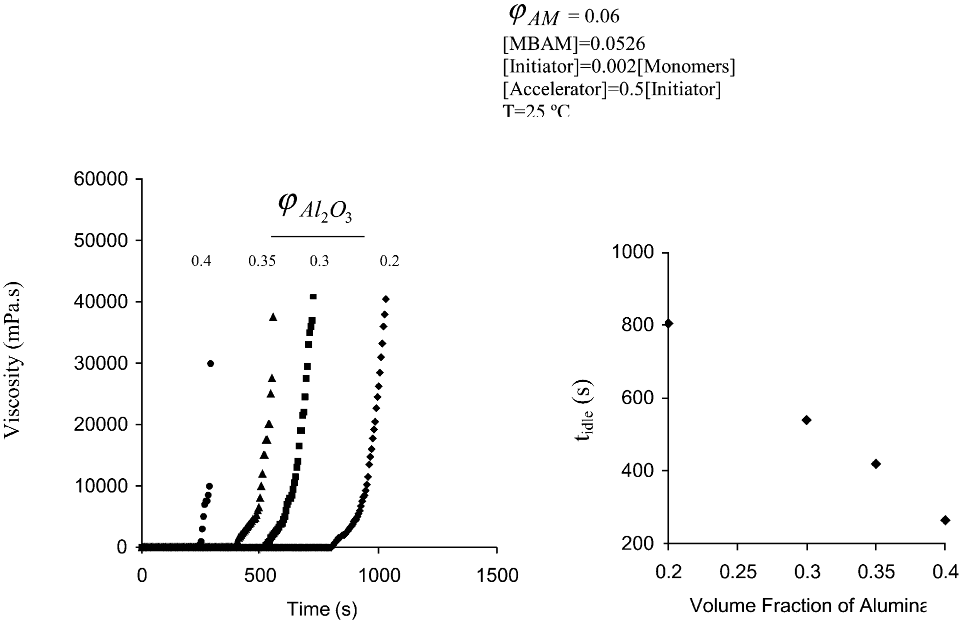
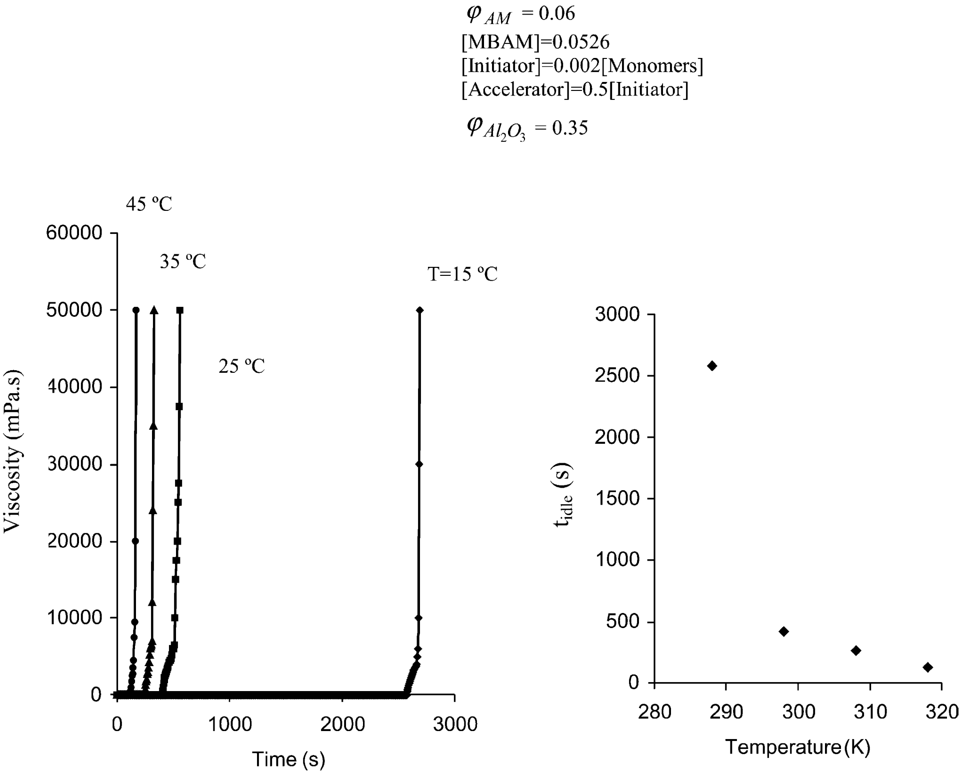


Fig. 9. (a) The apparent viscosity as a function of time, (b) idle time (t_{idle}) of solutions held in various temperatures.



(a) (b)

Fig. 10. (a) The apparent viscosity as a function of time, (b) idle time (t_{idle}) of suspensions for various ceramic loading levels.



(a) (b)

Fig. 11. (a) The apparent viscosity as a function of time, (b) idle time (t_{idle}) of suspensions held in various temperatures.

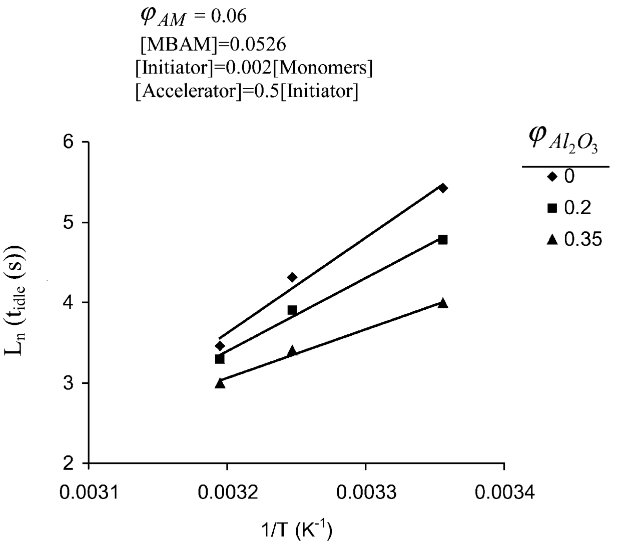


Fig. 12. Semi log plots of t_{idle} versus inverse of temperature.

Table 2
Curve fitting results of gelation kinetics

Ceramic loading in suspensions (volume fraction)	Solid lines slope $(\frac{E_a}{R})$	Activation energy (E_a, kJ/mol)	R-squared
0	11872	98.7	0.984
0.20	9084.7	75.5	0.989
0.35	6056.1	50.4	0.991

Table 3
The levels of variables affecting the idle time and processing time

Variables	Levels			
	L1	L2	L3	L4
Molar concentration of MBAM (mol/lit)	0.038	0.042	0.047	0.052
Volume fraction of AM (φ_{AM})	0.06	0.07	0.08	0.09
Molar ratio of initiator to the total monomers $\times 10^2$	0.2	0.3	0.4	0.5
Temperature (°C)	15	25	35	45
Volume fraction of ceramic loading ($\varphi_{Al_2O_3}$)	0.2	0.3	0.35	0.40

3.4. Qualitative evaluation of the results

Tables 3–7 were designed with the aim of qualitative evaluation and comparison of the effect of the various variables on the idle time and processing time, (i.e. the time interval which is started immediately after addition of initiator to the solution or suspension and terminated when viscosity reached to 50,000 mPas), which is needed for moulding samples that are geometrically stable and ejectable from the mould.

Table 4
The effect of various variables on the idle time of pre-mix solutions

Variables	Idle time (t_{idle}) (s)			
	Levels			
	L1	L2	L3	l4
MBAM	1780	1255	1050	790
AM	1780	985	740	580
Initiator	1780	660	495	320
Temperature	–	1780	605	250

Table 5
The effect of various variables on the processing time of pre-mix solutions

Variables	Processing time (s)			
	Levels			
	L1	L2	L3	l4
MBAM	2590	1795	1550	820
AM	2590	1370	1005	770
Initiator	2590	1110	900	325
Temperature	–	2590	695	255

Table 6
The effect of various variables on the idle time of suspensions

variables	Idle time (t_{idle}) (s)				
	Levels				
	L0 = 0	L1	L2	L3	l4
Ceramic loading	1780	805	540	420	265
Temperature	–	2580	420	260	125

Table 7
The effect of various variables on the processing time of suspensions

Variables	Processing time (s)				
	Levels				
	L0 = 0	L1	L2	L3	l4
Ceramic loading	2590	1055	755	560	295
Temperature	–	2685	560	330	170

In Table 3, all of the important parameters and the range of their changes in four levels are tabulated. The qualitative effect of each variable on the reduction of idle time based on its relative effectiveness is shown in Table 4. As it is seen, the temperature change in the evaluated range has the most significant effect on the reduction of idle time in comparison with the other variables. The corresponding results to the processing time show the same conditions (Table 5).

The comparison between Tables 4 and 6 clearly shows that the presence of ceramic in solution, i.e. ceramic suspension, has a significant effect on the reduction of idle time and this effect increases considerably with increasing the suspension temperature. The same conclusions are deduced for processing time, when the Tables 5 and 7 are compared.

In general, it is concluded that the temperature has the most significant qualitative effect on the reduction of the idle time and processing time, and this effect sharply increases in the presence of ceramics into pre-mix solution.

4. Conclusions

General conclusions are presented here on the work done in this research;

- *Rheological behaviour*. The rheological behaviour of ceramic suspensions in the alumina-aqueous acrylamide gelcasting systems were in good agreement with the original Casson model, i.e. the R-squared values for all of typical suspensions were higher than 0.98.
- *Chemorheological behaviour*. Among various parameters such as reactive monomers, initiator and accelerator concentrations, also ceramic loading level and temperature, the later parameter has the most significant effect on the reduction of idle time and processing time. The presence of ceramic powder causes the activation energy reduction of suspensions; therefore, shorter idle time and processing time are obtained.

An increase of reactive monomers, initiator and accelerator concentrations decreases the idle time and processing time, too, but their effects are not comparable with temperature or ceramic presence effects.

On the basis of these conclusions, process guidelines were established for fabricating advanced gelcast ceramic articles.

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