Persulfate−Amine Initiation Systems for Gelcasting of Ceramic Foams

P. Sepulveda*[†,‡] and J. G. P. Binner[‡,§]

Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN, Travessa R, 400- Cidade Universitária, São Paulo, SP, 05508-900, Brazil, and IPTME, Loughborough University, Leicestershire LE11 3TU, U.K.

Received May 1, 2001. Revised Manuscript Received July 26, 2001

The in situ polymerization of organic monomers to consolidate ceramic suspensions in the form of gelled bodies with very complex shapes has recently been employed for the manufacture of both dense and porous ceramics. The control of the polymerization rate is very important, particularly for the porous ceramics where there is the need for fast consolidation to retain the foamed suspension without damage to the pore structure or loss of pore volume. In the current work, ammonium acrylate and methylenebisacrylamide were used to promote gelation of foamed alumina suspensions. A variety of amine catalysts were tested in combination with ammonium persulfate as initiating systems for polymerization. Analysis of the exothermic profiles registered during polymerization revealed that the polymerization onset and rates are markedly influenced by the concentration and type of initiating species, with tertiary diamines being the most efficient accelerators.

Introduction

Application of the gelcasting technique to the setting of foamed ceramic suspensions has gained significant importance because it allows the manufacture of large and complex-shaped bodies with porosity levels as high as 95% and significantly improved mechanical properties compared to other related techniques.[1−3] The process is comprised of incorporation of organic monomers into ceramic aqueous suspensions, aeration of the suspensions, and in situ polymerization of organic monomers to consolidate the bodies. A gel retains the liquid films in the foams by the formation of a three-dimensional polymeric network. The organics are later burnt-out, and consolidation of the matrix is further accomplished by sintering.

An extensive list of monomeric additions has been used to set ceramic systems, including butyl methacrylate,[4] methyl methacrylate (MMA) and butyl acrylate (BA),[5] acrylamide (AM), 2-hydroxyethyl methacrylate (HEMA), methyl acrylate (MA), *N*-vinyl pyrrolidone (NVP), ethylene dimethacrylate (EDMA), and diethylene glycol diacrylate (DEGDA).[6−8] These are monomers typically used in aqueous solutions to produce gels with extensive branching and cross-linking during polymerization. Nevertheless, difficulties regarding the dispersion of powders incorporating some types of monomeric additions have been reported. Acrylamide (AM) and *N*,*N*-methylenebisacrylamide (MBAM), for instance, provided good characteristics in combination with alumina and dense suspensions of low viscosity could be attained. Butyl methacrylate or methyl methacrylate monomers on the other hand, only permitted the preparation of alumina slips containing up to 55 wt % solids.[8]

A variety of initiating systems can be used to bring about the polymerization reaction of these monomers, and they have a significant influence on the resultant reaction rate; some are thermally activated, i.e., radicals are generated spontaneously only upon heating at 50−150 °C.[9] In the gelcasting of ceramics “redox” type initiators have been also employed; these are based on a reducing and an oxidizing agent reacting to produce intermediate radical reactions at low temperatures.[9] The activation energy required to produce radicals using redox systems is much lower than for thermal initiation; therefore, significantly higher polymerization rates are produced. The important features of the redox systems are their solubility in water and fast and constant liberation of initiating radicals in the aqueous phase.[10,11] Commonly peroxy compounds can be suitable initiators,

---

[†] IPEN/CNEN.

[‡] Formerly of the Department of Materials Engineering & Materials Design, University of Nottingham, U.K.

[§] Loughborough University.

(1) Sepulveda, P. *Am. Ceram. Soc. Bull.* **1997**, *76* (10), 61−65.

(2) Sepulveda, P.; Binner, J. G. P. *J. Eur. Ceram. Soc.* **1999**, *19*, 2059−2066.

(3) Sepulveda, P.; Ortega, F. S.; Innocentini, M. D. M.; Pandolfelli, V. C. *J. Am. Ceram. Soc.* **2000**, *83* (12), 3021−3024.

(4) Landham, R. R.; Nahass, P.; Leung, D. K.; Ungureit, M.; Rhine, W. E.; Bowen, H. K.; Calvert, P. D. *Am. Ceram. Soc. Bull* **1987**, *66* (10), 1513−1516.

(5) Grader, G. S.; Zuri, L. *J. Am. Ceram. Soc.* **1993**, *76* (7), 1809−1814.

(6) Omatete, O. O.; Young, A. C.; Janney, M. A.; Adair, J. H. in Messing, G. L.; Hausner, H., Editors. Ceramic Powder Science III. *Ceram. Trans.* **1990**, *12*, 537−544.

(7) Janney, M. A.; Omatete, O. O.; Walls, C. A.; Nunn, S. D.; Ogle, R. J.; Westmoreland, G. *J. Am. Ceram. Soc.* **1998**, *81* (3), 581−591.

(8) Janney, M. A.; Marietta, M. U.S. Patent 4894194, 1990.

(9) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley and Sons: New York, 1991; pp 198−291 and pp 510−523.

(10) Bovey, F. A., Kolthoff, I. M., Medalia, A. I., Meehan, E. J., Eds. *High Polymers IX;* Interscience Publishers: New York, 1955; pp 59−93.

(11) Elias, H.-G. *Macromolecules 2, Synthesis and Materials*, 2nd ed.; Plenunm Press: London, 1984; pp 525−530 and pp 681−736.

10.1021/cm010437l CCC: $20.00

such as peroxydisulfates, peroxydiphosphates, and H_2O_2, which are combined with metallic ions as reducing agents such as Ag, Fe, Cu, and Co.[10] Other reducing agents have been preferred in processing of advanced ceramics because the presence of metallic compounds can be detrimental to the mechanical, electrical, magnetic, and optical properties.[12] Benzoyl peroxide has also been used in ceramic systems, either on its own when it decomposes at temperatures above 60 °C or combined with tertiary aromatic amines such as *N*,*N*-dimethyl-*p*-toluidine, initiating polymerization of acrylate monomers at room temperature.[4] Ammonium persulfate with *N*,*N*,*N′*,*N′*-tetramethylethylenediamine[13] has been shown to promote polymerization of monomers such as acrylamide, methacrylamide, and acrylic acid at room temperature.

As a result of the induced decomposition reactions taking place in redox systems, they are very sensitive to the medium; their decomposition rates depend very much on the concentration of the other participating reagents. The influence of type and concentration of monomer[8] and of processing conditions such as pH, initial temperature, and oxygen content[14] has been demonstrated previously. The concentration of initiating systems has also been investigated in the gelcasting of dense ceramics.[13] The initiator determines the number of free radicals that will interact with monomers to start polymerization, influencing polymerization rates, polymer yield, and the length of the polymer chains. These in turn alter the quality of the green ceramic body produced.

In the gelcasting of foamed systems a short onset time before polymerization and high polymerization rates are required. Any disruption to the liquid foams prior to setting, such as excessive drainage creating too thin or ruptured films, implies damage to the final microstructure and can compromise the mechanical strength of the ceramic foams.[15]

In the present work, the polymerization of acrylic monomers plus a cross-linking agent was investigated in aqueous systems containing ceramic powder for the processing of porous ceramics. Initiation was promoted with redox pairs including ammonium persulfate (APS) as initiator and different types of amines as catalysts. The concentration of the initiating species was evaluated as a means of controlling the parameters that dictate gelation kinetics.

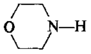
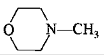
Experimental Procedure

Ceramic suspensions were prepared by mixing alumina (A-16 SG, average particle size 0.55 μm, Alcoa Aluminum S. A.), distilled water, dispersing agents, and organic monomers for setting the slurry in the percentages shown in Table 1. Ammonium polyacrylate and polymethacrylate aqueous solutions were used as the dispersing agents (Versicol KA11 and Dispex A40, Allied Colloids, Bradford, U.K.). The aqueous solution of monomers (Allied Colloids) contained approximately 29% of ammonium acrylate and 1 wt % of methylenebisacrylamide as the cross-linking agent to promote gel formation. The suspensions were homogenized by exposure to ultrasonic energy.

Table 1. Composition of the Alumina Suspensions

component	quantity/(wt %)	component	quantity/(wt %)
alumina	71.43	dispersant	0.66
water	21.40	monomer solution	6.51

Table 2. Description of Catalysts Used in Combination with Ammonium Persulfate To Initiate the Polymerization of Acrylic Monomers

Catalyst	**Structure**	**Description**
TEMED*	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	N,N,N',N'-tetramethylethylene diamine
THEED**	$[(HOCH_2CH_2)_2NCH_2—]_2$	N,N,N',N'-tetra (2-hydroxyl)ethylene diamine
MP**		Morpholine
NMMP**		4-Methylmorpholine

* Aldrich Chemical Co. **Fluka Chemie AG.

A total weight of 95 g of suspension was foamed up to 250 mL by vigorous agitation and with the addition of 0.16 wt % Tergitol TMN10. The latter is a poly(ethylene glycol) trimethylnonyl ether (Fluka Chemie AG) that lowers the surface tension and stabilizes the foam. The whole procedure of foam generation was conducted in a sealed glovebox under a nitrogen atmosphere to avoid the presence of oxygen, which can inhibit the polymerization reaction. The oxygen content was maintained at 0.0% and monitored with an oxygen analyzer (Servomex, Sussex, U.K.).

The polymerization process of foamed suspensions was promoted using chemical initiation by redox pairs of persulfate and different amines. The initiator was ammonium persulfate $(NH_4)_2S_2O_8$ (APS, Aldrich Chemical Co.) diluted in deionized water at a concentration of 0.52 g mL^{-1}. The amine catalysts were two tertiary aliphatic diamines, TEMED and THEED, and two cyclic amines, NMMP (secondary) and MP (primary), whose compositions are shown in Table 2. Polymerization was conducted with the addition 3.3×10^{-5} mol/g of APS and 3.5×10^{-5} mol/g of the relevant catalysts, in moles of reagent per gram of monomer.

A thermocouple probe monitored the temperature rise as a function of time. The exothermic profiles generated during polymerization provided an indication of the effectiveness of the reaction, as the rates of temperature increase correlated to the polymerization rates.[16] The curve in Figure 1 shows a schematic of typical temperature versus time curves produced during polymerization. The parameters that could affect polymerization were correlated with the data collected from the exothermic profiles as follows: induction time t_i, maximum rate of temperature increase R_p^{max} (by differentiation of the curve), and the area A_{peak} below the curve up to the maximum temperature (by integration of the selected area below the curve).

After preliminary evaluation of all catalysts, polymerization of foamed alumina suspensions was induced with the selected catalysts. The concentration of these reagents was varied within wide ranges to evaluate their effect on the polymerization rates.

Results and Discussion

Alternative Catalysts for Polymerization. The temperature profiles in Figure 2 present the polymer-

---

(12) Richerson, D. W. *Modern Ceramic Engineering—Properties, Processing and Use in Design*, 2nd ed.; Marcel Dekker: New York, 1992.

(13) Young, A. C.; Omatete, O. O.; Janney, M. A.; Menchhofer, P. A. *J. Am. Ceram. Soc.* **1991**, *74* (3), 612—618.

(14) Sepulveda, P.; Binner, J. G. P. Evaluation of the in Situ Polymerisation Kinetics for the Gelcasting of Ceramic Foams. *Chem. Mater.*, in press.

(15) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley and Sons: New York, 1989; pp 277—303.

(16) Zhu, S.; Hamiliec, A. *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 135—182.

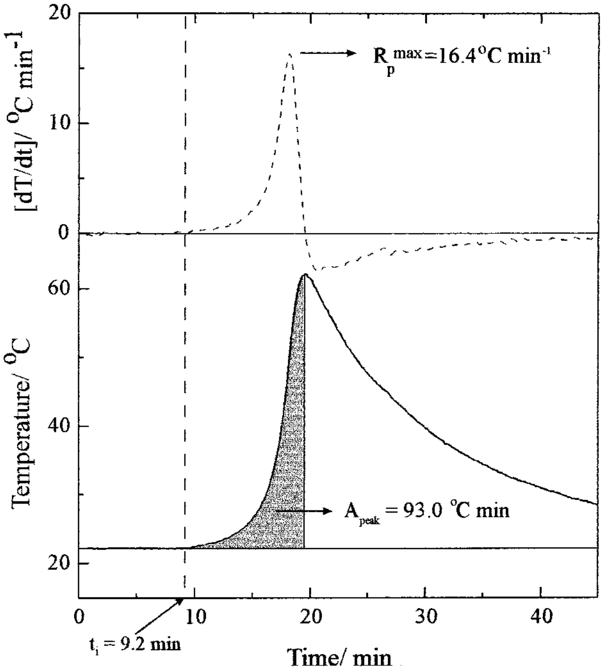


Figure 1. Schematic representation of temperature curves during polymerization and the corresponding plots of temperature increase rates. Parameters extracted from curves include induction time (t_i), maximum polymerization rate (R_p^{max}), and area below the curve up to the maximum temperature (A_{peak}).

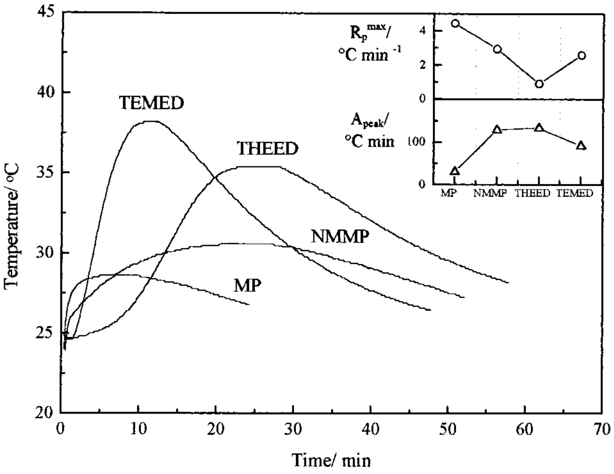


Figure 2. Temperature plots of the polymerization of 95 g alumina suspensions foamed up to 250 mL. The amines MP, NMMP, THEED, and TEMED were used as catalysts. [APS] = 3.3 × 10^{-5} mol g^{-1} and [catalyst] = 3.5 × 10^{-5} mol g^{-1}.

ization reaction behavior in foamed suspensions for four different amines, viz., MP, NMMP, TEMED, and THEED, with the corresponding R_p^{max} and A_{peak} values quoted from the related exothermic curves shown in the inset.

All four catalysts tested were effective promoters of polymerization and led to the formation of gelled bodies. The tertiary aliphatic diamines, TEMED and THEED, generated more exothermic reactions than the cyclic amines, MP and NMMP, whereas the latter produced higher reaction rates. On the basis of the maximum temperature reached during polymerization, the relative activities of peroxydisulfate−amine initiation systems are arranged in the following order: TEMED > THEED > NMMP > MP. The cyclic amines caused gelation with no observable induction time, and the initial reaction rates were higher than the rates at which gelation proceeded due to the faster formation of radicals with these compounds. During initiation in the presence of tertiary aliphatic diamines the radicals formed may be more prone to experience recombination by the solvent cage effect that leads to induction times,[9] probably because of their nature and size. The values of A_{peak}, which are proportional to the amount of heat released during polymerization reactions, were always inversely proportional to R_p^{max} values, indicating that in faster reactions the amount of converted monomer is smaller. This may explain why gelled bodies produced with the cyclic amines, which induced the fastest initial polymerization rates, in general presented weaker texture and were less stiff than the ones obtained with the tertiary aliphatic diamines.

These results agree with the findings of Xinqiu et al.[17] on the investigation of aliphatic and cyclic amines for acrylamide polymerization in aqueous solutions. The work demonstrated that tertiary aliphatic diamines, in particular TEMED, have high promoting effects on polymerization; thus, they may be used with peroxydisulfate as a good water-soluble redox initiation system for preparing hydrogels at ambient temperature. For instance, polymerization rates of ~6 × 10^4 mol L^{-1} s^{-1} have been reported for AAM polymerization using KPS-TEMED, while ~4 × 10 ^{4} mol L^{-1} s^{-1} were possible with cyclic amines under similar conditions.[17] The overall decrease of activation energy and increase of polymerization rates in the presence of cyclic amines compared to tertiary amines was also reported by Xinqiu et al.[17]

Mechanisms of initiation of vinyl monomer polymerization by peroxydisulfate−amine systems have been proposed by several authors,[17−21] although some detailed aspects of kinetic behavior in aqueous systems still produce some controversy. Since initiator contains ($-OSO_{3-}$) and ($-OH$) end groups, hydroxy ($HO^•$) and ($HO_3SO^•$) radicals are the initial free radicals in vinyl polymerization.[20] It has been demonstrated that in peroxydisulfate−amine initiation systems the amine component also takes part in the initiation reaction of vinyl polymerization. Amino alkyl radicals are in the form of $R-N^•$ for primary or secondary amine systems (RHNR)[17] and $R-NCH^•$ for tertiary amines such as $(CH_3)_2NCH_2CH_2(CH_3)NCH_2^•$ for TEMED.[19] The initiation by amine radical has shown to influence the polymer yield and molecular weight.[18]

Although all reducing agents tested in this work were good promoters of polymerization, for the production of porous ceramics fast initiation (as distinct from rapid polymerization) is undesirable because the process involves a casting stage. This would eliminate the use of primary and secondary cyclic amines for initiation, although in varied concentrations they could be useful for the processes that do not require long induction times and high gel strength. The tertiary diamines were the most effective in the present study; thus, they were

---

(17) Xinquo, G.; Kunyan, Q.; Xinde, F. *Sci. Sin., Ser. B* **1987**, *9*, 897−906.

(18) Gupta, M. K.; Bansil, R. *Polym. Prep.* **1981**, *22* (2), 375−376.

(19) Feng, X. D.; Guo, X. Q.; Qiu, K. Y. *Makromol. Chem.* **1988**, *189*, 77−83

(20) Ghosh, N. N.; Gupta, G. N.; Mandal, B. M. *Makromol. Chem.* **1986**, *187*, 2097−2102.

(21) Tanaka, T. *Sci. Am.* **1981**, *224*, 124−138.

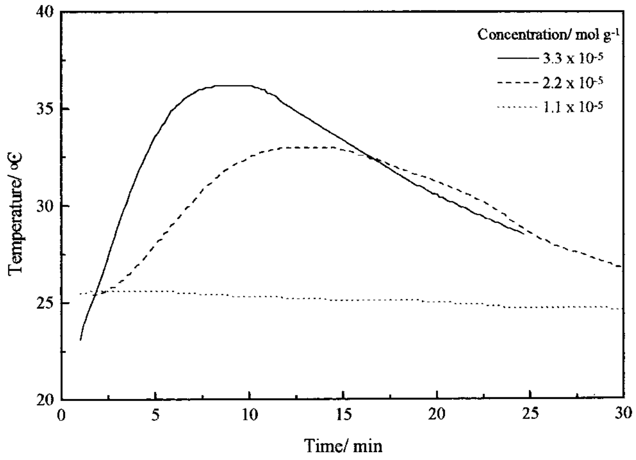


Figure 3. Exothermic profiles recorded during the polymerization of 95 g alumina suspension foamed up to 250 mL. TEMED/APS molar ratio was [1:1] added in concentrations of 3.3 × 10^{-5} mol g^{-1} (solid line), 2.2 $^{-}$ 10^{-5} mol g^{-1} (dashed line), and 1.1 × 10^{-5} mol g^{-1} (dotted line).

selected for further investigation. Tertiary diamines are also the most commonly used catalysts in the plastic foam industry, showing the highest promoting effect on the polymerization rates.[9,11]

APS-TEMED Redox System. Gelation of foamed alumina suspensions was initiated at various concentrations of APS and TEMED using a 1:1 molar ratio. This ratio was initially chosen because it has been reported to be optimum for producing free radicals, as the persulfate is fully used up by the catalyst and the polymer yield is also maximized.[18] The temperature profiles in Figure 3 correspond to the polymerization reactions at three different concentrations. As expected, faster and more exothermic reactions were produced with higher reagent concentrations. At the highest concentration used the induction period was less than 30 s, which is insufficient time for casting. The period could be extended to ~2 min, however, with lower reaction rates when the APS/TEMED concentration was lowered to 2.2 × 10^{-5} mol g^{-1}. An even lower concentration of 1.1 × 10^{-5} mol g^{-1} was insufficient to initiate gelation within the period of ~1 h, and subsequent collapse of the foamed suspension occurred. Intermediate concentrations to those investigated were not possible because of the small volumes involved and the delivering system's resolution limit (10 μL). Although the use of a 1:1 molar ratio of APS/TEMED implies the optimization of free radical production, it leads to a very limited range of induction times and reaction rates that are not interesting for the processing of ceramic foams.

The exothermic plots exhibited in Figure 4 provide an illustration of the influence of APS content on the gelation behavior of foamed suspensions when molar ratios of APS/TEMED other than 1:1 were employed. In general, very fast reactions were produced using very small amounts of the catalyst. The polymerization rates and maximum temperature levels reached during the reaction increased with increasing APS concentration. At too low an APS content value, however, only a few free radicals were formed and polymerization was consequently slow.

Figure 5a shows the data for induction times (t_i) for polymerization of foamed suspensions as a function of the square root of APS concentration, for various concentrations of TEMED. Because of the efficiency of this redox pair, extremely small amounts of the reagents were sufficient to produce very fast polymerization and only a limited range of concentrations was possible, which explains the scattered data. As expected, shorter

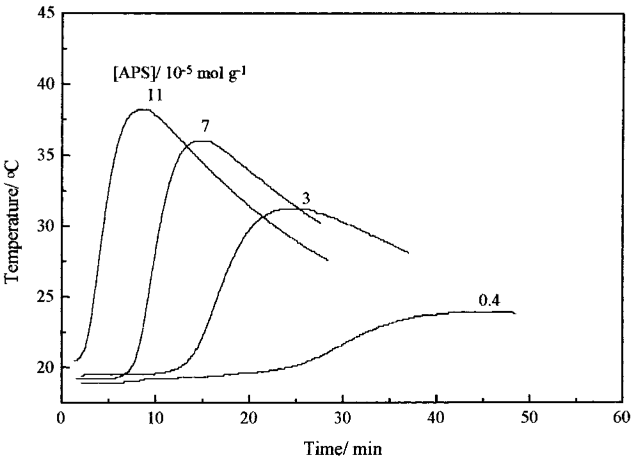


Figure 4. Temperature profiles monitored during the polymerization of 95 g alumina suspensions foamed up to 250 mL. APS concentration was altered as indicated. [TEMED] = 1.1 × 10^{-5} mol g^{-1}.

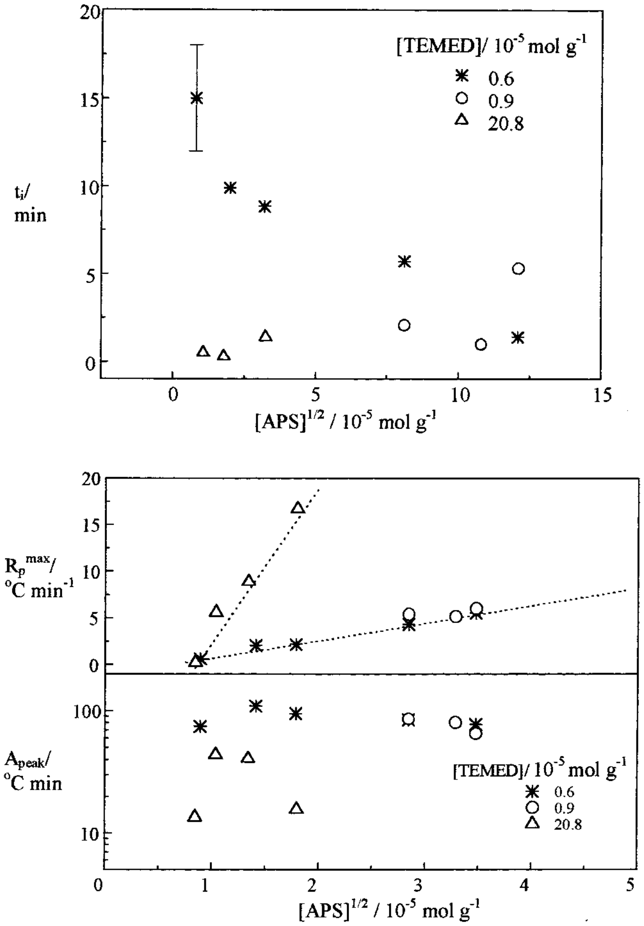


Figure 5. (a, top) Induction time as function of APS concentration and (b, bottom) R_p^{max} and A_{peak} data plotted as function of $[APS]^{1/2}$. Values were extracted from polymerization curves of 250 mL foamed alumina slips. TEMED concentrations used were 0.6 × 10^{-5} mol g^{-1} (star), 0.9 × 10^{-5} mol g^{-1} (circle), and 20.8 × 10^{-5} mol g^{-1} (triangle).

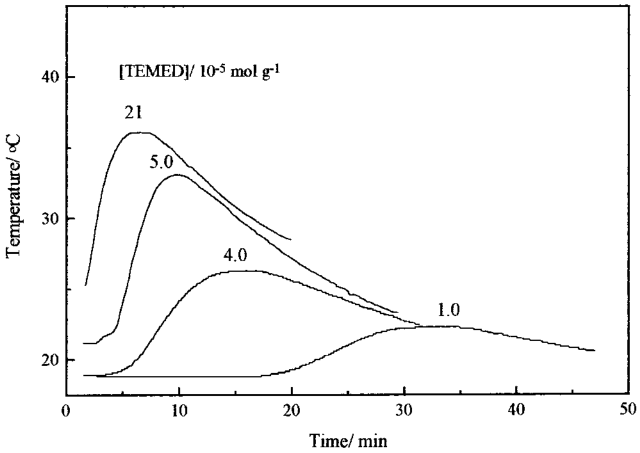


Figure 6. Temperature profiles during the polymerization of 95 g alumina suspensions, foamed up to 250 mL. TEMED concentration was altered as indicated. [APS] = 1.1 × 10^{-5} mol g^{-1}.

induction times (t_i) occurred when the APS and TEMED contents were increased. The data quote induction times varying from approximately 20 s up to 20 min, depending upon the reagent content. However, the gelled bodies produced appeared to have lowered strength as the polymerization onset was extended. A significant degree of bubble coarsening was noted in the foams gelled with t_i longer than ∼10 min, and the bodies fabricated yielded reduced mechanical strength. The longest induction time occurred with very little increase in temperature and although this was still sufficient to produce a solid body, the top layer of this sample suffered considerable collapse.

Trends of induction time being greatly shortened as the concentrations of APS and TEMED are increased were also reported by Young et al.[13] on the polymerization of acrylamide monomers for preparation of dense alumina compounds. Much longer induction periods of up to 120 min were reported for the production of dense ceramics.

Figure 5b depicts the calculated values of maximum temperature increase rate (R_p^{max}) and a value relative to the temperature produced (A_{peak}) as a function of the square root of the APS concentration. The R_p^{max} variation was described by linear relationships with the square root of the APS concentration, with a higher slope for higher TEMED concentrations. The R_p^{max} is proportional to the rate of monomer conversion; thus, the linearity implies that the rate of initiation is directly determined by the rate of persulfate dissociation at a constant TEMED concentration. For acrylamide systems using similar redox initiation, data have been reported showing polymerization rates proportional to a power smaller than 0.4 of the APS concentration curves.[17,19] A_{peak} showed no apparent dependence of $[APS]^{1/2}$.

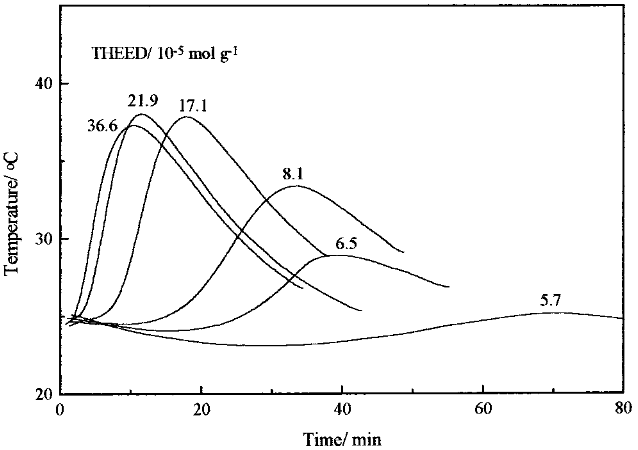


Figure 7. Exotherms recorded during the polymerization of 95 g alumina suspensions, foamed up to 250 mL. [THEED] was altered as indicated. [APS] = 7.2 × 10^{-5} mol g^{-1}.

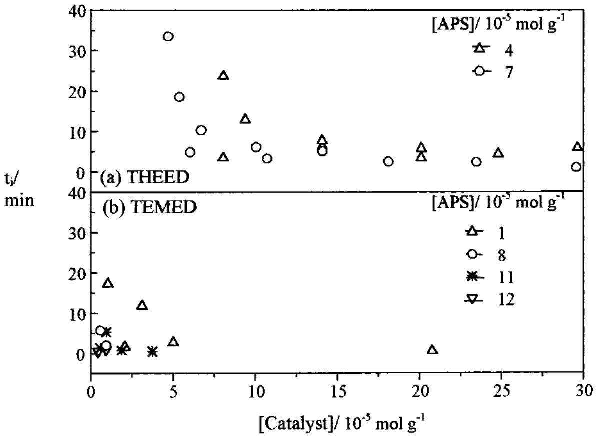


Figure 8. Induction time data extracted from polymerization exotherms of 250 mL foamed alumina suspensions as a function of catalyst concentration, at various APS concentrations as indicated. The catalysts used were (a) THEED and (b) TEMED.

Tertiary Aliphatic Diamines. *APS Initiating Systems.* The polymerization reactions of foamed suspensions employing TEMED and THEED as a catalyst are represented in the temperature profiles of Figures 6 and 7, respectively, using APS concentrations of 1.1 × 10^{-5} and 7.2 × 10^{-5} mol g^{-1}. The different efficiencies of these systems explain the use of such different concentrations to generate reactions in the desired rate ranges for the production of foams. The resulting ranges of induction times obtained in tests carried out with TEMED and THEED are shown in Figure 8. The effect of THEED concentration on R_p^{max} and A_{peak} is presented in Figure 9. The induction time decreased almost exponentially with increasing THEED concentration. Long induction times could be easily obtained with this catalyst. While the logarithm of A_{peak} appeared to be constant with the inverse of THEED content, a linear relationship described the dependence of the R_p^{max} logarithm with 1/[THEED]. The dependence of reaction rates on catalyst concentrations, given by the slope of a double log diagram, was found to be approximately 1 for TEMED (not shown). For THEED this value was 0.5, demonstrating the higher efficiency of the former. However, the induction periods could be varied over much wider ranges when THEED was used, albeit with some reduction in gel strength. The possibility of controlling the polymerization reaction with THEED was therefore much greater than with TEMED. The only practical difficulty found in the use of THEED was its high viscosity, which prevented the extraction of small amounts with the pipet. In the production of larger specimens this would not apply.

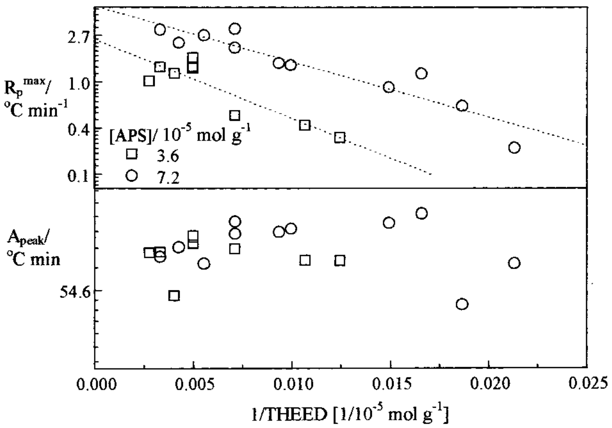


Figure 9. Influence of THEED content on R_p^{max} and A_{peak}. Data extracted from previous polymerization curves. Polymerization was promoted with APS in concentrations of 3.6 × 10^{-5} mol g^{-1} (solid square) and 7.2 × 10^{-5} mol g^{-1} (open square).

Influence of Polymerization Kinetics on Ceramic Foam Properties. Controlling the gelation reaction rates has been regarded as the main difficulty in processing of ceramic foams. The polymerization reactions are very susceptible to variations in viscosity, pH, temperature, oxygen, and suspension composition, as shown in previous work.[14] Despite these, the type and concentration of chemical species that initiate polymerization can determine the time for polymerization to start, as well as propagation rates, therefore providing the means to control the reaction kinetics.

In the processing of ceramic foams, the reagent concentrations should be combined so as to provide relatively short induction times, generally in the range of 1−4 min, i.e., short enough to avoid foam collapse, but sufficiently long for casting the fluid or foam into a mould. Due to the fragile and unstable nature of the liquid foams, liquid drainage, cell wall thinning, and bubble interpenetration take place prior to gelation, leading to bubble enlargement.[15] An adequate induction time solely does not guarantee the success of foam production. Adequate induction times have to be followed by fast reactions, including high polymerization rates (~R_p^{max}) and high-temperature gradients (A_{peak}). These characteristics have been shown to provide stronger gels,[22] as fast propagation of the polymer network helps maintain the foam integrity and high temperatures indicate optimized conversion of monomer into polymer.

The control of polymerization is of prime importance to the final characteristics of ceramic foams. Structural features, such as cell size and cell size distribution (bubbles), strut length (lamellae thickness), and the presence of microstructural flaws due to the rupture of films, have been shown to vary accordingly with the state of the liquid foam at the moment of gelation. Larger cell size, broader cell size distribution, and thinner struts occur for foams gelled with longer induction periods and lower reaction rates.[2] In addition to the effect on mechanical properties, the change in structure caused by different gelation reactions may also influence properties that depend directly on the cell and interconnection size such as permeability and thermal conductivity.[23,24] Therefore, the gelation process must proceed so as to maintain the foam structure, with minimum deteriorating effects to the mechanical properties of the final product.

Conclusions

The in situ polymerization reaction of acrylic monomers has been investigated in aqueous ceramic systems for the production of porous ceramics. A variety of amines, including secondary and tertiary aliphatic or cyclic amines, can be used in a redox pair with ammonium persulfate to promote polymerization of acrylic monomers in aqueous ceramic suspensions. The TEMED reducing agent was the most powerful catalyst for polymerisation, and the gelled bodies were very strong, although a strict control over induction periods was very difficult to obtain with this reagent. The other tertiary aliphatic diamine tested, THEED, enabled better variation of the induction time. However, the gelled bodies produced appeared to have lower strength as the polymerization onset was extended.

Acknowledgment. The authors wish to thank Dytech Corp., U.K., and CAPES, Brazil, for the financial support of this research.

CM010437L

---

(22) Ortega, F. S.; Sepulveda, P.; Pandolfelli, V. C. Monomer Systems for the Gelcasting of Foams. Submitted for publication in *J. Eur. Ceram. Soc.*

(23) Sepulveda, P.; dos Santos, W. N.; Pandolfelli, V. C.; Bressiani, J. C.; Taylor, R. *Am. Ceram. Soc. Bull.* **1999**, *78* (2), 61−66.

(24) Innocentini, M. D. M.; Sepulveda, P.; Salvini, V. R.; Pandolfelli, V. C.; Coury, J. R.*J. Am. Ceram. Soc.* **1998**, *81* (12), 3349−3352.