Evaluation of the in Situ Polymerization Kinetics for the Gelcasting of Ceramic Foams

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Recent processing technologies have employed the in situ polymerization of organic monomers to consolidate particulate suspensions of ceramics into dense and strong bodies. The same principle has been applied to solidify foamed ceramic suspensions with great success. In this work, the parameters that influence the polymerization kinetics of acrylic monomers were investigated in systems containing the separate components of a ceramic suspension, with and without the generation of foam. The main objective was to obtain control of the onset time for polymerization (I_d), which is a critical factor in the processing of foamed ceramics. Analysis of the exothermic profiles registered during polymerization revealed that the polymerization onset is markedly influenced by a number of variables, including the solids concentration, initial temperature, pH, and oxygen concentration.

Introduction

The gelcasting of foams is a recent technology used to manufacture macroporous ceramics with porosity levels as high as 95% and significantly improved mechanical properties as compared to other related techniques.[1−3] The process was independently developed at Oak Ridge National Laboratory but was focused on the production of dense ceramics. In the process, organic monomers are incorporated into a ceramic suspension and polymerized in situ to create a cross-linked, gelled structure that provides rigidity in the green bodies.[4] The manufacture of porous ceramics involves foaming of the suspension prior to gelation, and as a result additional considerations have to be made since the foam structure has a limited lifetime and can quickly deteriorate.[5]

The basic mechanisms of foam disruption involve drainage of the liquid in the film between two bubbles (lamellae) due to capillary pressure, coalescence of bubbles via film rupture, and bubble coarsening via gas diffusion as a result of differences in bubble curvature. Surfactants impart mechanisms that prevent film thinning; with their hydrophobic−hydrophilic nature they lower the surface tension of vapor−liquid interfaces. They also promote film cohesion and elasticity by the interaction between the surfactant chains around the film and diffusion of molecules and liquid to restore gradients in surface tension.[6] However, these mechanisms are limited in their ability to extend the life of foams produced with ceramic suspensions for the production of foams.

This in situ polymerization of monomers has been demonstrated to be an effective setting mechanism for retaining the structure of foamed ceramic suspensions and has led to their commercial production.[7] Many monomeric systems have been investigated for use in gelcasting, including methacrylamide,[8] hydroxymethylacrylamide,[9] methacrylic acid,[9] and ammonium acrylate.[2,3] Cross-linking is generally obtained by copolymerization using dienes, such as the *N*,*N′*-methylenebisacrylamide. Monomers must be water-soluble and have little interaction with the ceramic particles, so that the state of dispersion remains the same. At the beginning of the in situ polymerization process, the foamed system is stabilized by the viscosity increase that delays the drainage of the foam lamella, and, when gelation is finished, retention of liquid in the interstices of the polymeric network solidifies the structure.[5,10] Polymerization of the monomers can be effected by means of chemical substances wherein a period of inactivity may characterize the initial stages of polymerization; this is named the *induction period*[11] and is the time available for casting the fluid or foam into a mould. Generally, the induction period should be suf-

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ficiently long for casting to be completed before setting starts, but short enough to avoid foam collapse. The final cell size distribution (bubbles), strut length (lamellae thickness), as well as the presence of flaws due to the rupture of films, are some of the features that can vary accordingly with the state of the foam at the moment of gelation.[2]

The current work investigates several aspects of the in situ polymerization of acrylate monomers in media containing alumina as the ceramic component. The polymerization stage was investigated as a function of pH, initial temperature, oxygen content, solids concentration, and foam volume in terms of an analysis of the exothermic profiles recorded during polymerization.

Experimental Procedure

The aqueous ceramic suspensions were composed of a mixture of the 71.4 wt % powder (alumina A-16 SG, Alcoa Aluminum S.A., USA), distilled water, dispersing agents, and an organic monomer solution for setting the slurry. Poly(acrylic acid) dispersants were used as the dispersing agents, including Versicol KA11 and Dispex A40 (Allied Colloids, Bradford, U.K.). The aqueous solution of monomers (Allied Colloids, U.K.) used to set the slips contained approximately 29% of ammonium acrylate monomers and 1 wt % of methylenebisacrylamide monomers. The monomer content was kept constant in all slips, at approximately 6.5 wt %. The foaming agent used was Tergitol TMN10 (Fluka Chemie); this material is a poly(ethylene glycol) trimethylnonyl ether. 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 monitored with an oxygen analyzer (Servomex, Sussex, U.K.).

The polymerization process was performed using chemical initiation by the redox pair persulfate−diamine. The initiator was ammonium persulfate (APS, Aldrich Chemical Co.) prepared at a concentration of 0.52 g mL^{-1} and the catalyst *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine (TEMED, Aldrich Chemical Co.). A thermocouple probe was placed in the middle of the sample to enable the polymerization reaction to be monitored as a function of time. The exothermic profiles generated during polymerization were employed in this work to provide an indication of the effectiveness of the reaction, as the rates of temperature increase correlate to the polymerization rates.[10] The curve in Figure 1 shows a schematic of the 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).

Evaluation of Parameters that Influence Polymerization. *pH.* Polymerization of aqueous solutions of the acrylate monomer was performed in the absence of ceramic powder to diminish the effect of pH on viscosity.[12] Twenty gram samples of ammonium acrylate monomer solution (30 wt %) had their pH modified with additions of ammonia solution and nitric acid, respectively, the total solution volume being kept constant. Polymerization was promoted using APS and TEMED at 6.6 × 10^{-5} and 4.6 × 10^{-5} mol g^{-1}, respectively. Subsequently, the work was partially repeated using ceramic slips in which the pH was also varied. Eighty grams of 71.4 wt % alumina suspension containing hydrochloric acid solution were foamed up to 310 mL with 0.38 wt % Tergitol TMN10 and then gelled with 4.4 × 10^{-5} and 7.7 × 10^{-5} mol g^{-1} of APS and TEMED, respectively. Throughout this work, the initial temperature of the pure monomer solution was maintained at 15.8 ± 0.6 °C. For suspensions, the initial temperature was slightly higher, of approximately 19 °C, because of the inherent heating during foaming procedure.

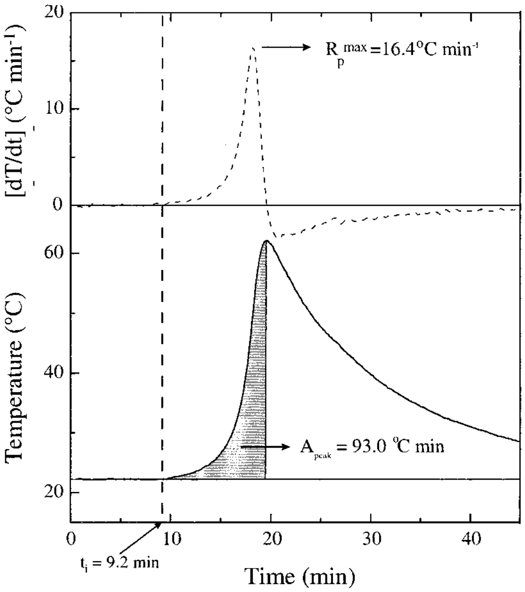

Figure 1. Schematic representation of temperature curves during polymerization and the corresponding plots of temperature increase rates. Parameters extracted from curves include: induction time (t_i), maximum polymerization rate (R_p^{max}), and area below the curve up to the maximum temperature (A_{peak}).

Table 1. Composition of Solutions Sol 1 to Sol 5

	monomer solution 30 wt % (g)	water (g)	dispersant (g)	alumina suspension (g of −wt %)
Sol 1	10			
Sol 2	10	2.22		
Sol 3	10	2.22	0.94	
Sol 4	10	2.22	0.94	10.77 of 45
Sol 5	10	2.22	0.94	30.71 of 70

Initial Temperature. The influence of initial temperature on polymerization parameters was studied, initially using pure ammonium acrylate solution and subsequently using both foamed and unfoamed alumina suspensions. Samples of 20 g ammonium acrylate solution (30 wt %) were polymerized at starting temperatures of 5 °C to 45 °C using a water bath. Polymerization was promoted by injecting APS and TEMED at 6.6 × 10^{-5} and 4.6 × 10^{-5} mol g^{-1}, respectively. Similar experiments were performed using 95 g of alumina suspensions foamed with 0.16 wt % (foam volume of approximately 250 mL), as a function of precisely monitored natural room temperature variations. Polymerization was promoted using a 1:1 molar concentration of APS and TEMED equal to 21.7 × 10^{-5} mol g^{-1}. Throughout these experiments, the pH of the pure monomer solution and the suspensions was maintained at 6.6 and 6.9, respectively.

Ceramic Suspension Components. An attempt was made to isolate the individual role of each substance comprising the slip formulation to verify its effect on the polymerization behavior. This was carried out by including each of the components into 10 g samples of a 30 wt % ammonium acrylate aqueous monomer solution. The solutions' composition is given in Table 1. Polymerization was induced with additions of 5.4 × 10^{-5} and 4.4 × 10^{-5} mol g^{-1} of APS and TEMED, respectively. The pH and initial temperature varied within the ranges 6.7 ± 0.2 and 21 ± 1 °C, respectively.

Oxygen. The oxygen content effect on polymerization behavior was also observed using 10 g samples of 30 wt %

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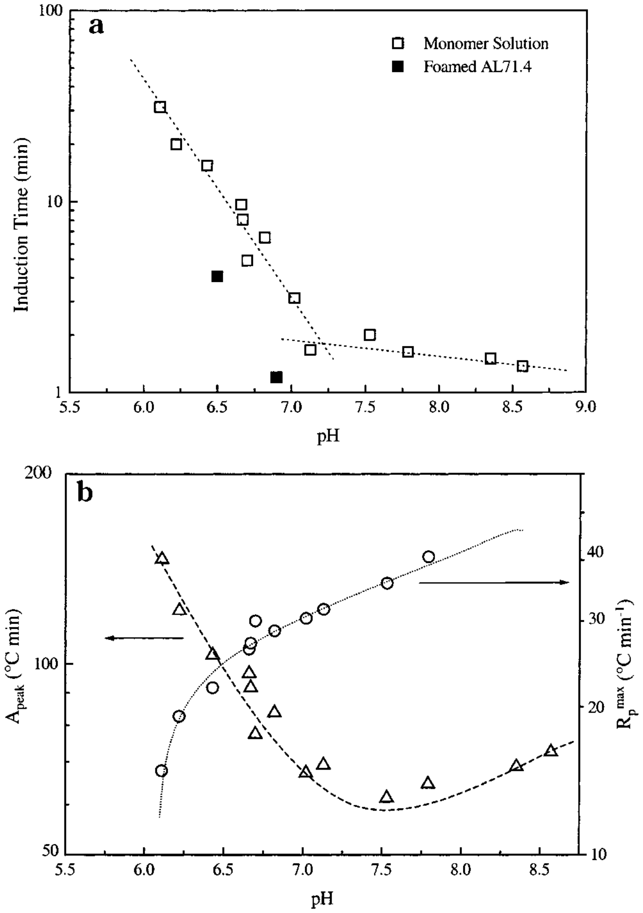

Figure 2. (a) Induction time, t_i, and (b) R_p^{max} (circle) and A_{peak} (triangle) retrieved from exothermic curves plotted as function of pH for monomer solutions (open symbols) and foamed suspensions (solid symbols). System compositions are given in the text.

ammonium acrylate aqueous monomer solutions and foamed alumina suspensions. For the former, APS and TEMED were used at 7.7×10^{-5} and 4.4×10^{-5} mol g^{-1}, respectively. In the foamed slurries, polymerization was induced with APS and TEMED at 3.7×10^{-5} and 3.2×10^{-5} mol g^{-1} (C1) and 4.5×10^{-5} and 5.4×10^{-5} mol g^{-1} (C2), respectively. Oxygen content was varied from 0.0 to 0.4%. Levels higher than 0.0% were obtained via small air inlets into the vessel before foaming and/or gelation were induced. The pH of the suspensions was 6.9, and the initial temperature was maintained at approximately 25 °C.

Foam volume. Slips were foamed at various levels with additions of 0.16, 0.26, and 0.45 wt % Tergitol TMN10 for 4 to 5 min by continuous and vigorous stirring at a 0.0% oxygen level in the glovebox. pH and initial temperature were maintained as for the above experiment. Polymerization was promoted using a 1:1 molar concentration of APS and TEMED equal to 21.7×10^{-5} mol g^{-1}. An unfoamed sample was also tested.

Foam Characterization. Alumina foams sintered at 1500 °C for 2 h were observed using scanning electron microscopy (SEM) for morphological characterization of the structure.

Results and Discussions

Influence of pH. The induction time values, t_i, extracted from the polymerization exotherms of monomer solutions and foamed slurries are shown in Figure 2a as function of pH, while Figure 2b provides the corresponding R_p^{max} and A_{peak} data for pure monomer solution. The results show that higher pHs lead to shorter induction times and faster propagation rates, as R_p^{max} is higher.

The amount of heat released during most polymerization reactions involved in this work, proportional to the calculated value for A_{peak}, was inversely proportional to the rates of polymerization, R_p^{max}. Thus, the overall monomer conversion into polymer decreases when reactions are faster. This result agrees with the postulation that longer polymerization reactions may lead to greater molecular weight and higher conversion levels.[10] A high initiator decomposition rate may cause significant amount of monomer to remain unreacted.

Polymerization appears to be significantly more affected by pH changes in the acidic range as compared to the alkaline range. This difference in behavior reflects the sensitivity of the initiating species to the variation of the solution ionic strength. The retardation observed with acidic pH variation has been attributed to the fact that acid catalyzed decomposition of persulfate does not give rise to the formation of free radicals. Thus, the H^+ released by the acid used to reduce the pH of the solutions might combine with the $S_2O_8^{2-}$ persulfate creating intermediate compounds that do not contribute to initiating polymerization. Some of the initiating species would be used up to form intermediate products that either do not propagate polymerization or become active only later in the process.[13] This would explain the observed decrease in polymerization rates and longer induction times with lower pH, as more H^+ ions are introduced into the system.

The reaction rates' dependence on the slip pH becomes a very important tool in the processing of ceramic fluid systems. Some ceramic powders may produce better dispersion in acidic medium, an effect that is associated with the powder's surface characteristics. Therefore, it is believed that the use of acidic ceramic suspensions to produce foams may influence polymerization in a negative manner. The reduction of reaction rates in these systems could occur to such an extent that deterioration of the polymeric network results. In the same way, the mechanical properties of the gelled foams produced would be also lowered. Moreover, reactions with long induction times would result in foams being solidified at advanced stages of lamellae drainage.

Influence of Initial Temperature. The induction time data retrieved from the exothermic profiles of monomer solution, foamed and unfoamed suspensions at various temperatures are illustrated in Figure 3a, while R_p^{max} data are shown in Figure 3b. As expected, the gelation kinetics revealed great dependence on the initial system's temperature. Induction time was shortened, and polymerization rates increased with a temperature increase. A higher temperature induces a higher decomposition rate for the initiator, producing a larger number of free radicals. The diffusion of monomers and growing chains in solution can also be enhanced at higher temperatures, facilitated by the decrease in the suspension's viscosity.[14]

The logarithm of the induction time appeared to be inversely proportional to the solution initial tempera-

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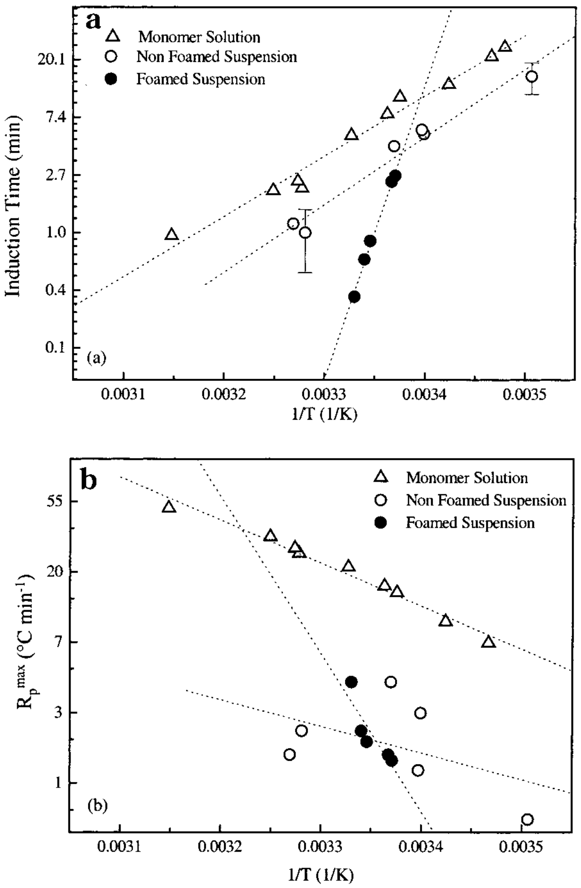

Figure 3. (a) Induction time, t_i, and (b) R_p^{max} retrieved from polymerization curves of foamed (solid circle) and nonfoamed (open circle) alumina suspensions and pure monomer solution (open triangle) as a function of initial temperature. System compositions are given in the text.

Table 2. Activation Energy Values for the Initiation of Ammonium Acrylate Polymerization in Three Systems

system	E_a for free radical generation (kJ mol^{-1})
aqueous solution	87
ceramic suspensions	98
foamed ceramic suspensions	426

ture. This relationship can be expressed by an Arrhenius-type equation: $t_i = t_0 e^{E_a/RT}$, where t_0 is a constant, R is the molar gas constant, and E_a is the activation energy of the free-radical generation process.[15] By fitting the data to this relationship, the initiation process in pure monomer solution may be described by $t_i = 3.9 \times 10^{-15}\, e^{87k/RT}$, while $t_i = 2.5 \times 10^{-17}\, e^{98k/RT}$ and $t_i = 2.8 \times 10^{-75}\, e^{426k/RT}$, respectively, for polymerization in unfoamed and foamed ceramic suspensions. It should be noted, though, that there was a considerable degree of scatter in the data for the unfoamed suspensions. Table 2 compares the resulting values of E_a obtained for the three systems. The values reflect the energy barrier levels that the species have to overcome to form the products and start polymerization. Similar values were observed for the aqueous solution and unfoamed suspension, 87 and 98 kJ mol^{-1}, respectively. These values are in agreement with those found in the literature for polymerizing monomers in solution.[15] An important feature of redox initiation is the low activation energy necessary for radical formation as compared to the system containing only a dissociative compound. For instance, in polymerization of acrylamide monomers thermally dissociated APS has an E_a of 150 kJ mol^{-1}, while in the redox system of TEMED-APS E_a is reduced to approximately 70 kJ mol^{-1}.[8] However, it should be noted that the similarities between the E_a value for the monomer solution and that for the unfoamed suspension does not necessarily imply that initiation and polymerization followed the same mechanism. Addition of solids and other polymeric species into the monomer solution system is expected to have altered the polymerization kinetics despite the apparent similarity in activation energy values.

The E_a values determined for the initiation process (t_i vs $1/T$ plots) in the foamed suspension, however, were significantly higher, viz. 426 kJ mol^{-1}. This value suggests that an increase in the energy barrier for the free radical generation process occurred as a result of foam generation, increasing the difficulty of initiation. For the propagation process (R_p^{max} vs $1/T$ plots), similar differences in E_a between foamed and unfoamed systems were detected. It is believed that this was due to the large viscosity increase that occurred as a result of foaming.

The "cage" effect is commonly used to explain the presence of an induction time in polymerization.[11,15] Since redox systems consist of an oxidizing and reducing agent forming free radicals in pairs, the two fragments can become locally trapped by the effect of the solvent molecules and recombine before they can diffuse out of the "cage" to interact with the monomers and initiate polymerization. The system viscosity will determine the diffusion rate of the radicals out of the "cage". Therefore, the large viscosity increase observed on foaming implies that the thin films created by the gas-phase trapped in the bubbles and the surfactant molecules interacting on the gas–liquid interfaces could have increased this "cage" effect. This would have created a limited path for extension of the polymeric network.

Taken as a whole, the results show that the variation in initial temperature alters the speed of reaction for polymerization in monomer solution, be it in aqueous solution, foamed or unfoamed ceramic suspension. In foamed suspensions, however, this temperature influence was much stronger. Therefore, even small variations in temperature can greatly alter reaction rates and induction times. This is of great importance for the production of ceramic foams, especially when the gelation stage needs to be carefully controlled to ensure an optimal structure.

Influence of Ceramic Solids and Dispersing Polymers. The polymerization of Sol 1 to Sol 5 produced the temperatures profiles presented in Figure 4. While the monomer quantity was kept constant, the overall mass of solution examined gradually increased from Sol 1 to Sol 5 as more additions were made, see Table 1. As expected, the dilution of monomer solution implied by Sol 2 as compared to Sol 1 led to a longer induction time. The compounds will have been more sparsely distributed in Sol 2, the extended distances that the free radicals needed to diffuse to reach the monomer or growing chains delaying polymerization

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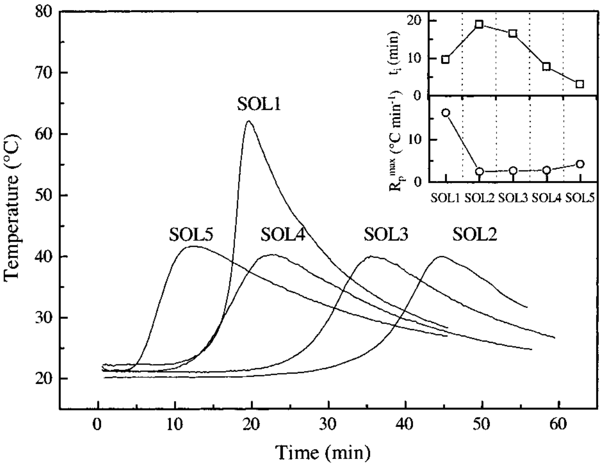

Figure 4. Exothermic curves of Sol 1 to Sol 5. The insert shows the correspondent values of t_i and R_p^{max}.

initiation and propagation. However, the induction time then steadily decreased with each new addition from Sol 2 through to Sol 5, although neither the maximum temperature reached nor the R_p^{max} values changed substantially after the initial big decrease from Sol 1 to Sol 2. Even though the pH increased from 6.5 for the pure monomer solution to approximately 6.9 for the suspensions, this rise was not sufficient to account for the variability in polymerization reactions.

It is believed that the powder particles and dispersant macromolecules might have provided additional surface energy for the radicals to be formed and for propagation to proceed, acting as nucleation sites in the polymerization process. This mechanism has been used to explain the polymerization of monomer solutions in the presence of impurities.[13] The slight increase in propagation rates as more particles are added to the system, relative to the slight upturn in R_p^{max} value from Sol 4 to Sol 5, may be due to the particles promoting greater physical entanglement of the growing chains and hence impeding the termination step.[10,17]

Effect of Oxygen. The curves in Figure 5a show the effect of atmosphere oxygen content on the polymerization of monomer solutions; there was comparatively little effect. In contrast, the curves in Figure 5b for foamed alumina suspensions show that the onset of polymerization was delayed by 5–10 min by the presence of 0.1% oxygen, depending on the precise level of initiator and catalyst, while just 0.2% oxygen was sufficient to inhibit the reaction completely. This latter foam collapsed within the 50 min of the test. The reaction rates also seemed to be influenced by the oxygen, decreasing as the oxygen content was increased.

It is believed that the insignificant effect of oxygen on the monomer solution was a result of the fact that oxygen could enter the system only through the top surface. With the foams, however, there was significant access for the oxygen to the monomer and initiator molecules as a result of the increased surface area and interconnected nature of the porosity. As a result, the foams are particularly susceptible to even small variations in oxygen content. The oxygen suppresses polymerization by reacting with the initiating and propagating radicals.[15] This results in nonradical species, or the reactivity of the radicals becomes so low that propagation does not proceed. Polymerization therefore decreases or even stops until all the inhibitor molecules are consumed.

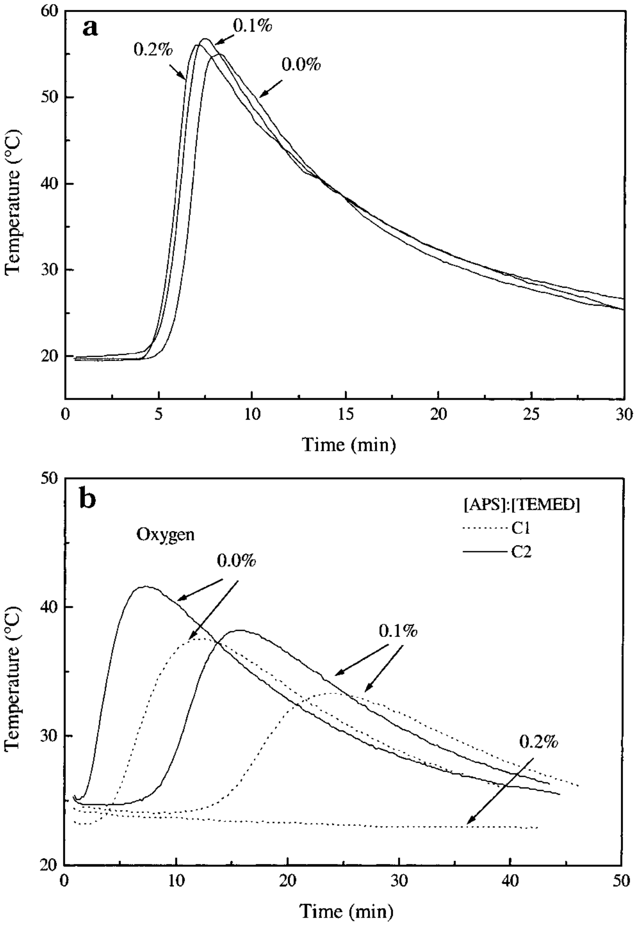

Figure 5. (a) Polymerization plots for 10 g monomer solutions at various oxygen contents. (b) Influence of oxygen content on the polymerization of alumina slurries foamed up to 250 mL. System compositions are given in the text.

Effect of Foam Volume. The exothermic curves in Figure 6 illustrate the polymerization results for suspensions foamed at different amounts. Increasing the level of foam produced resulted in a significant decrease in the ΔT during polymerization and a slight increase in the induction time. As the polymerization reaction produces heat, this must be dissipated through the liquid–gas interfaces. In general, the greater the degree of foaming, i.e., the more bubbles present, the lower the rate of temperature increase because of the larger gas–liquid interfacial area for heat exchange. Although the observed behavior was primarily thought to be a result of heat dissipation in the gaseous phase, the presence of bubbles could have influenced the polymerization process by causing a decrease in reaction rates. This effect could not be completely confirmed by these plots, but when the curves were normalized to eliminate the effect of heat dissipation marked differences were found in the heat produced by unfoamed and foamed systems.[5]

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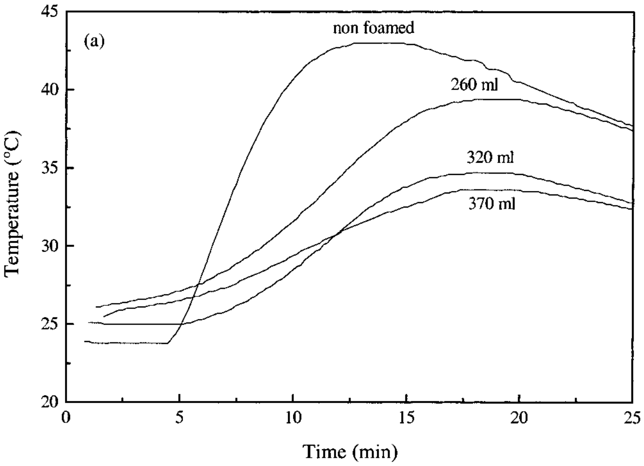

Figure 6. Polymerization plots for alumina suspensions. Nonfoamed slips and slips foamed up to 260, 320, and 370 mL were examined, as indicated. Suspension compositions are given in the text.

Influence of Induction Time on Ceramic Foam Properties. The characterization of gelcast foams has shown that aspects of foam morphology, such as pore volume, size, and size distribution, are all controllable by manipulation of specific parameters involved in the processing.[2] The induction time has been regarded as the most difficult parameter to control in the processing of ceramic foams via gelcasting. Because of 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.[6] Therefore, the gelation process must proceed so as to maintain the foam structure, with minimum deteriorating effects.

Previous work demonstrated that although the cell size distribution depends primarily on the density of foams, it is also greatly influenced by the induction time.[2] The increase in average cell size distribution and in the degree of interconnection on 12% dense alumina foams gelled with induction times of 90 and 200 s is illustrated in Figure 7. For longer induction times, the average cell size increases and the size distribution becomes wider with a simultaneous enlargement of cell windows.

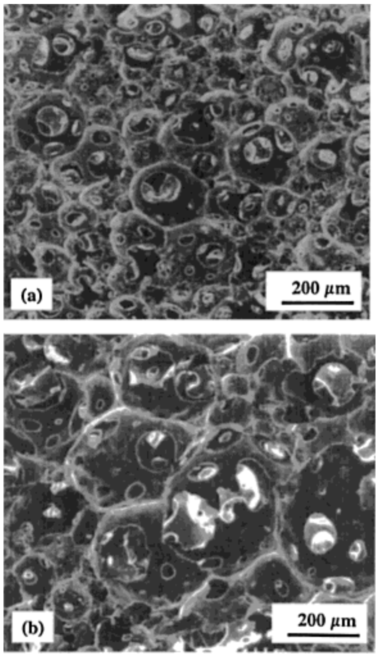

Figure 7. Scanning electron microscopy of 12% dense alumina foams gelled with induction times of (a) 90 and (b) 200 s.

The cell size distribution of foams is the major factor to define the potential application for these materials. Predominantly closed cell foams are preferable for thermal insulation, as the insulation to heat decreases as the cell size increases.[18] Open interconnected celled ceramics are needed for uses involving fluid transport, wherein the interconnecting window size is the determinant factor for properties involving permeability.[19] The mechanical properties of cellular ceramics have also been shown to depend on porosity, pore size, and strut strength.[20]

Conclusions

This study has focused on the in situ polymerization kinetics for the processing of porous ceramics via foaming and gelcasting. The influence of processing parameters including pH, temperature, oxygen content, and foam volume on the polymerization kinetics of acrylate monomer solutions and of foamed ceramic suspensions has been evaluated. The results show that the time for polymerization, which is of prime importance for porous ceramics processing, is very sensitive to variations in pH, temperature, and oxygen content. Faster polymerization reactions with shorter induction times can be produced at higher and more alkaline pHs, higher temperatures, and lower atmosphere oxygen contents. As compared to unfoamed systems, foaming appears to cause a significant change in polymerization kinetics, which reduces reaction rates and makes the systems more sensitive to small temperature variations.

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