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Gelation process in low-toxic gelcasting systems

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Abstract

Gelcasting has been recognized as a very high-potential method in fabricating complex three-dimensional ceramic parts. The main component of the original gelcasting system (i.e. acrylamide) is a neurotoxic and industry is reluctant to use gelcasting instead of the other ceramic forming methods. Hence, developing of gelcasting systems with similar or superior properties to the original system and low toxicity is required. In this study, gelation kinetics of acrylic acid-based system as a low-toxic gelcasting system were investigated and compared with the original acrylamide-based system, using the Taguchi statistical method.

Statistical analysis showed that in both of the gelcasting systems, initiator and accelerator concentrations had the strongest effects on the gelation behaviour. Also, monofunctional monomers had the same effects on the gelation behaviour in both of the gelcasting systems. Between the rest variables (ceramic loading level and crosslinker concentration) a counter interacting term existed which caused to weak the pure effects of these variables on the gelation behaviour of gelcasting systems. In the acrylic acid-based system, unlike the original one, the precise monitoring of the idle time was possible. In this system, in spite of very low activity in the gelcasting process all of the undesirable neurotoxic effects of the original gelcasting system were omitted.

Keywords: Al_2O_3; Gelcasting; Shaping; Suspensions

1. Introduction

Of the various ceramic manufacturing techniques, gelcasting has been recognized as a very high-potential process: controllable casting, rapid forming cycle, minimal moulding defects, fabricating green bodies with high mechanical strength and stiffness, low shrinkage during drying and sintering processes, and the capability of processing complex shape and near-net-shape ceramic parts.[1–5]

After pouring an aqueous slurry of ceramic powder together with small quantities of reactive monomers, crosslinkers, initiators, and accelerators into a mould, the in situ polymerisation (gelation) is initiated. A macromolecular network is created to hold the ceramic particles very near to each other.[6] The gelcast ceramic part is dried to remove the solvent from green gelcast part,[7,8] is heated to burn out the polymer gel and is subsequently sintered for densification. The final product is a near-net-shape part that requires very little machining.[6]

Industry has been reluctant to use gelcasting because the main component of the original gelcasting system, acrylamide, is a neurotoxic.[1,2] To solve this problem, an effort was initiated to develop gelcasting systems that had similar or superior properties to the acrylamide-based system and yet were low in toxicity.[9] Ortega et al.[10] investigated two harmless alternative gelling agents: first polyvinyl-alcohol crosslinked by an organotitanate and second gelatin-based system, for gelcasting of ceramic foams. Ovoalbumin and its hydrolysate proteins were developed as economical and environmental friendly (low toxicity) gelation agents for the production of engineering ceramics from micrometric- and nanometric-sized powders.[11]

Monomers for gelcasting systems, must have the following attributes: preferably water soluble (at least 20% by weight for monofunctional monomers and 2% by weight for difunctional monomers (crosslinkers)), low toxicity and inexpensive.[9] A list of potential monomers that might be useful for their gel-forming tendencies is presented in Table 1. For each new gel compositions, evaluation of the numerous combinations of monofunctional and difunctional monomers, together with the free-radical initiators and ceramic powders, presents a significant experimental challenge. Hence, it seems the study of gelation behaviour

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Table 1
A list of potential monomers that might be useful for their gel-forming tendencies[6]

Monomer	Abbreviation	Functionality
Monofunctional monomer		
Acrylic acid	AA	Acrylate
Dimethyl aminoethyl methacrylate	DMAEMA	Acrylate
Dimethyl aminopropyl methacrylamide	DMAPMAM	Acrylamide
Hydroxyethyl acrylate	HEA	Acrylate
Hydroxyethyl methacrylate	HEMA	Acrylate
Hydroxypropyl acrylate	HPA	Acrylate
Hydroxypropyl methacrylate	HPMA	Acrylate
Methoxy poly(ethylene glycol) monomethacrylate	MPEGMA	Acrylate
Methacrylamide	MAM	Acrylamide
Methacrylatoethyl trimethyl ammonium chloride	MAETAC	Acrylate
Methacrylamidopropyle trimethyl ammonium chloride	MAPTAC	Acrylate
Methacrylic acid	MAA	Acrylate
p-Styrene sulfonic acid (sodium salt)	SSA	Vinyl
n-Vinyl pyrrollidone	NVP	Vinyl
Difunctional monomer		
Diallyl tartardiamide	DATDA	Allyl
N,*N*′-methylene bis acrylamide	MBAM	Acrylamide
Poly(ethylene glycol XXX) diacrylate	PEG(XXX)DA	Acrylate
Poly(ethylene glycol XXX) dimethacrylate	PEG(XXX)DMA	Acrylate
Trialyl amine	TAA	Allyl

of suspensions made with the new gel precursor solutions is required.

Surprisingly, little attention was given to the study of the gelation behaviour aspects of the new gelcasting systems. Morissette and Lewis,[12] investigated chemorheology of aqueous-based alumina-poly(vinyl alcohol) suspensions during gelation process. The chemorheology of alumina-aqueous acrylamide gelcasting systems was investigated in our previous work.[13] In this study, gelation kinetics of acrylic acid-based system as a low-toxic gelcasting system, were investigated and compared with the original acrylamide-based system.

2. Experimental

2.1. Materials

The characteristics of materials used in this work are given in Table 2.

2.2. Procedure

An appropriate amount of monomers was dissolved in deionized water to make pre-mix solution. 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.[14] Suspensions were mechanically stirred for at least 2 h.

A digital thermometer (i.e. pH–mV–temperature meter with an accuracy of $\pm 0.8\,^{\circ}C$, Lutron TM-905, Taiwan) was used to measure the temperature of suspensions during the progress of gelation.

2.3. Statistical survey of the gelcasting systems

Experimental design is generally applied to determine the dependence of a target variable such as idle time, t_{idle}, i.e. the time interval between the addition of the initiator or the initiator/accelerator and the commencement of polymerisation, on the rest of the variables.

The effects of four variables at four levels (Table 3) on the gelation behaviour of the gelcasting systems were investigated. To reduce the total number of experiments, a fractional factorial design was employed. The Taguchi statistical method[15] is well suited to the study of a process that has many factors that need to be evaluated at several levels. This method was chosen for investigating of the gelation properties of the gelcasting systems.

An M_{16} (4^4) orthogonal array of experiments was chosen for the initial set of experiments. This M_{16} array can be used, in principle, to examine the effects of four variables at four levels on a target variable (t_{idle}) in only 16 experiments.[16]

Table 2
Characteristics of materials

Materials	Function	Molecular formula	Characteristics	Supplier
α-Alumina	Ceramic phase	$\alpha\text{-}Al_2O_3$	Average particle size (3 μm)	Good Fellow[a]
Acrylamide (AM)	Monofunctional monomer (neurotoxic)	$C_2H_3CONH_2$	Mw. 71.08 solid white powder	Merck[b]
Acrylic acid (AA)	Monofunctional monomer (low toxicity)	$C_3H_4O_2$	Mw. 72.06 liquid, transparent	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. 15000 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., P.O. Box 14508, St. Louis, MO 63178, USA.
[d] R.T. Vanderbilt Co., Norwalk, CT, USA.

Table 3
The levels of variables affecting the gelation behaviour of gelcasting systems

Variable	Gelcasting system	Level 1	Level 2	Level 3	Level 4
Monofunctional monomer (vol.%)	Acrylamide	6	7	8	9
	Acrylic acid	20	25	30	35
Ceramic powder (vol.%)	Acrylamide	20	30	35	40
	Acrylic acid	30	35	37.5	40
Molar ratio of monofunctional monomer to the crosslinker	Acrylamide and acrylic acid	16	18	20	22
Molar ratio of initiator to total monomers	Acrylamide[a]	0.2	0.3	0.4	0.5
	Acrylic acid[b]	1	1.2	1.4	1.6

[a] [Accelerator] = 0.1[initiator].
[b] [Accelerator] = [initiator].

3. Results and discussion

3.1. Gelation process and statistical analysis

The gelation process of the low-toxicity acrylic acid gelcasting system and the original acrylamide-based system, in the M_{16} orthogonal array of experiments, are shown in Table 4 and Figs. 1 and 2. In the new low-toxic gelcasting system, unlike the original acrylamide-based system, the temperature of the system decreases slowly and then increases sharply. Decreasing of temperature in the acrylic acid-based system is due to endothermic reactions in the initiation step of chain polymerisation of acrylic acid, as presented by Caykara and Guven.[17] Therefore, the idle time (t_{idle}) in this system is very distinct and can be determined exactly. This is the point, where the thermal behaviour of reaction changes from endothermic to exothermic.

The experimental results for the idle time and processing time (i.e. the time interval, which is started immediately after

Table 4
The M_{16} orthogonal array of experiments

System	Experiment number (vol.%)	Monofunctional monomer	Ceramic powder (vol.%)	Molar ratio of monofunctional monomer to the crosslinker	Molar ratio of initiator to total monomers
Acrylamide	1	6	20	16	0.2
	2	6	30	18	0.3
	3	6	35	20	0.4
	4	6	40	22	0.5
	5	7	20	18	0.4
	6	7	30	16	0.5
	7	7	35	22	0.2
	8	7	40	20	0.3
	9	8	20	20	0.5
	10	8	30	22	0.4
	11	8	35	16	0.3
	12	8	40	18	0.2
	13	9	20	22	0.3
	14	9	30	20	0.2
	15	9	35	18	0.5
	16	9	40	16	0.4
Acrylic acid	1	20	30	16	1
	2	20	35	18	1.2
	3	20	37.5	20	1.4
	4	20	40	22	1.6
	5	25	30	18	1.4
	6	25	35	16	1.6
	7	25	37.5	22	1
	8	25	40	20	1.2
	9	30	30	20	1.6
	10	30	35	22	1.4
	11	30	37.5	16	1.2
	12	30	40	18	1
	13	35	30	22	1.2
	14	35	35	20	1
	15	35	37.5	18	1.6
	16	35	40	16	1.4

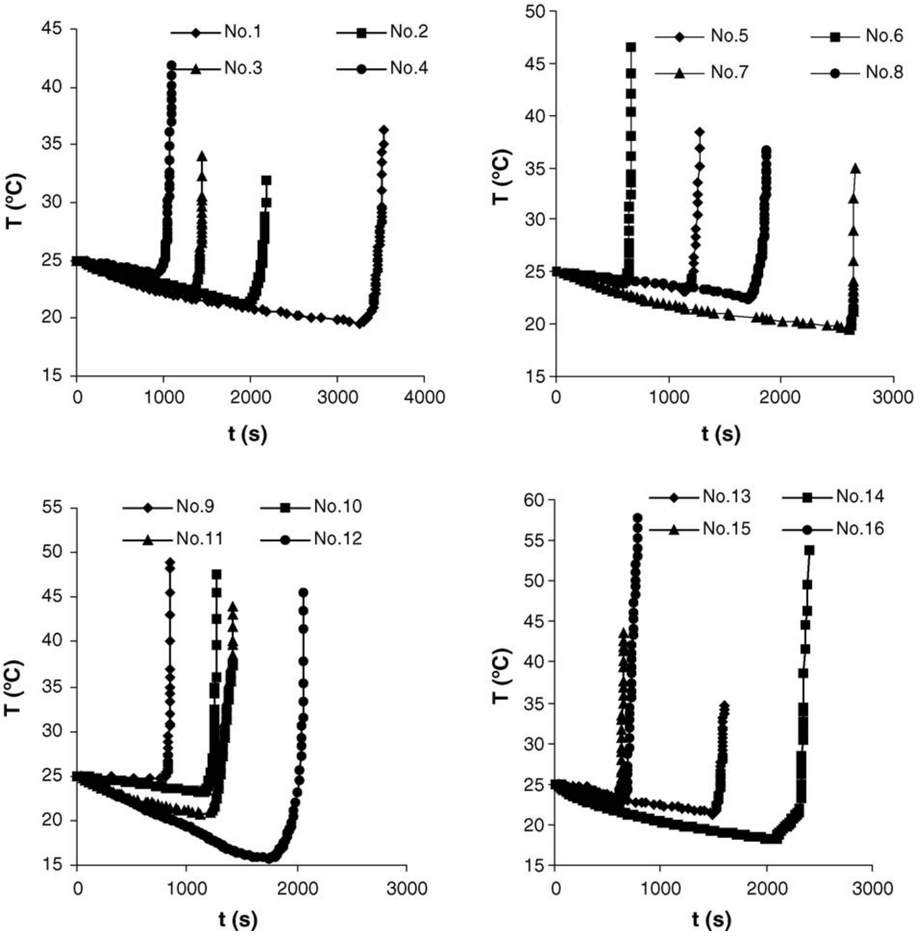

Fig. 1. The gelation behaviour of the low-toxic acrylic acid-based gelcasting system in the M_{16} orthogonal array of experiments.

addition of initiator to the suspension and terminated when the temperature rising is stopped) for both of the systems in the M_{16} orthogonal array of experiments are given in Table 4.

A statistical analysis of the results has been carried out to identify the effects of individual variables and their interactions. The statistical technique popularly known as analysis of variance (ANOVA) was used to determine the significance of each variable and their interaction effects. The signal-to-noise ratio (S/N) was used in the statistical analysis of the results. In fact, it is a way of isolating the sensitivity to noise factors.[16] The results are set out as shown in Tables 5 and 6 for both of the investigated systems.

Table 5
The statistical analysis of the idle time experimental results

Idle time (t_{idle})							
System	Variables	DOF (f)	Sum of squares (S)	Variance (V)	F-ratio (F)	Pure sum (S')	Percent (P)
Acrylamide	Monofunctional monomer (vol.%)	3	72.895	24.298	313.689	72.663	18.969
	Ceramic powder (vol.%)	3	4.559	1.519	19.63	4.326	1.129
	Molar ratio of initiator to total monomers	3	26.585	8.886	114.471	26.353	6.879
	Molar ratio of initiator to total monomers	3	278.776	92.925	1200.333	278.544	72.717
	Other/error	3	0.231	0.077	–	–	0.306
	Total	15	383.049	–	–	–	100
Acrylic acid	Monofunctional monomer (vol.%)	3	57.156	19.052	36.118	55.574	16.273
	Ceramic powder (vol.%)	3	16.641	5.547	10.515	15.058	4.409
	Molar ratio of initiator to total monomers	3	8.369	2.789	5.288	6.786	1.987
	Molar ratio of initiator to total monomers	3	257.745	85.915	162.873	256.163	75.012
	Other/error	3	1.581	0.527	–	–	2.319
	Total	15	341.495	–	–	–	100

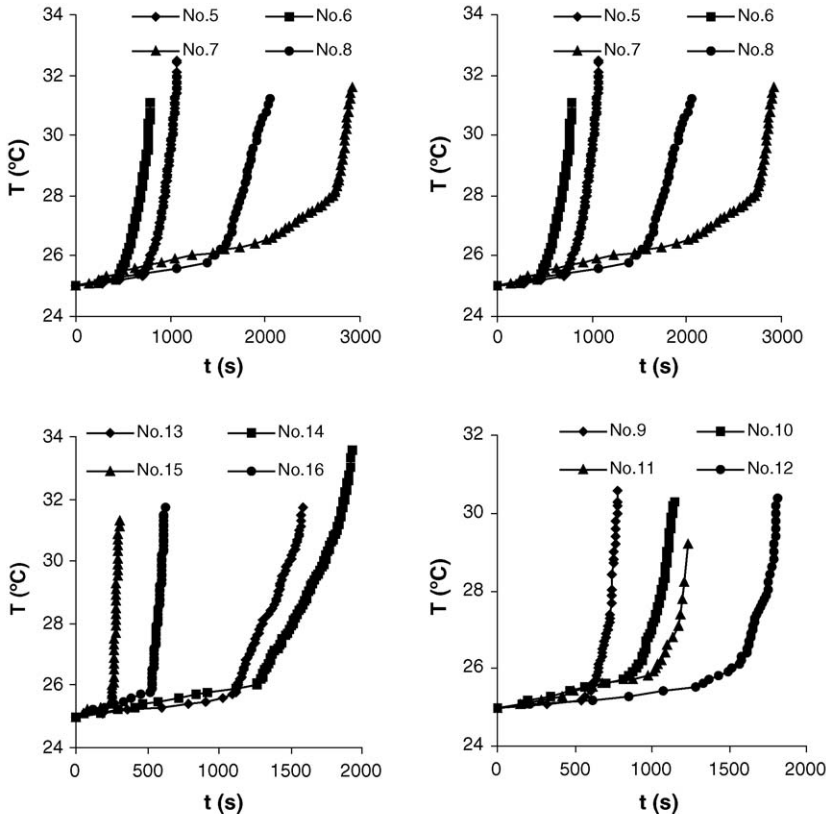

Fig. 2. The gelation behaviour of the original acrylamide-based gelcasting system in the M_{16} orthogonal array of experiments.

The statistical analysis of the results shows that, within the selected range of variables, concentration of the initiator has the strongest effect on the gelation behaviour of gelcasting systems. This effect is the combination of the effects of initiator and accelerator, because in the gelcasting systems the concentration of accelerator is directly attributed to the initiator concentration as presented in Table 3.

Both the monofunctional monomers acrylamide and acrylic acid show similar effects on the idle and processing times in their own gelcasting systems, which are valid in the range of their changes mentioned in Table 3. The rest of variables (i.e. volume fraction of powder and molar ratio of monofunctional monomer to crosslinker) do not have strong effects on gelation behaviour of gelcasting systems. The statistical analysis of the results shows

Table 6
The statistical analysis of the processing time experimental results

Processing time							
System	Variables	DOF (*f*)	Sum of squares (*S*)	Variance (*V*)	*F*-Ratio (*F*)	Pure sum (*S*′)	Percent (*P*)
Acrylamide	Monofunctional monomer (vol.%)	3	122.436	40.812	27.551	117.992	26.762
	Ceramic powder (vol.%)	3	8.287	2.762	1.865	3.843	0.871
	Molar ratio of initiator to total monomers	3	38.598	12.866	8.685	34.155	7.746
	Molar ratio of initiator to total monomers	3	267.124	89.041	60.11	262.68	59.579
	Other/error	3	4.443	1.481	–	–	5.042
	Total	15	440.891	–	–	–	100%
Acrylic acid	Monofunctional monomer (vol.%)	3	41.72	13.906	18.354	39.447	13.059
	Ceramic powder (vol.%)	3	10.337	3.445	4.547	8.064	2.669
	Molar ratio of initiator to total monomers	3	4.807	1.602	2.115	2.534	0.839
	Molar ratio of initiator to total monomers	3	242.915	80.971	106.868	240.642	79.668
	Other/error	3	2.272	0.757	–	–	3.765
	Total	15	302.054	–	–	–	100%

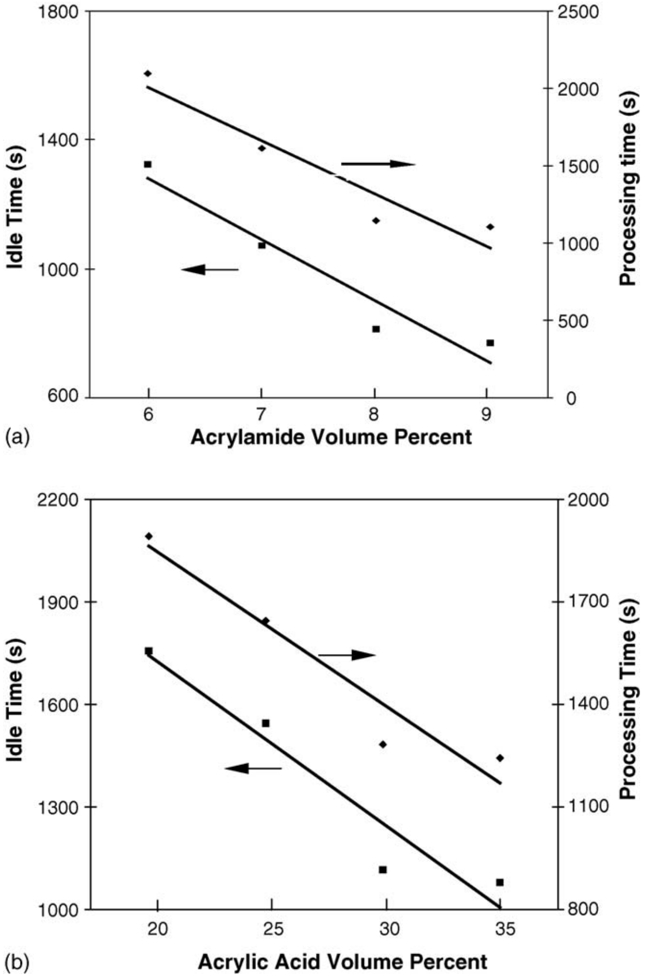

Fig. 3. The idle and processing time of (a) acrylamide-based system and (b) acrylic acid-based system as a function of monofunctional monomer volume percent.

that the counter interacting term of these variables is significant (i.e. 69% for acrylamide-based system and 56% for acrylic acid-based system). This counter interaction term reduces the pure effects of these variables on the gelation behaviour of gelcasting systems.

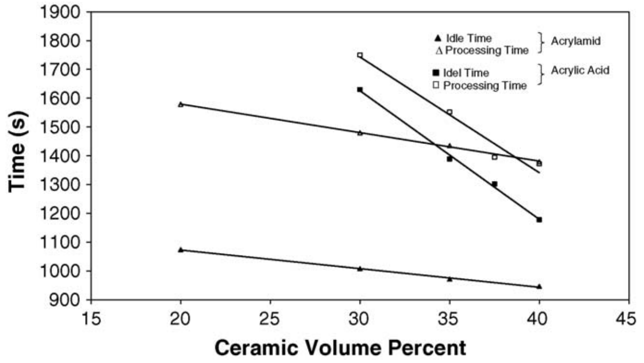

Fig. 4. The idle and processing time of acrylamide and acrylic acid-based systems as a function of ceramic loading levels.

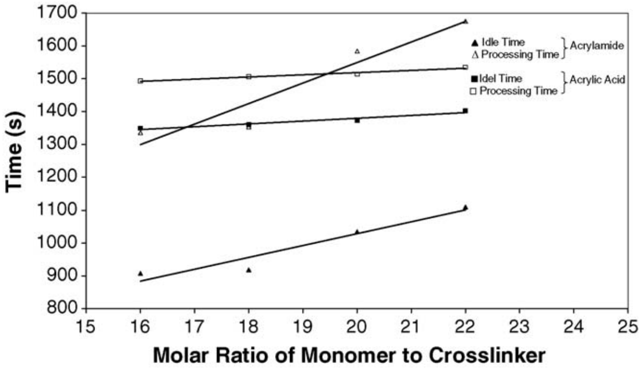

Fig. 5. The idle and processing time of acrylamide and acrylic acid-based systems as a function of molar ratio of monofunctional monomer to the crosslinker.

3.2. Evaluation the effects of variables on gelation behaviour

3.2.1. Monofunctional monomers

The idle and processing time of the suspensions decrease by increasing the monofunctional monomer concentration in both

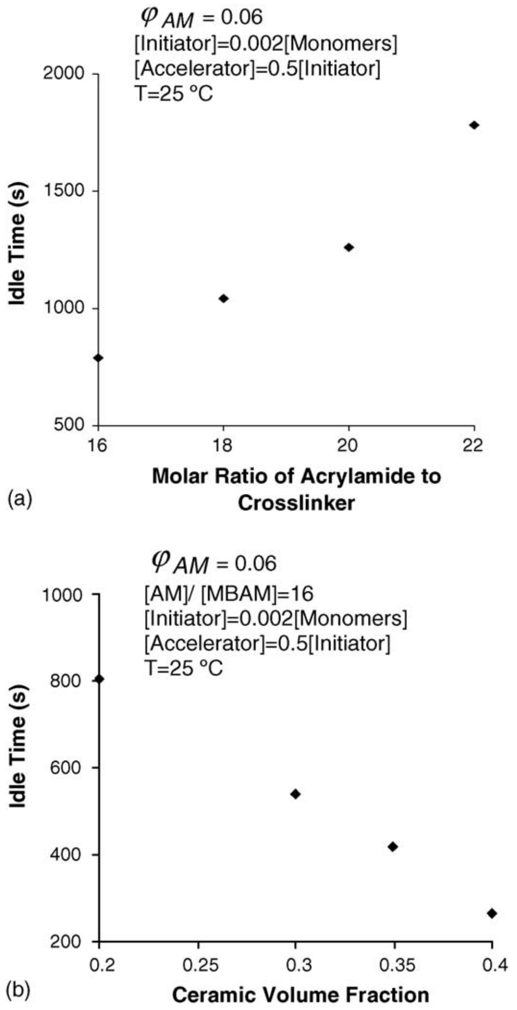

Fig. 6. The pure effects of (a) crosslinker and (b) ceramic loading on the idle time of acrylamide-based gelcasting system.[13]

of the gelcasting systems, as shown in Fig. 3. These results are in a good agreement with the theories which have been presented for the free radical polymerisation.[18]

3.2.2. Ceramic powder

Fig. 4 shows that the idle and processing time of gelcasting systems are linear functions of ceramic loading level. The gelation kinetics are influenced by the volume fraction of Al_2O_3 ($\phi_{Al_2O_3}$). This observation indicates that the ceramic powder has a catalytic effect. The catalytic effect of Al_2O_3 is probed by the decreasing of idle time and processing time with increasing volume fraction of alumina powder.[13]

3.2.3. Crosslinker

The idle and processing time of suspensions increase by increasing the molar ratio of the monofunctional monomer to the crosslinker and/or decreasing the crosslinker concentration, as shown in Fig. 5. It is probably attributed to the reaction of crosslinker with the monofunctional monomer at high concentrations, to form very tight net.[19]

Figs. 4 and 5 show that the effects of the crosslinker and ceramic powder loading level on the gelation behaviour of both gelcasting systems are very weak, while in the pervious work, the pure effects of crosslinker and ceramic powder have been reported contrary for the acrylamide-based system, as shown in Fig. 6.[13] The comparison between these two experimental works confirms the existence of counter interaction effect between ceramic powder loading level and molar ratio of monofunctional monomer to the crosslinker.

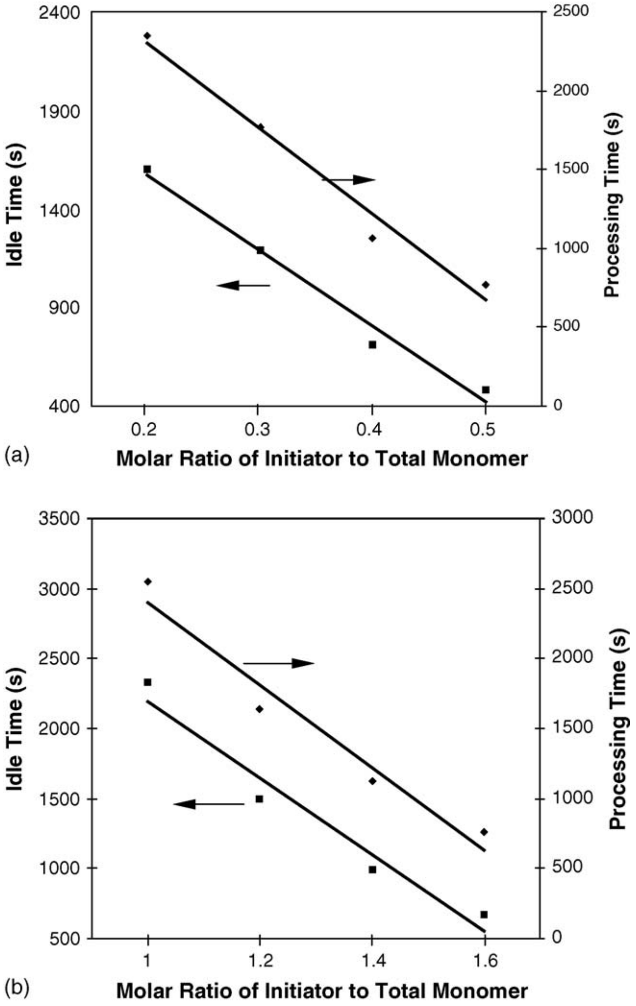

Fig. 7. The idle and processing time of (a) acrylamide-based system and (b) acrylic acid-based system as a function of initiator concentration.

3.2.4. Initiator and accelerator

Fig. 7 shows the variation of the idle and processing time of gelcasting systems with respect to the amount of initiator and accelerator. The experimental results are in a good agreement with the previous theoretical work.[18]

As mentioned earlier, initiator and accelerator concentrations have the strongest effects on the idle and processing time of gelcasting systems, as compared with the rest of variables.

4. Conclusion

In this study, the gelation behaviour of a low-toxic gelcasting system, i.e. acrylic acid-based system, was investigated and compared with the original acrylamide-based system. The obtained results are presented as follow:

- In the acrylic acid-based system, unlike the original acrylamide-based system, temperature of the suspensions decreases before the commencement of polymerisation, hence, the precise monitoring of the idle time (t_{idle}) is possible in this system.
- The effects of monofunctional monomers on the idle time and processing time in both of the gelcasting systems are alike.
- In both gelcasting systems, initiator and accelerator have the strongest effects on the gelation process.
- The statistical analysis of results shows that in both gelcasting systems the counter-interacting term of ceramic powder loading level and molar ratio of monofunctional monomer to crosslinker is significant.
- In the acrylic acid-based system, the amount of monofunctional monomer is about four times more than the acrylamide-based system.
- The molar concentration of initiator and accelerator in the acrylic acid-based system, are about 12 and 120 times more than the original acrylamide system, respectively.

The results show in the acrylic acid-based system in spite of very low activity in the gelcasting process all of the undesirable neurotoxic effects of the original gelcasting system were omitted.

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References

1. Young, A. C., Omatete, O. O., Janney, M. A. and Menchhofer, P. A., Gelcasting of alumina. *J. Am. Ceram. Soc.*, 1991, **74**(3), 612–618.
2. Omatete, O. O., Janney, M. A. and Srehlow, R. A., Gelcasting, a new ceramic forming process. *Ceram. Bull.*, 1991, **70**(10), 1642–1649.
3. Janney, M. A. and Omatete, O. O., Method for moulding ceramic powders using a water-based gel casting process. U.S. Patent 5,145,908, September 8, 1992.
4. Gu, Y., Liu, X., Meng, G. and Peng, D., Porous YSZ ceramics by water-based gel casting. *Ceram. Int.*, 1999, **25**, 705–709.
5. Kokabi, M., Pirooz, A. and Nekoomanesh, M., Gel-casting of engineering ceramics. *Iranian Polym. J.*, 1998, **7**(3), 169–175.
6. Omatete, O. O., Janney, M. A. and Nunn, S. D., Gelcasting: from laboratory development toward industrial production. *J. Eur. Ceram. Soc.*, 1997, **17**, 407–413.
7. Barati, A., Kokabi, M. and Famili, N., Modeling of liquid desiccant drying method for gelcast ceramic parts. *Ceram. Int.*, 2003, **29**, 199–207.
8. Barati, A., Kokabi, M. and Famili, N., Drying of gelcast ceramic parts via the liquid desiccant method. *J. Eur. Ceram. Soc.*, 2003, **23**, 2265–2272.
9. Janney, M. A., Omatete, O. O., Walls, C. A., Nunn, S. D., Ogle, R. J. and Westmoreland, G., Development of low-toxicity gelcasting system. *J. Am. Ceram. Soc.*, 1998, **8**(3), 581–591.
10. Ortega, F. S., Valenzuela, F. A. O., Scuracchio, C. H. and Pandolfelli, V. C., Alternative gelling agents for the gelcasting of ceramic foams. *J. Eur. Ceram. Soc.*, 2003, **23**, 75–80.
11. Schilling, C. H., Tomasik, P., Li, C. and Sikora, M., Protein plastisisers for aqueous suspensions of micrometric- and nanometric-alumina powder. *Mater. Sci. Eng. A*, 2002, **336**, 219–224.
12. Morissette, S. L. and Lewis, J. A., Chemorheology of aqueous-based alumina-poly(vinyl alcohol) gelcasting suspensions. *J. Am. Ceram. Soc.*, 1999, **82**(3), 521–528.
13. Babaluo, A. A., Kokabi, M. and Barati, A., Chemorheology of alumina-aqueous acrylamide gelcasting systems. *J. Eur. Ceram. Soc.*, 2004, **24**, 635–644.
14. Barati, A., Kokabi, M. and Babaluo, A. A., The effect of poly(methacrylic acid) polyelectrolytes in stability of alumina suspensions. *Iranian J. Polym. Sci. Technol.*, 2002, **15**(2), 131–141.
15. Weiser, M. W. and Fong, K. B., Application of Taguchi method of experimental design to improving ceramic processing. *Am. Ceram. Soc. Bull.*, 1993, **73**(1), 83–86.
16. Phadke, M. S., *Quality Engineering Using Robust Design*. Prentice-Hall International, Inc., AT & Bell Laboratories, USA, 1989, pp. 98–128.
17. Caykara, T. and Guven, O., Kinetic analysis of the radiation induced polymerisation of an acrylic acid-silica system. *Eur. Polym. J.*, 1999, **35**, 113–119.
18. Sun, S. F., *Physical Chemistry of Macromolecules*. John Wiley and Sons, New York, 1994, pp. 36–42.
19. Peppas, N. A. and Bell, C. L., Equilibrium and Dynamic Swelling of Polyacrylates. *Polym. Eng. Sci.*, 1996, **36**, 1856–1861.